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FERROELECTRICITY IN CRYSTALS

CONTENTS

1. INTRODUCTION	page 1
1. Dielectric hysteresis 2. The Curie point 3. Dielectric constant 4. Crystal symmetry and the existence of spontaneous polarization 5. Dipole moment and dipoles 6. Nature of transition at the Curie point: pseudosymmetric structures 7. Twinning and domain formation 8. Other materials 9. Summary of properties of ferroelectrics; definition 10. Antiferroelectrics 11. Relation between ferroelectrics and antiferroelectrics: line and cone ferroelectrics 12. Polymorphism in ferroelectric and antiferroelectric materials; 'multiple structures', sub-cells and superlattices 13. Paraelectrics.	
2. ROCHELLE SALT	20
1. Orthorhombic crystal structure 2. Evidence for monoclinic symmetry, and location of hydrogen atoms 3. Chemical discontinuity at the Curie point 4. Isomorphous substances 5. Curie points and effects of pressure 6. Thermal expansion and change of lattice parameters 7. Specific heat 8. Dielectric constant 9. Spontaneous polarization and coercive field 10. Barkhausen jumps and Weiss domains: pyroelectric effect 11. Discussion: mechanism of the transition.	
3. THE TETRAGONAL PHOSPHATES	35
1. Introduction: potassium dihydrogen phosphate 2. Crystal structure at room temperature 3. Low-temperature structure 4. Domain texture 5. Isomorphous substances 6. Ammonium salts 7. Lattice parameters and thermal expansion 8. Specific heat and entropy 9. Spontaneous polarization and coercive field 10. Effect of field on crystal structure 11. Dielectric constant 12. Discussion: nature of transition.	
4. BARIUM TITANATE	58
1. Introduction 2. Cubic (high-temperature) structure 3. Tetragonal structure 4. Orthorhombic structure; choice of axes of reference 5. Rhombohedral structure 6. Hexagonal barium titanate 7. Cell dimensions and thermal expansion 8. Twinning and domain texture; twin laws, X-ray and optical evidence 9. Optical properties 10. Latent heat, specific heat, and change of entropy 11. Spontaneous polarization and coercive field 12. Pyroelectric effect 13. Dielectric constant 14. Changes in the Curie point: effects of pressure, solid solution, and biasing field 15. Domain boundaries and effect of field 16. Nature of transition.	
5. THE PEROVSKITE FAMILY	83
1. Introduction: Goldschmidt's rules for ionic structures, and classification of the perovskite family 2. Titanates of alkaline earth metals 3. Zirconates and hafnates of alkaline earth metals 4. Niobates and tantalates of sodium, potassium, and rubidium 5. Lithium niobate	

CONTENTS

type 6. Tungsten trioxide 7. Lead titanate 8. Lead zirconate 9. Lead hafnate 10. Solid solutions of lead compounds 11. Lead compounds: summary.	
6. DISCUSSION OF DISTORTED PEROVSKITE STRUCTURES	124
1. Introduction: two types of distortion 2. Packing distortion or crumpling: tilting of octahedra 3. 'Off-centre' distortion: rôle of covalent bonds 4. Behaviour of lead compounds 5. Relation of distortion to ferroelectricity and antiferroelectricity 6. Multiple cell: relation to electrical properties 7. Summary.	
7. MISCELLANEOUS STRUCTURES	135
1. Introduction 2. Double tartrates of lithium 3. Guanidine aluminium sulphate hexahydrate 4. Lithium niobate (referred to perovskite family) 5. Periodates 6. Pyrochlore group: cadmium niobate and isomorphous compounds.	
8. THEORIES OF FERROELECTRICITY: THE PHENOMENOLOGICAL APPROACH	150
1. Introduction: comparison of phenomenological and model theories 2. Devonshire's theory of barium titanate 3. Mueller's theory of Rochelle salt 4. Comment on the phenomenological theories 5. Phenomenological theory of antiferroelectricity: existence of 'mixed states' (cone ferroelectrics).	
9. MODEL THEORIES: GENERAL BACKGROUND	165
1. Introductory ideas: origin and nature of dipoles; long-range and short-range forces 2. Polarization and susceptibility in terms of long-range forces 3. The internal field 4. Polarizability: Clausius-Mosotti relation; additivity of polarizabilities of atoms; electronic and ionic polarizabilities 5. Construction of a model theory: necessary postulates.	
10. MODEL THEORIES: PARTICULAR APPLICATIONS	179
1. Introduction 2. Rochelle salt: theories of Kurchatov and of Fowler 3. Mason's theory of Rochelle salt 4. Slater's theory of potassium dihydrogen phosphate 5. Mason's treatment of potassium dihydrogen phosphate 6. Pirenne's theory of potassium dihydrogen phosphate 7. Mason and Matthias's theory of barium titanate 8. Devonshire's model theory of barium titanate: potential energy of atom 9. Slater's theory of barium titanate: relation to Devonshire's treatment of ionic and electronic polarizabilities, and field factor 10. Jaynes's mechanical-deformation treatment of barium titanate 11. Jaynes's electronic theory of barium titanate 12. Structural approach: postulates and outline of treatment in terms of short-range forces.	
APPENDIX: GLOSSARY OF CRYSTALLOGRAPHIC TERMS	203
INDEX	212

PREFACE

THE subject of ferroelectricity is still very young, and it is growing so fast that the writing of a book about it presents particular difficulties. In attempting it I have been constantly aware that the subject spreads across conventional boundaries between branches of science, and that those interested in knowing more about it will come to it with very different backgrounds. I have therefore tried to take nothing for granted beyond a familiarity with elementary principles of physics, chemistry and mathematics, and to define and explain all the specialized concepts of the subject either in an introductory chapter or later in the text when they are first introduced. With regard to crystallographic notation, a dilemma becomes apparent. Few physicists and chemists have had a formal training in crystal geometry; but those who have had such a training know it for a very powerful tool in increasing our knowledge of solids. For the first group, crystallographic notation is a difficulty which perhaps they cannot give time to surmount; for the second, it is the most elegant, concise and objective way of conveying the experimentally-derived information needed for a proper understanding of the material and as a basis of further advance. I have tried to meet the needs of both groups by using the notation freely in compiling a record of facts about each material, and by adding a verbal explanation, based on first principles, at every point where it is needed to understand the argument or the description of what is happening. In this way I hope the book will be intelligible and readable to the first group without inducing a sense of frustration in the second. As an additional help, a short glossary of some of the crystallographic terms is included; those who wish to go further in learning to use the notation are referred to the preface to the *International Tables for X-ray Crystallography* (1952), Vol. I.

This book sets out primarily to be a record of experimental facts. Theoretical treatments are kept to a late stage when an assembly of facts has been gathered by which they can be judged. Our knowledge is advancing so rapidly that no theories can yet be regarded as established; the fact which is evidence for one theory today may be found equally in support of another quite different theory tomorrow (as has happened once or twice already in the history of the subject). It might therefore be actively misleading, as well as logically unsatisfactory, to record the observed facts only in a context where their relevance to some theoretical treatment could be made plain. On the

PREFACE

other hand, the disadvantage of beginning with a compilation of unexplained facts is its dullness, for our interest is generally only aroused when we see relationships. It is a price that must be paid, however, for a comprehensive understanding of the subject. Readers who prefer to see the conclusions first and the evidence later can go straight from Chapter 1 to Chapters 6, 8, 9 and 10; cross-references to the earlier chapters are provided.

Underlying the whole treatment is the assumption that the physical properties of a solid are closely related to its structure, and that the first step in understanding the physical properties is to understand the structure. Any explanation of the unusual electrical properties in terms of interatomic forces must recognize that forces of the same kind are responsible for holding the atoms in their equilibrium positions. It is therefore relevant to draw on our knowledge of structures of chemically-related compounds which are not electrically abnormal. The crystallographic approach draws attention on the one hand to the great variety of structures which can actually exist, on the other hand to regularities and recurrence of certain features which allow us to classify and compare them. The kind of approach which substitutes a simplified structure for that actually observed in ferroelectrics is to be avoided, for it is in danger of throwing out the real hope of an explanation along with the mathematical difficulties—the baby with the bath-water.

Two omissions should be mentioned. Very little is said about the mechanical properties of the substances dealt with, or their relation to the electrical properties through piezoelectricity. These properties are of great technical importance and have been much studied, but they are not fundamental to our understanding of the nature of ferroelectricity. Good accounts of them are available (notably in Cady's *Piezoelectricity*), and to describe them adequately here would have taken up a disproportionate amount of space. An account of the evidence from infra-red and Raman spectra is omitted for the opposite reason: very few facts are available, and it is too early yet to see them in any perspective.

With these exceptions, I have tried to make the account of the materials dealt with as complete as possible, collecting together data scattered through the literature not only for ferroelectrics but also for antiferroelectrics and substances closely related to them chemically and structurally. As yet we lack a word covering this whole class of materials; since the others are of interest for their relation to ferroelectrics I hope that the title of the book, chosen on grounds of brevity, will not prove too misleading.

In a subject advancing as rapidly as this, it is inevitable that any survey should have many omissions and many statements that will

PREFACE

need revision before even the book is in print. It will have achieved its aim, however, if it displays our existing knowledge in such a way that the foundations can be clearly seen; that their strength can be tested; and that as rebuilding and extension become necessary these can be done economically and with an understanding of their place in the edifice as a whole.

I wish to express my thanks to all those who have read and commented on parts of the book in manuscript, and particularly to Dr R. E. Newnham who read it in proof and helped me to remove numerous errors. I owe a special debt of gratitude to Dr W. H. Taylor for his encouragement from the time when the idea of writing the book first began to take shape.

I wish also to thank the various authors whose diagrams I have used as illustrations, and the editors and publishers of the following journals for permission to reproduce them: *Acta Crystallographica*; *Helvetica Physica Acta*; *Journal of the Physical Society of Japan*; *Philosophical Magazine*; *Physical Review*; *Proceedings of the Physical Society*; *Proceedings of the Royal Society*. I am particularly grateful to the following, who let me have photographs or drawings from which to make reproductions: to Mr H. S. Pease for Fig. 3.3 (a) and (b), to Dr W. J. Merz for Fig. 4.6 (d), (e) and (f), and to Dr H. F. Kay for Fig. 5.4.

Finally, I should perhaps say that I have not tried to give a systematic account of work published after about the middle of 1955; a few later papers are mentioned, however, where they are immediately relevant to topics discussed in the text and happened to come to my notice while the book was being prepared for the press.

HELEN D. MEGAW

Cambridge
February 1956

Chapter 1

INTRODUCTION

Wisdom will repudiate thee, if thou think to enquire
WHY things are as they are, or whence they came: thy task
is first to learn WHAT is.

BRIDGES: *Testament of Beauty*

1 Dielectric hysteresis

1.1. The discovery of the phenomenon later to be known as ferroelectricity was made in 1921 by Valasek in an investigation of Rochelle salt (sodium potassium tartrate tetrahydrate). This substance was believed to belong to the crystal class 222 (orthorhombic hemihedral-holoaxial)*; it is water-soluble, easily prepared, easily grown in large crystals, and has been much studied for its physical properties since the time of Pasteur, who demonstrated its optical activity. It has no centre of symmetry, and is therefore capable of showing piezoelectricity—that is, the production of electrical charges by the application of mechanical stress, and conversely of mechanical deformation by an electric field. The magnitude of its piezoelectric effect gives it technological importance, and for this reason it has been extensively studied.

The new effect discovered by Valasek was a dielectric hysteresis. He showed that for one direction in the crystal, parallel to the x axis, the electric displacement D (measured by the charge on a condenser) was not determined uniquely by the applied field E , but depended also on its previous values. If the field was alternately increased to a maximum and decreased through zero to a maximum in the opposite sense, the displacement traced out a hysteresis loop, as shown in Fig. 1.1. The resemblance to a ferromagnetic hysteresis loop (which connects B , the induction, with H , the field) is immediately obvious. The analogy between them was pointed out in Valasek's first paper, and it inspired much of the work that followed. It will be shown later that it must not be pressed too far or it becomes misleading, but it provides a useful approach.

It is to this analogy with ferromagnetism that ferroelectricity owes

* The crystal notation used throughout this book is that defined in the *International Tables for X-ray Crystallography*, Vol. I (1952: Kynoch Press, Birmingham), to which the reader may be referred. It will only be explained in this book when the understanding of the argument depends upon it. A glossary of crystallographic terms is given in the Appendix.

FERROELECTRICITY IN CRYSTALS

its name. The word seems to have been first used by Mueller in 1935. The name is illogical, because the analogy is not perfect, and the reference to iron is misleading. An earlier name, 'Seignette-electricity', derived from its first discovery in Rochelle salt (Seignette salt), was introduced by Kurchatov (1933) and has been widely used, particularly on the Continent. It too can be challenged, since we now know that Rochelle salt is far from typical; but perhaps the real reason for its rejection by many writers is its failure to fit comfortably into the English language. As an adjective, 'ferroelectric' is euphonious, while 'Seignette-electric' grates on the ear.

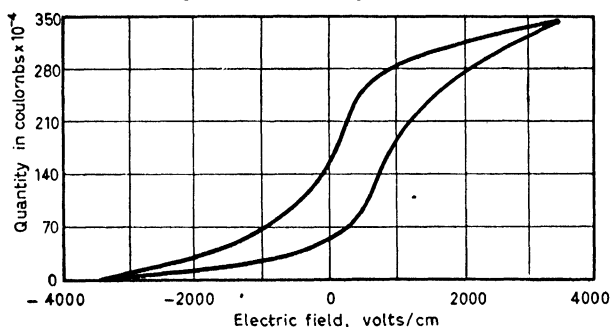


Fig. 1.1. Dielectric hysteresis loop for Rochelle salt (Valasek, 1921).

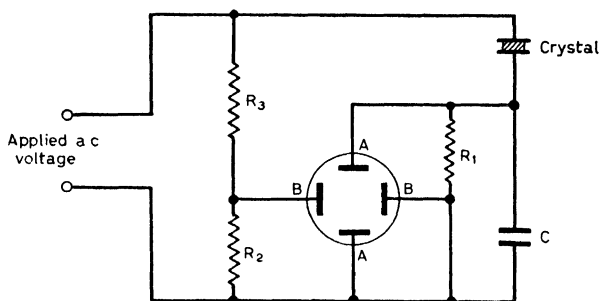


Fig. 1.2. Circuit for investigating hysteresis loop (Sawyer and Tower, 1930).

1.2. Experimental methods of recording the hysteresis loop are generally based on that of Sawyer and Tower (1930). The crystal under test is in the form of a parallel plate with electrodes connected to its surfaces, which are commonly silvered. The circuit is shown in Fig. 1.2. A cathode-ray oscillograph is used. One pair of plates *AA* measures the potential applied across the crystal itself, which is proportional to the field, while the other *BB* measures the potential across a condenser *C* in series with the crystal, which is proportional to the charge on the crystal and hence to the displacement.

1. INTRODUCTION

1.3. The existence in any substance of a dielectric hysteresis loop implies that the substance possesses a *spontaneous polarization*, that is, a polarization which persists when the applied field is zero. This

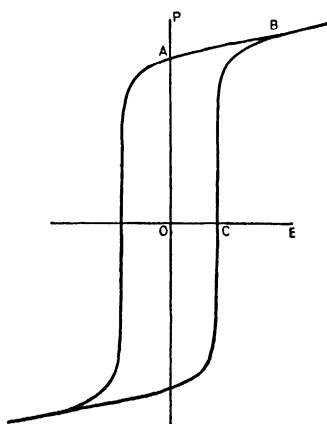


Fig. 1.3. Dielectric hysteresis loop: illustrative diagram.

is illustrated in Fig. 1.3, which shows a loop of polarization P versus field E (which is qualitatively similar to the loop of D versus E , since $D = E + 4\pi P$). The length OA represents the spontaneous polarization P_s ; OC represents the coercive field E_c , the minimum field needed to reverse the direction of polarization.

Spontaneous polarization corresponds to intrinsic magnetization in a ferromagnetic, but there is a very important difference. A magnetic moment in a specimen can be detected and measured by its external field. An electric polarization can only be similarly detected if the specimen retains electric charges on its surface. Such charges become neutralized in time—by leakage through moisture films or ionized air, even if the material itself is perfectly non-conducting—and then no external effect can be observed. If however the sense of the polarization can be reversed, new charges are formed and can be detected. But if the applied field is less than the coercive field, reversal will not occur and the polarization will remain unobservable.

1.4. The exact shape of the loop obtained experimentally depends on a number of factors: the dimensions of the specimen, the temperature, the humidity (since Rochelle salt can change its composition appreciably by loss of water on standing in air), the texture of the crystal and its previous thermal and electrical history. It is now recognized that a curve such as that of Fig. 1.1 does not represent a true single crystal; it results from the superposition of loops due to smaller crystallites. In some cases, abrupt changes in polarization of

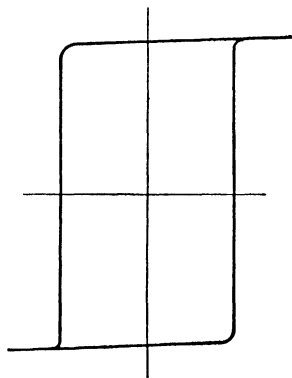


Fig. 1.4. Dielectric hysteresis loop for a true single-domain crystal.

individual crystallites can be observed as discontinuous jumps in the curve, similar to the 'Barkhausen jumps' in ferromagnetic materials (see Fig. 3.8). For very good single crystals, in favourable circumstances, the loop approximates to a parallelogram, as illustrated in Fig. 1.4, and the change in polarization at the coercive field happens in a single discontinuous jump.

However, actual crystals are never perfect, but are subject to local stresses; and because of the piezoelectric effect, local stresses imply local fields. According to the direction of these, the external field required for reversal will be greater or less than the coercive field. Thus even for the best available single crystals the loop is always somewhat rounded at the corners.

2 The Curie point

With increase of temperature above 0°C , the hysteresis loop of Rochelle salt changes its shape. The height decreases slightly, the width decreases very much, until at about 24°C the sides of the loop

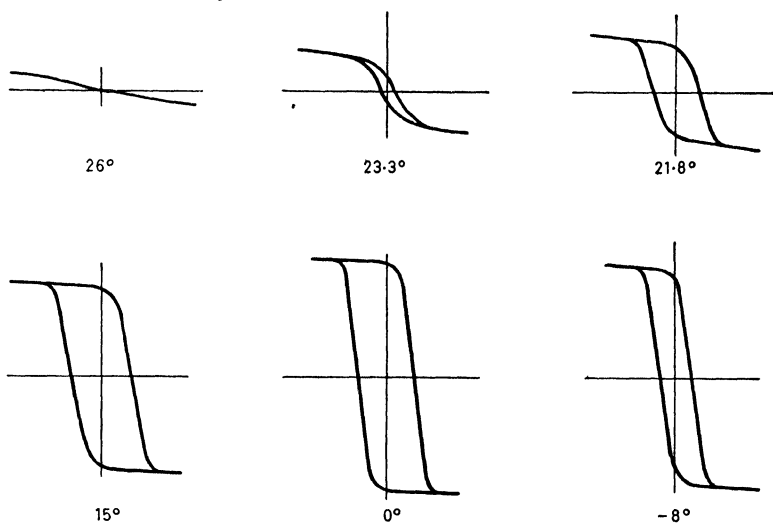


Fig. 1.5. Dielectric hysteresis loops for Rochelle salt at different temperatures (Sawyer and Tower, 1930).

have merged into one line. Fig. 1.5 shows some early observations with a cathode-ray oscillograph. The disappearance of spontaneous polarization in Rochelle salt is comparable to the disappearance of magnetization in iron at the Curie point, and Rochelle salt is therefore said to have a *ferroelectric Curie point*, at 24°C . Below 0°C the hysteresis loop closes up as the temperature *decreases*; the first

1. INTRODUCTION

stages of this effect are shown in Fig. 1.5. At about -20°C the spontaneous polarization disappears, and does not recur at any lower temperature; this temperature is known as the *lower Curie point*. This effect is quite without a parallel in ferromagnetism, where there is no lower temperature limit to the ferromagnetic range. Subsequent work shows that it is also unusual among ferroelectrics, most of which retain their spontaneous polarization down to the lowest temperatures investigated.

When a constant biasing field is used, it is found that the range of spontaneous polarization is extended: the upper Curie point is raised, and the lower Curie point lowered.

3 Dielectric constant

3.1. Another striking feature of Rochelle salt is its very high dielectric constant parallel to the x axis within the ferroelectric range. At the upper Curie point it rises to a peak value of as much as 4000 as compared with about 10 along the y axis (see Chap. 2, Fig. 2.2). At higher temperatures it decreases according to a Curie-Weiss law (Fig. 2.3): that is, the dielectric constant ϵ and the temperature T are related by an equation of the form

$$\epsilon - 1 = \frac{C}{T - T_c}$$

where T_c is a temperature close to the Curie point and C is a constant with the dimensions of temperature. At the lower Curie point it has a second peak, dropping to low values according to a Curie-Weiss law on the low temperature side.

3.2. The reason for the high dielectric constant can be seen qualitatively from the hysteresis loop (Fig. 1.3). It is first necessary, however, to consider our definitions. Dielectric susceptibility η is ordinarily defined as P/E , and permittivity or dielectric constant ϵ as $1 + 4\pi\eta$. In a normal material, P is proportional to E , and the definition is adequate; here it is not. We may distinguish

- (1) the overall susceptibility P_B/E_B , the ratio of the values of P and E at the tip of the loop,
- (2) the differential susceptibility, the slope $\partial P/\partial E$ at any point,
- (3) the initial or 'small-signal' susceptibility, the slope $\partial P/\partial E$ at zero external field,
- (4) the saturation susceptibility, the slope at B .

If the material has been taken round the hysteresis loop already, the initial susceptibility measures the slope at A ; it can be shown to be equal to the slope for small fields applied to a new specimen.

It is clear that the overall susceptibility is much greater than the saturation susceptibility, which is the value when the continuously-applied field is too great to allow reversal of polarization by the testing field, and which is therefore of the same order of magnitude as for materials—or for directions in the same material—not possessing spontaneous polarization. It can also be seen in a qualitative way how the susceptibility increases as the loop narrows in the neighbourhood of the Curie point; for the square loop of a true single crystal, as the sides close together into a vertical line the susceptibility becomes infinite.

3.3. It follows from any of the definitions that the susceptibility and the dielectric constant derived from it are strongly dependent on the shape of the hysteresis loop, and hence, as we have seen, on the texture of the crystal and its approximation to a true single crystal. It is therefore not surprising that there is a good deal of disagreement among different authors about the absolute values they report for the dielectric constant of the same substance. Many of them have not stated their definition of the constant, nor specified the conditions under which it was measured—for example, whether the crystal was clamped or free. Later writers generally measure the initial dielectric constant of a free crystal. In this book, no attempt is made at critical assessment of the values; the figures are only given to illustrate relative orders of magnitude.

As an illustration of the different values based on different definitions, the work of Merz (1953) on a very good single crystal of barium titanate may be quoted. This crystal showed a very square hysteresis loop. The initial dielectric constant, derived from the slope at *A* (Fig. 1.3), was about 200, while the differential dielectric constant, derived from the slope at *C*, was of the order of 10^6 .

4 Crystal symmetry and the existence of spontaneous polarization

4.1. The existence of spontaneous polarization in Rochelle salt raises a difficulty, for it is not compatible with the symmetry which the crystal was originally believed to possess. This is a point which it is worth looking into rather fully.

The existence of a symmetry element means that any vector in a crystal is repeated according to certain geometrical laws which are characteristic of the symmetry element. The resultant vector descriptive of the crystal as a whole is obtained by adding all the separate vectors derived from the initial one by the operation of the symmetry elements. For many combinations of symmetry elements the resultant is zero. Consider for example a crystal having diad axes

1. INTRODUCTION

along x and y . The first diad repeats a vector with components $u\ v\ w$ to give another with components $u\ \bar{v}\ \bar{w}$. The second repeats them both to give two more, $\bar{u}\ v\ \bar{w}$ and $\bar{u}\ \bar{v}\ w$. (It can be seen that this implies a third diad axis along z .) The sum of the components along each axis is zero, and therefore the resultant is zero. If the diad axis along x had been the only symmetry element, the resultant would have had a component $2u$ in this direction. Hence the crystal class 2, with only one diad axis, allows a resultant vector along the axis; the class 222, with three diads at right angles, has zero vector. The possible combinations of symmetry elements represented by the thirty-two crystal classes can be divided in this way into those which allow a resultant vector (the polar classes) and those which do not.

4.2. The importance of the distinction comes in connection with physical properties which must be represented by a unidirectional vector. Of these, *pyroelectricity* has received most attention in the past. *True pyroelectricity* is the development of electric charges of opposite sign at opposite ends of an unstressed crystal which is heated (or cooled) uniformly. '*False*' *pyroelectricity* is the similar development of charges when there is a temperature gradient or when the heated crystal becomes subject to stress. It is difficult to distinguish between these experimentally, and for this reason they have often been treated together, but the theoretical distinction is important. True pyroelectricity implies a resultant vector in the crystal, and can therefore only occur in the polar classes (sometimes called, for this reason, the pyroelectric classes). (Neumann's rule, which relates geometrical crystal symmetry to the symmetry of physical properties, provides a different formulation of the same statement.) Piezoelectricity and false pyroelectricity, on the other hand, must be described by tensors, and the above argument does not apply; they can occur in any crystal class (such as 222) which lacks a centre of symmetry (except the cubic class 432).

Spontaneous polarization is also represented by a resultant vector and can therefore only occur in the polar classes. We have just seen that the class 222 is not polar; yet the evidence that Rochelle salt belonged to that class seemed well established. The solution was provided by Jaffe in 1935. He realized that the evidence of spontaneous polarization implied a lowering of the symmetry to class 2 (more correctly written 211, since the polar axis is still chosen to be the x axis, and the y and z axes are now associated with no symmetry repetition). This is monoclinic, and he predicted a departure of the interaxial angle from 90° by $3'$. Later work detected this and confirmed his explanation; the details are given in Chap. 2. The position may be summed up by saying that the true symmetry is monoclinic in the

Curie range, but that the departure from orthorhombic is so small it may easily escape detection except by very sensitive methods.

4.3. There is a close relation between spontaneous polarization and pyroelectricity. The latter (as Lord Kelvin realized) implies the existence in the crystal of a polarization which changes with temperature. The difference between this and the spontaneous polarization of a ferroelectric lies in the fact that the latter is reversible. Suppose for a given material the coercive fields were large and the applied fields small; then the crystal would remain polarized in one direction, and behave like a pyroelectric. Ferroelectrics in fact are all pyroelectrics. The pyroelectric behaviour of Rochelle salt was demonstrated by Mueller (see Chap. 2).

It does not follow that all pyroelectrics would become ferroelectric if we could apply a large enough field. It may happen that the internal forces resisting reversal of polarity are so large that they cannot be overcome without breaking down the structure completely.

5 Dipole moment and dipoles

5.1. Spontaneous polarization may be defined in an alternative way as the dipole moment per unit volume. This terminology may suggest that we ought to be able, from the crystal structure, to pick out dipoles each with its own dipole moment: that is, pairs of equal and opposite charges, the product of charge and separation giving the dipole moment. Unfortunately this procedure is generally not legitimate at the present stage of knowledge. There is a dipole moment per unit cell, but it cannot be broken up into separate dipoles without introducing assumptions about the interatomic bonds. The reason is clear: if the dipole is to have any physical meaning (as distinct from a formal mathematical significance) the charges must be bound to each other more rigidly than to other charges outside the dipole.

It is easiest first to consider examples where this holds good. Thus, in a gas where each molecule has oppositely charged ends, the molecules are dipoles; in an ionic crystal subjected to an external electric field, so that there is a relative displacement of positive and negative charges within the same ion, each ion is a dipole. In a crystal structure containing molecules which may change orientation as a whole with respect to the rest of the structure, these molecules may be dipoles. The first theory attempting to explain the dipole moment of Rochelle salt attributed it to the water molecules, which were supposed to be able to rotate relative to the rest of the structure; they constituted permanent dipoles. As we shall see later, this theory proved unsatisfactory.

1. INTRODUCTION

In non-molecular crystals, however, the atoms are linked together in a three-dimensional network by forces which, in general, are of the same order of magnitude throughout. We cannot pick out pairs of atoms which retain their special relationship whatever happens to the rest, because they are bound to their other neighbours by the same sort of forces as to each other. If the environment of the atoms is symmetrical, this is exactly true. In sodium chloride, for example, each sodium is equally associated with six chlorines. We can then formally pair off each sixth-of-a-sodium with a sixth-of-a-chlorine, and all these bonds have equal strength ('electrostatic valence'). But if an atom is in an unsymmetrical environment, there is no way (except guesswork) of making an electrostatic division of its charge between the various bonds, unless we know the distribution of its charge (no longer spherical) in the field of all its neighbours. The assumption of electrostatic point charges is no longer adequate; we need a chemical approach, which can deal with bonds of homopolar character.* No detailed theoretical treatment is yet available for ferroelectric materials, where the bonds are probably semi-polar. Such a theory is a goal to aim at, but cannot yet provide an unquestioned starting-point for identifying individual dipoles.

5.2. It is however possible that dipoles may be identified empirically. The recurrence of certain geometrically-polar groupings of atoms in crystals with abnormal electrical properties is evidence suggesting that the dipoles are associated with these groupings (cf. Chap. 6, § 5.1). In some types of materials the evidence already accumulated makes the identification reasonably convincing, in others it is no more than guesswork. We may hope for advances in knowledge as more work is done on single crystals, correlating the electrical properties in particular directions with the directional features of the various structures.

It must nevertheless be emphasized that, while the dipole moment of the unit cell is directly determined from observable quantities—the spontaneous polarization and the cell volume—the identification of the whole or any part of it with any particular part of the unit cell is a step introducing further assumptions whose experimental justification is always less direct and sometimes entirely lacking. It is therefore necessary to avoid using the idea of individual dipoles in stating the experimental results of X-ray structure determination, which are independent of electrical evidence. This has not always been done in the literature, and it has sometimes led to confusion.

Various attempts which have been made to identify dipoles and to estimate their magnitude will be considered in Chap. 10.

* For an account of homopolar or covalent bonds, see for example A. F. Wells, *Structural Inorganic Chemistry*, 2nd edition (Oxford University Press, 1950).

6 Nature of transition at the Curie point: pseudosymmetric structures

6.1. Outside the Curie range, Rochelle salt becomes truly orthorhombic, and has the symmetry 222. Inside, it is monoclinic, with symmetry 211. The change is a transition between two solid states, from one crystal form to another. It happens reversibly without breakdown of the structure as a whole. From the thermodynamic standpoint the question arises, is it a first-order or a second-order transition?

A first-order transition is one in which there is a discontinuous change of volume and energy; the energy appears as a release of latent heat in an infinitely narrow temperature range. A second-order transition shows no discontinuity in the volume or energy—there is no latent heat; but their temperature derivatives, the expansion coefficient and the specific heat, show anomalies extending over a finite temperature range. Other properties, such as the polarization, show discontinuity in a first-order change but not in a second-order change.

If, however, the discontinuities are very small, they are liable to be masked or smeared out by other effects; for example, the transition temperature may be very sensitive to applied stress. The detection of discontinuities is then likely to depend on the refinement of experimental methods and the perfection of the material available. Indirect thermodynamic arguments (which will be referred to in Chap. 8) can be used to formulate other criteria, but it is not at all clear how far the distinction between first- and second-order transitions has any physical significance in such a limiting case. In Rochelle salt, so far as is yet known, the transition appears to be continuous. An attempt has been made to collect the evidence concerning continuity and discontinuity in the chapters dealing with individual substances.

6.2. A more fundamental distinction has to be made from the structural standpoint, between transitions which occur with and without breakdown of the structure as a whole. The latter can occur reversibly within a single crystal. It follows that the atomic displacements at the transition must be small, and hence the change of volume and of energy must also be small. The transitions which occur in ferroelectrics are all of this type, but the type is by no means confined to ferroelectrics; there are many important examples among minerals. Some of these have been discussed by Buerger (1951). He defines *displacive transitions*, which only involve very small distortions of the atomic network, and contrasts them with *reconstructive transitions*, in which the network is broken up into small parts and reassembled. Thus, for example, the α - β transition in quartz, which

1. INTRODUCTION

occurs reversibly at about 550° C and involves a change of symmetry but no breakdown of the structure as a whole, is displacive, while the transition between quartz and tridymite or cristobalite, which involves a change of linkage of the Si-O network, is reconstructive.

Burger's definition of displacive transition probably covers the transitions in ferroelectrics, though it emphasizes only the crumpling of the framework and not the small movements of atoms relative to the framework which are important in ferroelectrics. A more useful definition is that of *pseudosymmetric structures*. A pseudosymmetric structure is one derived from a structure of higher symmetry by small displacements of the atoms, such that atoms which in the high-symmetry form were on special positions (i.e. mirror planes, rotation axes, or centres) are released from them by the disappearance of a particular symmetry element. In consequence, either the unit cell changes its shape to a more general one—for example, a cube may become a square prism, or a parallelepiped with a rectangular base may become oblique-angled—or else a larger unit cell is formed from two or more of the original units, which are now not truly but only approximately identical. Examples of these will be met in the following chapters. In either case, the change is a topological one—by which we mean that there are no interchanges of atoms on different sites, and no creation or destruction (geometrically speaking) of linkages between atoms, though their relative lengths may be altered.

From an experimental point of view, it is generally easier to learn the shape and size of the unit cell than the positions of atoms within it; indeed there are only a few pseudosymmetric structures for which the exact atomic coordinates are known. This does not matter seriously for a qualitative understanding of such structures, provided their symmetry has been determined unambiguously, since the symmetry requirements, taken in conjunction with the fact that all displacements from the high-symmetry form must be small, are often enough to fix the atomic positions within narrow limits and give us an idea of the general features.

6.3. Rochelle salt, within its Curie range, is a pseudosymmetric structure. It appears unusual in the very small distortion of its unit cell; but it may be that distortions as small as this occur elsewhere and are overlooked because the substances concerned have not been studied in as much detail.

It should be noted that there is no conclusive evidence that the structure of orthorhombic Rochelle salt below -20° C is identical with that above 24° C, though both are related by pseudosymmetric transitions to the same monoclinic form.

7 Twinning and domain formation

7.1. Pseudosymmetric structures commonly give rise to twin formation, especially when they involve changes in shape of the unit cell. It is easy to understand why this should be so. Suppose an orthorhombic unit cell (seen in plan in Fig. 1.6 (a)) becomes monoclinic, retaining the axis perpendicular to the paper as symmetry axis. It can do so with two orientations (Fig. 1.6 (b) and (c)) which are physically equivalent; for a perfect single crystal, not clamped in any way, there is nothing to choose between them. If however the crystal is embedded in an elastic medium, there will obviously be smaller stresses developed at the boundary if it can keep its overall shape as little changed as possible, and this it can do by twinning, as in Fig. 1.6 (d),

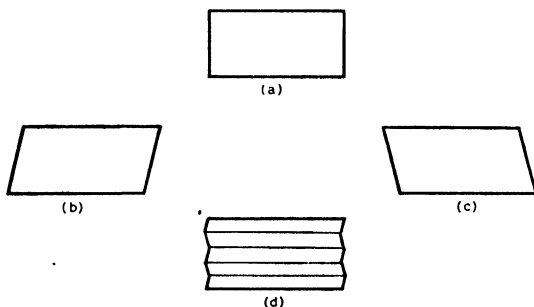


Fig. 1.6. Diagrammatic illustration of twinning in a pseudosymmetric structure.

- (a) Crystal above transition point (high-symmetry form)
- (b), (c) Low-symmetry form: two possible orientations
- (d) Twinned crystal, with low-symmetry form in both orientations.

so that alternate lamellae have the orientation of (b) and (c). Actual crystals are generally clamped in some way, either by their neighbours or their supports, or, if they are large, by their own inertia. Thus twin formation is very likely, unless special precautions are taken to ensure that the crystal is free. The arrangement of twins in any given substance depends on the detailed geometry of the two structures, the case chosen for illustration being a specially simple one; but, whatever it is, an alternation of individuals is always to be expected. In ferroelectric crystals such individuals are often known as *domains*, since their rôle is somewhat comparable to that of ferromagnetic domains, but the analogy is by no means exact.

7.2. Since twinning takes place at the transition from higher to lower symmetry, the details of the texture can be influenced if, during this

1. INTRODUCTION

transition, the crystal is subjected to conditions which favour one particular orientation. If, for example, pressure perpendicular to the polar axis in the low-symmetry crystal raises the Curie point, then linear compression of the solid just above the Curie point will encourage the growth of domains with their polar axis perpendicular to the applied force. An electric field applied in a particular direction can have a similar effect. In practice, good single-domain crystals are prepared by an operation called 'poling', in which the crystal is heated and cooled a number of times through its transition point while subject to an electric field along the polar axis or to appropriate mechanical stresses or to both together.

8 Other materials

Though Rochelle salt remained for some years the only known example of a ferroelectric, others were discovered later. The known ferroelectrics mostly fall into three main groups; the rest must still be classified as 'miscellaneous'. They will be dealt with in the chapters that follow.

- (1) *Rochelle salt*. This group includes, as pure substances, only Rochelle salt itself and its deuterium-substituted analogue. Solid solutions in which there is a small amount of isomorphous replacement of K and Na by other ions are also ferroelectric. Ferroelectricity has not been conclusively demonstrated in any of the pure isomorphous tartrates such as $\text{NH}_4\text{NaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, though there are anomalous properties below room temperature.
- (2) *Potassium dihydrogen phosphate, KH_2PO_4* . The group of isomorphous substances comprises the dihydrogen phosphates and arsenates of the alkali metals K, Rb, Cs, and their deuterium-substituted analogues. Ferroelectricity in certain members of the group was discovered by Busch in 1935, and the others have been added by later work.
- (3) *Barium titanate, BaTiO_3* . The first published evidence on ferroelectricity in this substance came in 1945 from Wul and Goldman in Russia; it had however been described a year or two earlier by von Hippel and co-workers in reports with a limited circulation in America. There are many substances belonging to the same structure family (the perovskite group), and of these there is evidence for ferroelectricity in PbTiO_3 , KNbO_3 , NaNbO_3 , KTaO_3 , WO_3 , and certain solid solutions. Another substance which should be included here is LiNbO_3 .
- (4) *Miscellaneous*. Certain other substances are believed to be ferroelectric. They include cadmium niobate, $\text{Cd}_2\text{Nb}_2\text{O}_7$, which has

the structure of pyrochlore; guanidine aluminium sulphate hexahydrate; and lithium thallium tartrate monohydrate, $\text{LiTlC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$, which, though a tartrate of monoclinic symmetry, is not isomorphous with Rochelle salt.

9 Summary of properties of ferroelectrics: definition

The properties which have been illustrated in the foregoing paragraphs by Rochelle salt are also possessed by most other ferroelectrics. It will be useful to summarize them, and consider which must be regarded as fundamental and which as derived.

- (1) They possess a dielectric hysteresis loop, indicating reversible spontaneous polarization.
- (2) They show disappearance of hysteresis at a certain temperature, the Curie point.
- (3) They have a domain structure, which may be visible in polarized light.
- (4) They have a high dielectric constant, rising to a peak at the Curie point.
- (5) The falling-off of their dielectric constant above the Curie point follows a Curie-Weiss law.
- (6) They possess a pseudosymmetric structure.
- (7) Their symmetry places them in a polar class.
- (8) They have a transition at the Curie point to a form of higher symmetry.
- (9) The Curie point is raised (or a lower Curie point lowered) by the application of a biasing field.
- (10) There is a sudden appearance of surface charges at the transition.

Of these, item (1) is characteristic of ferroelectrics and may be used to define them:

A ferroelectric is a crystal possessing reversible polarization, as shown by a dielectric hysteresis loop.

Items (6) and (7) are conditions that must be satisfied, and ferroelectricity may be looked for in any crystal that does so; but unless the pseudosymmetry is close to the true symmetry the coercive field may be too large. Items (2) and (8) describe the effect of changing temperature, provided that the ferroelectric form remains stable, but it is quite possible that a transition to a different polymorph, or even chemical breakdown, may intervene before the Curie point is reached (see for example Chap. 7, § 3). Items (9) and (10) are useful confirmation of (1), in cases where the Curie point is attainable. Item (3) is a normal effect in pseudosymmetric structures, as we have seen, and is in no way limited to ferroelectrics. Item (4) cannot be used as a

1. INTRODUCTION

criterion, since the shape of the curve is texture-sensitive, and not distinctly different from that of substances which show no hysteresis loops; also it is hard to define what is meant by 'high'. It is nevertheless a useful clue. Item (5) refers wholly to the high-temperature side of any possible Curie point, and provides no proof that the material ever achieves a ferroelectric state.

Other criteria, based on various physical properties and their dependence on temperature, stress, and applied field, are less direct; since they are all ultimately dependent on the existence of a spontaneous polarization and polar symmetry, they will not be discussed in detail here.

10 Antiferroelectrics

The analogy with ferromagnetism suggested that, just as there are substances (called antiferromagnetics) with no external magnetic moment because the individual magnetic moments of the atoms are in antiparallel array, so there may be substances with no spontaneous polarization because individual parts of the structure have polarizations in opposite senses. Kittel (1951) predicted these, and called them antiferroelectrics. It was not long before substances were found which were considered to fulfil the prediction. The first of these was lead zirconate, PbZrO_3 . It had a transition point at which there was an anomaly in the dielectric constant; the low-temperature structure gave no dielectric hysteresis loop, but certain of the atoms had antiparallel displacements from their positions in the high-temperature form (see Chap. 5 for details). These features were regarded as characteristic of antiferroelectrics.

Unfortunately the early definitions treated atomic displacements (incompletely known) as equivalent to dipoles, a procedure which (as we have seen in § 5) introduces presuppositions which are themselves ill-defined. It is desirable to look for something more exact, and more easily stated in terms of observable properties. A definition must include some reference to the electrical properties, otherwise it would be too wide to be useful; but it cannot be based on the dipole moment of the unit cell, since this is zero, nor on the dipole moments of parts of the cell, since any identification of these comes at best from rather indirect arguments, and at a later stage in our knowledge of the material. It seems best to use the dielectric constant as a criterion. The anomalies in this only appear at the transition point, and therefore an antiferroelectric can only be recognized as such at or near the transition. It may be defined provisionally as follows:

An antiferroelectric is a substance of non-polar symmetry, showing no dielectric hysteresis, which has a pseudosymmetric transition to

a high-symmetry form accompanied by a sharp anomaly in the dielectric constant.

This definition suffers from the drawback that the pseudosymmetric character of the transition is not always easy to establish experimentally. It is then useful to have a further criterion, based on the fact that a biasing field applied to an antiferroelectric lowers the temperature at which the anomaly occurs, i.e. *decreases* the antiferroelectric range (by contrast with its effect of *increasing* the ferroelectric range).

In practice the anomaly at the transition point of an antiferroelectric generally has a shape more like a cliff than a peak (see Fig. 3.11). It is very much like that of the dielectric constant at right angles to the polar axis in a ferroelectric (for example ϵ_a in KH_2PO_4 , Fig. 3.10).

11 Relation between ferroelectrics and antiferroelectrics: line and cone ferroelectrics

11.1. The point noted in the last paragraph leads us on to the question whether a substance may at the same time be ferroelectric and antiferroelectric. With the definitions as they stand, it clearly cannot be; but something more needs to be said. The spontaneous polarization of a ferroelectric is in one direction only. If we restrict our investigation to directions at right angles to this, it has no spontaneous polarization, and therefore (ideally) gives no hysteresis loop; on the other hand, it may (though it need not) show the pseudosymmetry and anomalous dielectric constant of an antiferroelectric. In other words, a ferroelectric may have antiferroelectric properties at right angles to its polar axis. These effects are only likely to be detectable in single crystals, since they depend on direction.

The origin of these effects is clearly that there exist in separate parts of the unit cell dipole moments so arranged in space that the sum of their components in all directions except one is zero. If we assume that the individual dipoles are all similar, then they must make the same angle with the unique direction, and can be represented (in direction, not in position) by a set of vectors lying on a cone about that direction. The material is ferroelectric, because of the non-vanishing component; it may therefore be called a *cone ferroelectric*.*

* These substances were originally called ferrielectrics (Cross, 1956); but the analogy with ferrimagnetic materials is not very close. The characteristic features of the latter are due to two kinds of atomic dipoles not related by the crystal symmetry, and therefore (in principle) physically distinct, whereas cone ferroelectricity results from a single set of related dipoles. Ferrimagnetism is essentially one-dimensional, cone ferroelectricity three-dimensional.

1. INTRODUCTION

In directions perpendicular to the polar axis it has the properties of an antiferroelectric.

The cone ferroelectric is the most general type of ferroelectric. Possible examples include Rochelle salt itself; others are considered in Chap. 5, § 4.11, and Chap. 7, § 2.3 and § 6.4. The point is discussed theoretically in Chap. 8, § 5.2.

An important special case occurs when all the dipoles are necessarily parallel because they lie on rotation axes of symmetry, as for example must happen in tetragonal BaTiO_3 , where all atoms lie on such axes. In this case the semi-angle of the cone is zero. To distinguish these structures, where necessary, from the more general type, they may be called *line ferroelectrics*. Most theoretical work up to about 1955 limited itself to structures of this special type.

11.2. In preliminary work on any substance, it is not always easy to distinguish whether it is ferroelectric, or antiferroelectric, or neither. Investigation of the dielectric hysteresis may be difficult if the material is electrically-conducting; and where single crystals are not available the shape of the dielectric anomaly may not be very distinctive.

An illustration occurs in the work of Gränicher and Jakits (1954) on solid solutions of the perovskite family. They found transitions accompanied by no anomaly in the dielectric constant, and others accompanied by an anomaly whose temperature was independent of the biasing field. Such transitions are neither ferroelectric nor antiferroelectric.

A good many substances originally reported as ferroelectric are now considered probably antiferroelectric; they are classed as such in the next paragraph.

11.3. Examples of antiferroelectrics arranged according to structure include the following:

- (1) *Rochelle salt group*. It is possible that solid solutions $(\text{K}, \text{NH}_4)\text{NaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ may be antiferroelectric, as may also be Rochelle salt itself below -20°C , but further work is needed.
- (2) *KH_2PO_4 group*. $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{ND}_4\text{D}_2\text{PO}_4$, which are isomorphous with the rest of the group in their high-temperature form, have a transition point below which they become antiferroelectric.
- (3) *Perovskite group*. PbZrO_3 is antiferroelectric, though solid solutions with small amounts of impurities are ferroelectric. It is probable that NaNbO_3 and WO_3 have forms which are antiferroelectric as well as others which are ferroelectric.

- (4) *Miscellaneous*. It is probable that $\text{Pb}_2\text{Nb}_2\text{O}_7$ is antiferroelectric, and also $(\text{NH}_4)_2\text{H}_3\text{IO}_6$ and $\text{Ag}_2\text{H}_3\text{IO}_6$. The evidence about $\text{LiNH}_4\cdot\text{C}_4\text{H}_4\text{O}_6\cdot\text{H}_2\text{O}$ is conflicting. Low-quartz, which has no related ferroelectric, is nevertheless itself an antiferroelectric; the anomaly in its dielectric constant has been demonstrated by Perez (1950).

12 Polymorphism in ferroelectric and antiferroelectric materials

It is easy to see that a variety of pseudosymmetric structures may be derived from the same high-symmetry form, if this contains several independent sets of symmetry elements, any one of which may be removed alone. Thus for example a cube retaining its original volume can suffer three different distortions, according to whether the symmetry axis retained is the tetrad (cube edge), the triad (body diagonal) or the diad (face diagonal), and in each the atomic displacements will be different. Again, the atomic displacements may be such that a true repeat only occurs after twice the original cell length (or even some higher multiple of it). The true cell is then some multiple of the original cell, which is known as a *sub-cell*. The lattice corresponding to the true cell is sometimes called a *superlattice*. Multiple structures can be built up in a great variety of ways.

Since the structures are all nearly alike it is not surprising that the same compound should sometimes occur in more than one low-symmetry form (possibly under the influence of traces of impurities). Some examples of this polymorphism are mentioned in § 11, and these and others are discussed in more detail later in the book.

13 Paraelectrics

The word paraelectric has sometimes been used, by analogy with paramagnetic, to denote the high-symmetry form of a substance which, below its transition temperature, is ferroelectric or antiferroelectric. It has also been extended to cover substances possessing high-symmetry structures in a family which contains ferroelectrics, even if they themselves never undergo a pseudosymmetric transition. Both these usages are rather vague.

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See also p. 149.

Chapter 2

ROCHELLE SALT

One said it was a hedgehog
The second he said, Nay;
The third, it was a pincushion
The pins stuck in wrong way, . . .
And a hunting they did go.

ANON: *The three jovial huntsmen*

1 Orthorhombic crystal structure

1.1. The crystal structure of Rochelle salt was first determined by Beevers and Hughes in 1941. Later work (reported by Shirane, Jona and Pepinsky, 1955) has resulted in slight changes of atomic parameters*, but no major changes in arrangement, except as regards the hydrogen atoms, which were only located indirectly in the earlier work. The structure determination of Beevers and Hughes was made at room temperature, but their results must be taken as applying to the high-temperature orthorhombic form, since their resolution was not great enough to show the effects of monoclinic symmetry, which will be discussed later.

The cell dimensions at 20° C (determined by Ubbelohde and Woodward (1946)) are as follows:

$$\begin{aligned}a &= 11.891 \pm 0.007 \text{ \AA} \\b &= 14.264 \pm 0.008 \text{ \AA} \\c &= 6.225 \pm 0.004 \text{ \AA}\end{aligned}$$

The space group is No. 18, $P2_12_12$, and there are 4 formula-units, $\text{KNa}(\text{COO}.\text{CHOH}.\text{CHOH}.\text{COO}).4\text{H}_2\text{O}$, in the unit cell. The potassium ions lie in special positions on the diad axes parallel to z , forming two pairs not related to each other by symmetry; all the other atoms are in general positions, giving sets of four which are crystallographically equivalent. Atomic parameters according to Beevers and Hughes are given in Table 2.1.

The structure is most easily seen in projection on (001) (Fig. 2.1). The tartrate ions lie inclined to this plane, and some of their atoms overlap in projection. All sodium ions are in equivalent positions and have the same arrangement of six nearest 'oxygen' neighbours lying

* The numerical values are not yet available.

2. ROCHELLE SALT

TABLE 2.1

Atomic parameters in (orthorhombic) Rochelle salt (Beevers and Hughes, 1941), expressed as hundredths of the cell edge. These were originally measured in sixtieths of the cell edge (Beevers, personal communication); hence there is a rounding-off error in the second figure.

Crystallographically equivalent positions are:

$$x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \bar{z}; \frac{1}{2} - x, \frac{1}{2} + y, \bar{z}; \bar{x}, \bar{y}, z.$$

Atom	Parameters		
	x	y	z
K ₁	0	0	05
K ₂	0	50	15
Na	23	99	52
O(1)	12	10	37
O(2)	22	20	12
O(3)	23	40	82
O(4)	06	37	85
OH(5)	16	36	32
OH(6)	29	24	63
H ₂ O(7)	40	08	50
H ₂ O(8)	25	05	87
H ₂ O(9)	44	30	05
H ₂ O(10)	42	40	45
C(1)	15	18	28
C(2)	12	28	42
C(3)	17	27	65
C(4)	15	35	80

roughly at the corners of an octahedron. (We include hydroxyl groups and water molecules under the term 'oxygen'.) Of the two different potassium ions, K₁ has four near 'oxygen' neighbours only (the next nearest being at more than 3.2 Å distance), while K₂ has eight. The distances are given in Table 2.2.

FERROELECTRICITY IN CRYSTALS

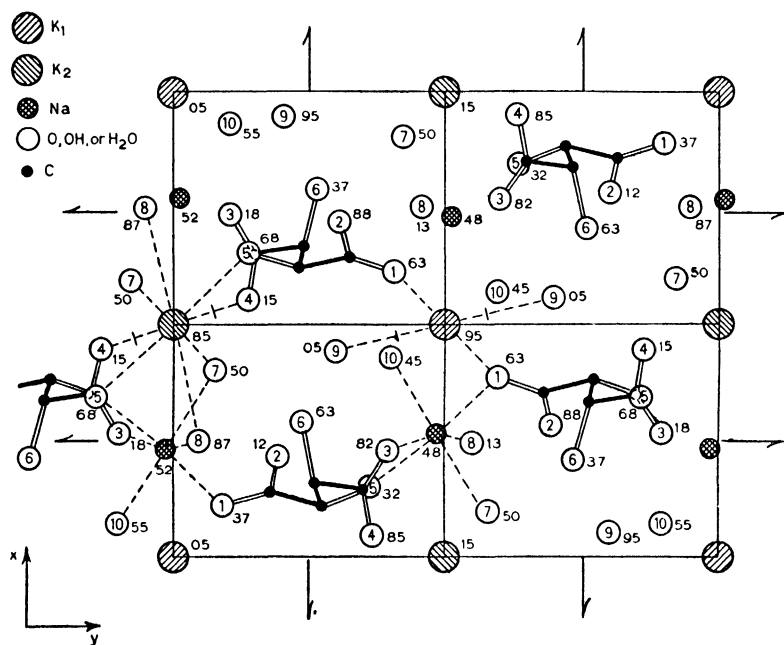


Fig. 2.1. Rochelle salt: projection of structure on 001. Figures beside atom give heights above plane $z = 0$ in hundredths of cell edge; to convert into Ångstrom units multiply by $c/100$. Positions of screw axes indicated by arrows. Environments of representative atoms shown by dotted lines; where these are crossed by a short line at right angles, they involve an atom in the cell vertically above or below that whose height is marked.

TABLE 2.2

Cation-oxygen distances in Rochelle salt (Beevers and Hughes, 1941)

	Å		Å
$K_1-O(1)$	2.79	$Na-O(1)$	2.29
$K_1-O(9)$	3.01	$Na-O(10)$	2.31
$K_1-O(8)$	3.29	$Na-O(8)$	2.34
$K_1-O(10)$	3.52	$Na-O(7)$	2.39
		$Na-O(3)$	2.49
$K_2-O(4)$	2.75	$Na-O(5)$	2.52
$K_2-O(7)$	2.75		
$K_2-O(5)$	2.96		
$K_2-O(8)$	3.07		

2. ROCHELLE SALT

1.2. The positions of the hydrogen atoms were not found directly, but were inferred from the short 'oxygen'-'oxygen' distances, which indicate the existence of hydrogen bonds. The relevant interatomic distances are given in Table 2.3. Beevers and Hughes, considering

TABLE 2.3
Oxygen-oxygen distances

Atoms involved	Coordinates of atoms (in hundredths of cell edge)				Distance Å
O(1)-O(10)	112, 10, 37	92, 10, 55			2.56
O(2)-O(8)	22, 20, 112	25, 05, 87			2.67
O(2)-O(5)	22, 20, 12	16, 36, 32			2.69*
O(3)-O(6)	23, 40, 82	29, 24, 63			2.66*
O(3)-O(8)	23, 40, 82	25, 55, 113			2.89*
O(4)-O(7)	106, 37, 85	90, 42, 50			2.96
O(4)-O(9)	106, 37, 85	94, 20, 95			2.83
O(6)-O(7)	29, 24, 63	40, 08, 50			2.73
O(6)-O(10)	29, 24, 63	42, 40, 45			2.99
O(9)-O(10)	44, 30, 05	42, 40, 45			2.86
O(2)-O(9)	22, 20, 12	44, 30, 05			3.07
O(6)-O(8)	29, 24, 63	25, 05, 87			3.14
O(6)-O(9)	29, 24, 63	44, 30, 105			3.20

* Distances calculated from Beevers and Hughes' published coordinates (other distances as given by Beevers and Hughes).

these distances, put forward a system of hydrogen bonds intended to account for the ferroelectric behaviour; in particular they emphasized the significance of the short bond O(1)-O(10), which lies parallel to the *x* axis, the direction of spontaneous polarization. The theoretical treatments based on this will be considered in Chap. 10. Here it must be emphasized that their experimental evidence is not sufficient to enable the hydrogen bonds to be recognized with certainty. There are certain points, however, which should be noted (cf. Megaw, 1954). It may be taken for granted on chemical grounds that atoms 5 and 6 are hydroxyl groups carrying one hydrogen atom each, atoms 7, 8, 9, 10 water molecules carrying two hydrogens. It cannot be assumed that all of these necessarily take part in hydrogen bond formation. (The hydrogen atoms attached directly to carbon are in any case not concerned in this, and will not be further discussed.) It seems unlikely that distances of more than 3 Å represent a hydrogen bond.

2 Evidence for monoclinic symmetry

2.1. As we have seen in Chap. 1, the existence of a spontaneous polarization along the x axis requires that the symmetry should be lowered from orthorhombic (space group No. 18, $P2_12_12$) to monoclinic (space group No. 4, $P2_111$). (It is more conventional in a monoclinic crystal to let the symmetry axis be y , and write the space group $P2_1$; but in this case it would mean re-naming the axes at the transition point, which is undesirable. The space-group symbol as written records a diad screw axis in the x direction, and no axes of symmetry or normals to planes of symmetry in the y or z directions.)

The first clear statement of this change of symmetry was made by Jaffe (1937). He recognized that the apparent orthorhombic features in the Curie region are due to twinning of monoclinic individuals in which the interaxial angle α (i.e. $\widehat{yoz}$) differs very slightly from 90° . From measurements of the converse piezoelectric effect he estimated that the change of angle was about $3'$. This prediction was verified by Mueller (1940a), who took a rectangular block of Rochelle salt with a base 1 cm. square, glued mirrors on the four faces parallel to the x axis, and made accurate measurements of the angles between them as the temperature changed. He found a change of nearly $4'$ at 0°C , while at 25°C and above no change was detectable.

2.2. X-ray evidence

The monoclinic symmetry might be expected to affect the X-ray diffraction pattern in three ways, (a) difference in spacing between hkl and $h\bar{k}l$ planes, (b) difference in intensity between hkl and $h\bar{k}l$, (c) appearance of $0k0$ reflections with k odd, which are forbidden in the space-group $P2_12_12$. These will be considered separately.

(a) It is sufficient to illustrate this from spacings in the $0kl$ zone. The spacing of the planes $0kl$, $0k\bar{l}$ are given respectively by

$$\sin \alpha [k^2/b^2 + l^2/c^2 - (2kl \cos \alpha)/(bc)]^{-\frac{1}{2}}$$

and
$$\sin \alpha [k^2/b^2 + l^2/c^2 + (2kl \cos \alpha)/(bc)]^{-\frac{1}{2}}.$$

If α is nearly 90° the difference between these will be small, but may be observable for high-angle reflections. If the crystal transforms as a whole, rather accurate measurement of the positions of the spot will be needed, but if it twins, both spots will appear close together on the photograph, and from their separation α can be found. In this way Ubbelohde and Woodward (1946) were able to determine the angle from the splitting of the $0,12,6$ reflection, and found for the departure from 90° a maximum value of about $1.8'$; outside the Curie range the spots were single. It is worth noting that their crystals were from 0.7 to 1.6 mm. in size, and that the individual domains were smaller than those observed by Mueller (1933); further, the hysteresis effects to

2. ROCHELLE SALT

which they attribute a scatter in individual measurements of lattice dimensions in the Curie range (see § 6) might equally affect the values of the interaxial angle.

(b) The very small change of angle, and consequent difficulty of observing the doubling of reflections which should characterize a twinned monoclinic crystal, explains a fact which had hitherto puzzled workers on the subject—why intensities of hkl and $h\bar{k}l$ always appeared to be equal, as required by orthorhombic symmetry. We can now see that the two components of the monoclinic twin will give reflections which overlap; it is only careful work on high-angle reflections that allows any of them to be resolved.

Nevertheless it is possible to use the measured intensities to show that the true symmetry is monoclinic, with the help of a Fourier synthesis. In projection on (001), the orthorhombic structure possesses a centre of symmetry which the monoclinic lacks. This means that the structure factors of the monoclinic structure are complex numbers; if we ignore this and replace them by their moduli, we are introducing a centre of symmetry which should not be there. If we take these moduli—the square roots of the observed intensities, with signs calculated from the orthorhombic structure—and use them as coefficients in the Fourier synthesis of an electron-density map, the result is composite, and consists of a true map of the crystal superposed on a ghost map related to the first by the operation of the symmetry centre. Thus the atoms appear as double peaks, or, if their departure from centrosymmetric positions is small, as unresolved elongated peaks. From the map itself it is not, of course, possible to tell which of each doublet is a 'true peak' and which a 'ghost peak'; other methods must be used. But the existence of doubled peaks indicates the monoclinic symmetry. Similar arguments are applicable to the other projections; the artificially introduced symmetry is not necessarily a centre, but depends on the plane-group of the projection, which is known in each case.

Work of this kind has been carried out by Sundara Rao, Frazer and Pepinsky (see Shirane, Jona and Pepinsky, 1955). They used the deuterium-substituted salt, which has a higher Curie point (see Table 2.4) and is more stable against loss of water at room temperature. They were able to detect doubling of the peaks, notably that due to displacement of the K atoms from their special positions.

It should be noticed that this method uses information from a large number of reflecting planes. Earlier work which tried to study the changes in individual intensities at the transition point was inconclusive because of the difficulty of making corrections for extinction effects, which may be very large, and which themselves change at the transition.

(c) In the orthorhombic space group $P2_12_12$, the screw diad axis parallel to y requires the systematic absence of $0k0$ reflections with k odd. In the monoclinic space group $P2_111$ this diad does not exist and the reflections are allowed. Experimentally they have not been detected by X-rays in spite of search (but see below, § 2.3). Though this fact speaks in favour of orthorhombic symmetry it is not conclusive, since we cannot say for certain that the reflections are completely absent—they might merely be extremely weak. When there is other evidence for the lower symmetry their non-appearance merely shows that any departure of atoms from the ‘orthorhombic’ positions must be very small.

2.3. *Hydrogen atoms in the monoclinic structure*

The question of the hydrogen atoms is important, and needs special consideration. Since the scattering of X-rays by hydrogen is small, their exact position has not much effect on the observed intensities, and the arguments used above do not apply to them. It seems very possible that the whole system of hydrogen bonds may be different in the orthorhombic and monoclinic forms; and that in the latter they may not satisfy even approximately the orthorhombic requirements, but that the two halves of the unit cell in Fig. 2.1 may contain entirely different bond arrangements. Small changes of position of ‘oxygens’ might easily change O–O distances by a few tenths of an Ångström, and therefore make available quite different sites for the hydrogen bonds. Table 2.3 indicates some of the possibilities, but is probably not exhaustive. It is quite possible that the structures above 24°C and below -20°C are different in their bond systems, though alike in their general arrangement of oxygens and cations and in their orthorhombic symmetry.

Though the effect of the hydrogen atoms on the X-ray diffraction is so small it is not wholly negligible, and if accurate intensity measurements are available their positions can be found, both indirectly from accurate O–O distances and directly as peaks in a ‘difference synthesis’; but this comes only at the end of a long and careful process of refinement. The situation is quite different with neutron diffraction, in which the scattering by hydrogens is relatively large, and their contribution to the observed intensities is much more conspicuous. Investigations of Rochelle salt and its deuterium analogue by neutron diffraction have been made by Frazer, McKeown and Pepinsky (1954). They obtained $0k0$ reflections of appreciable magnitude with k odd, showing that the departure of hydrogen atoms from positions of orthorhombic symmetry is much greater than that of the atoms which contribute significantly to the X-ray intensities. It is also reported (Shirane, Jona and Pepinsky, 1955) that there are

2. ROCHELLE SALT

differences in certain hydrogen bonds, but the details are not yet fully known.

3 Chemical discontinuity at the Curie point

An interesting effect has been noticed by Hedvall and Pauly (1935). Pastilles of Rochelle salt, carefully prepared to ensure uniformity, were allowed to dissolve in 80% alcohol. The rate of solution depended reproducibly on the temperature, but dropped sharply by about 40% at 22°C. The effect can be understood if the transition involves a change in the hydrogen bond system, since the process of solution probably begins with an attack on the hydrogen bonds; it is not clear whether the difference between the temperature of the discontinuity and that of the electrically-determined Curie point is significant.

4 Isomorphous substances

4.1. There are other tartrates isomorphous with Rochelle salt, notably $\text{NH}_4\text{NaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, $\text{RbNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, and $\text{TiNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$. None of these, however, has been conclusively shown to be ferroelectric, though the sodium ammonium salt has anomalous electrical properties at low temperatures (Jona and Pepinsky, 1953), and this is true too of the solid solutions it forms with Rochelle salt. The ferroelectric behaviour persists only in solid solutions with very small amounts of the other constituent.

4.2. Other tartrates which have been reported to show ferroelectricity at low temperatures, for example $\text{LiTiC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$, are not isomorphous with Rochelle salt and are dealt with in Chap. 7.

The only pure substance isomorphous with Rochelle salt which is known to be ferroelectric is its deuterium-substituted analogue. The properties of this (where they are known) are described in the following section along with those of normal Rochelle salt.

5 Curie points and effect of pressure

5.1. The Curie points for normal Rochelle salt and its deuterium analogue are given in Table 2.4.

TABLE 2.4

	H compound	D compound
Upper Curie point	24° C	35° C
Lower	-18° C	-21° C

The difference is rather small (cf. KH_2PO_4 , Table 3.3).

FERROELECTRICITY IN CRYSTALS

5.2. The dependence of the Curie point of normal Rochelle salt on hydrostatic pressure is interesting. Bancroft (1938) has shown that the temperatures of both upper and lower points increase linearly with pressure, the upper more rapidly. For a pressure of 2500 kg./cm.², the temperatures are about 50°C and -10°C respectively.

6 Thermal expansion and change of lattice parameters

Measurements of thermal expansion have been made by Valasek (1922), Vigness (1935), Hablützel (1935) and Ubbelohde and Woodward (1946). Their results are summarized in Table 2.5.

TABLE 2.5
Thermal expansion of Rochelle salt
(Figures give expansion coefficients in deg.⁻¹ × 10⁶)

	x axis				y axis				z axis			
	Va	Vi	H	UW	Va	Vi	H	UW	Va	Vi	H	UW
Below -20° C			55	60				30				41
Between Curie points	60	58	35 to 70	50 to 82	38	36		30 to 53	45	42		42 to 58
Above 25° C		58		60		40		54		44		54

Key

Va: Valasek (1922). Optical interferometer; reports average value of coefficients between -10° and 20° C.

Vi: Vigness (1935). Optical lever; reports change of dimensions at about 10 different points in temperature range 12° to 35° C.

H: Hablützel (1935). Abbé-Pulfrich dilatometer; reports expansion coefficient, but not actual change of dimensions, at about 12 points in temperature range -110° to 40° C. Few experimental details given.

UW: Ubbelohde and Woodward (1946). X-ray determination of lattice parameters; report only average values of expansion coefficients over temperature ranges -60° to 30° C., -30° to 25° C., and 25 to 40° C.

The agreement between different observers is not very satisfactory. Hablützel found a definite anomaly in the expansion coefficient parallel to the x axis, and also along the normal to (011); there were maxima at the two Curie points and a sharp dip between them, but no discontinuous jump. Vigness, examining a smaller temperature range in greater detail, found that at the upper Curie point the x

2. ROCHELLE SALT

coefficient did not change but there were small abrupt increases in the y and z coefficients. Ubbelohde and Woodward found differences of the same sign but larger magnitude between the y and z coefficients above and below the Curie range as a whole, and no change in the x coefficient.

The explanation of the discrepancies may lie, partly at least, in the existence of thermal hysteresis. Ubbelohde and Woodward remarked that in the Curie region 'the lattice expansion could assume a range of values, probably due to hysteresis'. This may be associated with the development of pyroelectric charges on the surface of the crystal; if these are wholly or partly retained the field to which they give rise will affect the dimensions of the crystal. There is agreement among the different workers that for reproducible results, at least in the Curie range, the crystal must be held at constant temperature for some hours. It was also suggested by Ubbelohde and Woodward that variations in water content of the crystal might occur; some of the electrical properties have been found to depend on the humidity.

None of these authors detected a discontinuity of spacing at either Curie point. An explicit search for this was made by Valasek, but under conditions where it might have been masked by thermal hysteresis. Ubbelohde and Woodward also looked for it, but do not state an upper limit to the size of a discontinuity which could have escaped detection.

7 Specific heat

Measurements of specific heat have been made by Kobeko and Nelidow (1932), Rusterholz (1935), Wilson (1938), Hicks and Hooley (1938) and Bantle (1942). They are not in good agreement. At the upper Curie point Rusterholz found an anomaly of peak height $6 \text{ cal. mol.}^{-1} \text{ deg.}^{-1}$, area $2.1 \text{ cal. mol.}^{-1}$, and characteristic λ shape. Wilson on the other hand found no anomaly here outside his experimental error of about $0.5 \text{ cal. mol.}^{-1} \text{ deg.}^{-1}$, but a small anomaly of opposite sign and magnitude $1.0 \text{ cal. mol.}^{-1} \text{ deg.}^{-1}$ at the lower Curie point (which had not been studied by Rusterholz). Later workers could detect no measurable anomaly.

Wilson made the half-serious comment that the discrepancies 'would seem to indicate some difference in the properties of Rochelle salt of European and American origin', but Bantle (1942) obtained the same results in Europe as Wilson in Canada. The question of variable water content is perhaps relevant here. It is also worth noticing the kind of material used; Wilson worked with 'small

crystals', Rusterholz with a powder, Bantle with crystal plates. If thermal hysteresis plays any part, it might be more effective in masking an anomaly in the larger specimens. On the other hand, Wilson's result is in better agreement with accepted theory than is Rusterholz's (cf. Chap. 10).

8 Dielectric constant

Measurements of the dielectric constant along the x axis for the free crystal have been made by Mueller (1935), Bancroft (1938), Hablützel (1939), Mason (1939) and Holden and Mason (1940) and are in satisfactory agreement. Hablützel's results for ordinary

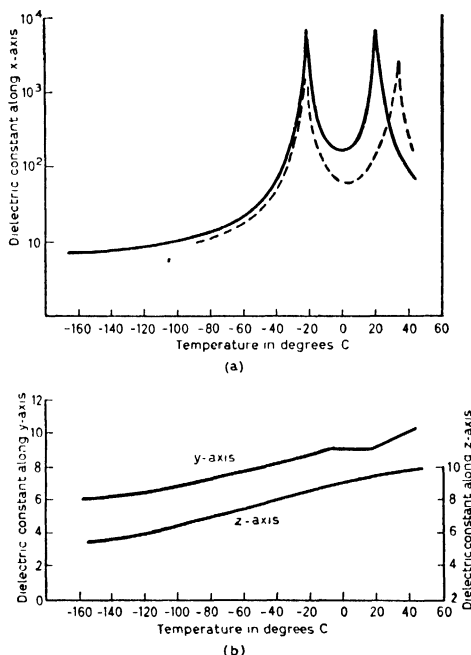


Fig. 2.2. Dielectric constant of Rochelle salt (Hablützel, 1939):

- (a) in direction of x axis (full line, ordinary Rochelle salt; dotted line, deuterium-substituted compound)
- (b) in direction of y and z axes (ordinary Rochelle salt)

Rochelle salt and its deuterium analogue are shown in Fig. 2.2 (a). The peak values are about 4000 and 2000 respectively. Fig. 2.3 (taken from Mueller, 1940) shows on a larger scale the dielectric constant and the reciprocal susceptibility above the Curie point. The experimental values are represented by the dashed lines. (For a discussion

2. ROCHELLE SALT

of the quantities represented by the full lines, see Chap. 8, §3.2.) If the Curie-Weiss law held, the temperature variation of the reciprocal susceptibility should be a single straight line. This is nearly but not perfectly true.

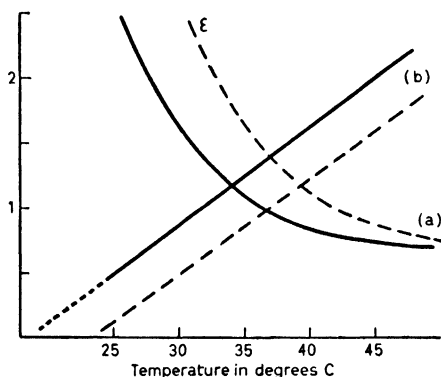


Fig. 2.3. Rochelle salt above the Curie point (Mueller, 1940):

(a) Dielectric constant $\times 10^{-2}$, (b) Reciprocal susceptibility $\times 10$.

Dashed lines give experimental values for free crystal, full lines values for clamped crystal calculated with the help of other observed data.

The dielectric constants along y and z have also been determined by Hablützel. These are shown in Fig. 2.2 (b) for ordinary Rochelle salt; the deuterium-substituted salt follows very nearly the same curve. It is noteworthy that these show only a slight anomaly at the Curie point. At low temperatures, well below the Curie range, all three constants are of the same order of magnitude.

9 Spontaneous polarization and coercive field

These have been determined by Hablützel (1939), and his results are shown in Figs. 2.4 and 2.5. For the ordinary and deuterium-substituted salts the maximum spontaneous polarizations are 0.25×10^{-6} and 0.37×10^{-6} coul. cm.⁻² respectively, the coercive fields 200 and 400 volt. cm.⁻¹ respectively. A set of hysteresis loops at different temperatures is shown in Fig. 1.5.

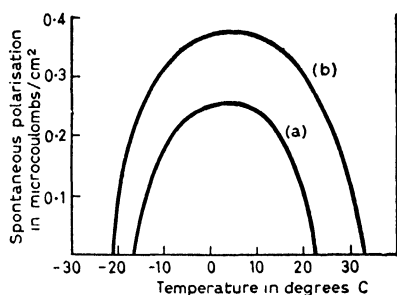


Fig. 2.4. Spontaneous polarization of Rochelle salt (Hablützel, 1939):

(a) ordinary, (b) deuterium-substituted.

FERROELECTRICITY IN CRYSTALS

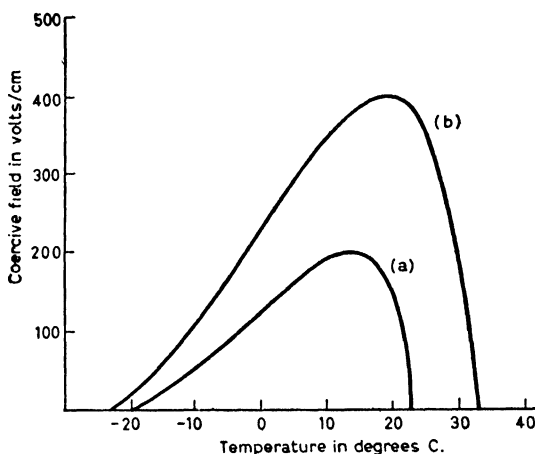


Fig. 2.5. Coercive field of Rochelle salt (Hablützel, 1939):
(a) ordinary, (b) deuterium-substituted.

It has been shown that actual crystals have a spontaneous polarization in the virgin state, which is very stable against external fields (Takahashi and Hara, 1949).

10 Barkhausen jumps and Weiss domains

Mueller (1933, 1935) made some interesting observations on Barkhausen jumps in Rochelle salt. In series with a crystal of Rochelle salt he had an induction coil, loosely coupled with another which was connected to a loud speaker. When the field in the crystal was slowly and continuously increased within a certain range of values sharp clicks were heard. This range corresponded to the steep part of the hysteresis loop. Above the saturation field no clicks occurred; nor did they at any field for temperatures outside the Curie range. They are caused by the sudden release of charge brought about when large regions of the crystal acting as a single unit reverse their polarity.

In some crystals Mueller was able to make these regions visible by taking advantage of their pyroelectric properties. If a finely-divided powder of sulphur, lycopodium and carmine is blown over a charged crystal, oppositely charged faces attract red and yellow particles and become correspondingly coloured. Mueller found that this happened with small crystals, on faces parallel to (100), but for large crystals the faces were covered with patches of red and yellow, indicating opposite polarities in oppositely coloured areas. Occasionally he obtained a regular chequered pattern of spots about 2 to 3 cm. apart. The pattern indicates the domain structure of the crystal,

2. ROCHELLE SALT

which in turn is determined by the particular array of internal stresses imposed on the crystal in its growth from solution and modified by subsequent thermal, electrical and mechanical treatment.

The domain texture has also been observed under the polarizing microscope (Klassen-Neklyudova, Chernysheva and Shternberg, 1948; Furuichi and Mitsui, 1950; Chernysheva, 1950). It can be altered by pressure, such as the application of a needle to the thin section, but the original pattern generally reappears on removal of the pressure. When there is considerable deformation, hysteresis may occur. Miyake (1947), using X-ray intensities to study the domain texture, found that the changes produced on bending a plate disappeared an hour after the plate had been released. The domain texture can also be changed by applying an electric field. Mitsui and Furuichi (1953) observed the propagation of domain walls, and found they moved with a velocity of $0.2 \text{ cm. sec.}^{-1}$ for a field of $100 \text{ volt. cm.}^{-1}$. They also calculated the thickness of the domain wall, and found it very small, of the order of 20 to 30 Å—i.e. about two cell widths.

11 Discussion: mechanism of the transition

It follows from the symmetry of Rochelle salt (§ 1.1) that the K atoms play an essential part in the transition. Whatever displacement or rearrangements are needed by the other atoms in consequence of temperature changes, if they are achieved in one part of the structure they can be achieved in the symmetrically-related part, since the atoms are all in general positions. Further, any forces they exert on the K atoms will be symmetrical, and will not tend to displace it from its special position. Only if the K atom itself requires a different environment will it move from the diad axis, and in so doing lower the symmetry.

In this connection we notice the rather curious environment of K_1 . According to Table 2.2, only four neighbours, two O(1) and two O(9), are reasonably close, and even the distance to O(9) is somewhat on the long side for K—O. It is not surprising to find that the K is easily displaced, and that at a certain temperature it becomes unstable. This does not seem likely to be a direct effect of thermal expansion, which is very small, producing changes of distance which are less than the usual limits of tolerance of ionic radii. On the other hand, it may be an indirect effect, since the interatomic distance has an influence on the degree of covalent character in the bond. In any case, there is evidence that conditions are rather critical with respect to K from the small amount of substitution of other atoms either for it or for Na (which acts as a spacer) which can be tolerated without destroying the ferroelectricity.

The contribution of the hydrogen bonds to the transition is of secondary importance, as can be seen from the rather small effects of substituting D for H.

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Chapter 3

THE TETRAGONAL PHOSPHATES

And the mind must sweat a poison
... that, discharged not thence
Gangrenes the vital sense
And makes disorder true.
It is certain we shall attain
No life till we stamp on all
Life the tetragonal
Pure symmetry of brain.

C. DAY LEWIS: *Transitional Poem*

1 Introduction: potassium dihydrogen phosphate

The most important member of this group of substances is potassium dihydrogen phosphate, KH_2PO_4 . Like Rochelle salt, it is a colourless, water-soluble substance, which can be grown in large crystals from solution. Its Curie point is at -150°C . At room temperature it is tetragonal, belonging to a class without a centre of symmetry. Its ferroelectric properties were discovered in 1935 by Busch and Scherrer. The magnitude of the effect is bigger than in Rochelle salt, and the crystal structure is simpler; hence it has proved a very interesting substance to study.

2 Crystal structure at room temperature

2.1. The room temperature structure was determined by West (1930). It has been confirmed by later work (Frazer and Pepinsky (1953a) using X-rays; Bacon and Pease (1953) using neutrons); as a result of this, small amendments were made to the atomic coordinates, and more direct information was obtained about the position of the hydrogen atoms.

The space group is No. 122, $I\bar{4}2d$; this belongs to the class $\bar{4}2m$ of the tetragonal system. The cell-dimensions* (Ubbelohde and Woodward, 1947) are $a = b = 7.453 \text{ \AA}$, $c = 6.959 \text{ \AA}$. There are 4 formula-units per cell.

It is sometimes convenient to refer the crystal to new axes rotated through 45° with respect to the first set. Then the space-group

* It is clear from the original paper that the lengths there called $\text{\AA}$ were in fact kX (see appendix) and they have been corrected accordingly throughout this chapter. Other workers have used the figures without correction.

FERROELECTRICITY IN CRYSTALS

symbol must be written $F\bar{4}d2$; the new cell-dimensions are $a = b = 10.534 \text{ \AA}$, $c = 6.959 \text{ \AA}$, and the cell contains 8 formula-units.

The small cell is shown in Fig. 3.1, in projection on (001). (The

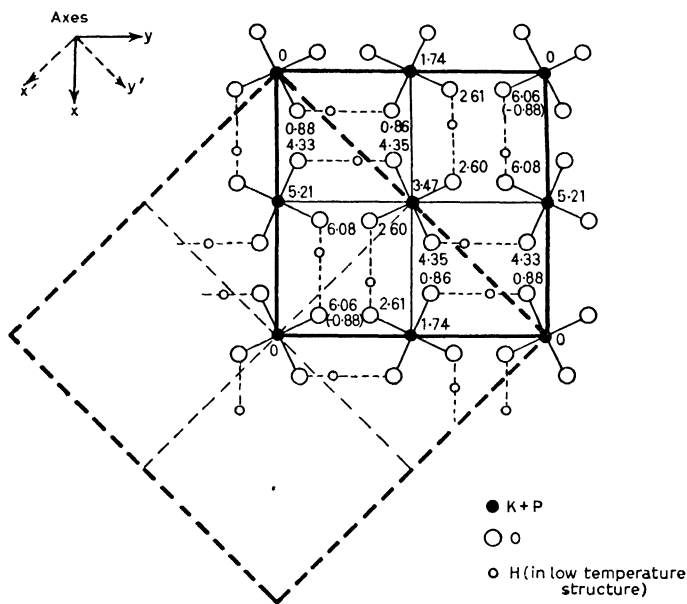


Fig. 3.1. Structure of KH_2PO_4 , projected on (001), showing relation of small unit cell (heavy solid lines) and large unit cell (heavy dashed lines). The z axis is directed upwards in both. Dotted lines show hydrogen bonds (with displacement of H from the centre slightly exaggerated). Figures give heights of atoms in $\text{\AA}$. Heights of K are omitted for clarity; they lie $3.47 \text{ \AA}$ above the corresponding P. (Note that the addition of $6.94 \text{ \AA}$ to the height of any atom will give the corresponding atom in the unit cell above.)

hydrogen atoms should be disregarded for the time being; they will be discussed later.) The relation to the larger cell is indicated. Atomic coordinates are given in Table 3.1.

2.2. The structure is most easily pictured as built up from K atoms and PO_4 groups. These latter each consist of one P atom surrounded by four O's at the corners of a tetrahedron which is nearly but not quite regular, being compressed by about 2% along the tetrad axis. The K and P atoms lie vertically above one another, separated by a height $c/2$. Tetrahedra which adjoin each other in projection are separated by $c/4$ in height, and this means that the upper oxygens of one tetrahedron lie nearly in the same (001) plane as the lower

3. THE TETRAGONAL PHOSPHATES

TABLE 3.1
Cell dimensions * (in Å) and atomic coordinates of KH_2PO_4 (Bacon and Pease)

	Room temperature (Small cell, $I4_2d$)	Room temperature (Large cell, $F4d2$)	132°K (Large cell, $F4d2$)	77°K (Orthorhombic cell, $Fdd2$)
$\left. \begin{matrix} a \\ b \\ c \end{matrix} \right\}$	7.453 6.959	10.534 6.959	10.495 6.919	$\left\{ \begin{matrix} 10.540 \\ 10.458 \\ 6.918 \end{matrix} \right.$
K	$\begin{matrix} x \\ y \\ z \end{matrix}$	$\begin{matrix} 0 \\ 0 \\ \frac{1}{2} \end{matrix}$	$\begin{matrix} 0 \\ 0 \\ \frac{1}{2} \end{matrix}$	$\begin{matrix} 0 \\ 0 \\ \frac{1}{2} + 0.016 \pm 0.002 \end{matrix}$
P	$\begin{matrix} x \\ y \\ z \end{matrix}$	$\begin{matrix} 0 \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ 0 \\ 0 \end{matrix}$	$\begin{matrix} 0 \\ 0 \\ 0 \end{matrix}$
O	$\begin{matrix} x \\ y \\ z \end{matrix}$	$\begin{matrix} 0.1487 \pm 0.0003 \\ 0.0828 \pm 0.0003 \\ 0.1262 \pm 0.0006 \end{matrix}$	$\begin{matrix} 0.0328 \pm 0.0004 \\ 0.1158 \pm 0.004 \\ 0.1261 \pm 0.006 \end{matrix}$	$\begin{matrix} \text{(OH)} & \text{(O)} \\ 0.0339 & 0.1164 \\ 0.1161 \pm 0.0003 & 0.1158 \pm 0.0003 \\ 0.1270 \pm 0.0003 & 0.139 \pm 0.002 \end{matrix}$
H	$\begin{matrix} x \\ y \\ z \end{matrix}$	$\begin{matrix} 0.1476 \pm 0.0014 \\ \left\{ \begin{matrix} 0.226 \\ 0.274 \end{matrix} \right\} \pm 0.025 \\ 0.125 \pm 0.003 \end{matrix}$	$\begin{matrix} \left\{ \begin{matrix} 0.961 \\ 0.937 \end{matrix} \right\} \pm 0.002 \\ \left\{ \begin{matrix} 0.187 \\ 0.211 \end{matrix} \right\} \pm 0.002 \\ 0.125 \pm 0.002 \end{matrix}$	$\begin{matrix} 0.963 \pm 0.001 \\ 0.187 \pm 0.001 \\ 0.138 \pm 0.004 \end{matrix}$

General positions in $I4_2d$ are $x, y, z; y, \bar{x}, \bar{z}; \bar{x}, \bar{y}, z; \bar{y}, x, \bar{z}; \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z; x, \frac{1}{2} - y, \frac{1}{2} + z; y, \frac{1}{2} - x, \frac{1}{2} + z$; together with 8 other positions derived from these by the lattice translation $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

* See footnote on p. 35.

FERROELECTRICITY IN CRYSTALS

oxygens of its neighbour. Thus there are short oxygen-oxygen distances lying nearly in the plane of the diagram (shown by dotted lines in Fig. 3.1). These short distances are explained if they are assumed to be hydrogen bonds, linking the tetrahedra together into a three-dimensional network. The tetrahedra are also linked by the cations. Each K has eight O neighbours, which may be grouped into two interpenetrating tetrahedra, a steep one whose corners are shared with PO_4 groups above and below the K atom, and a flat one whose corners are shared with PO_4 groups in the same (001) plane as the K atom (see Fig. 3.2). Thus there are two independent K-O distances, which are nearly but not exactly equal (see Table 3.2).

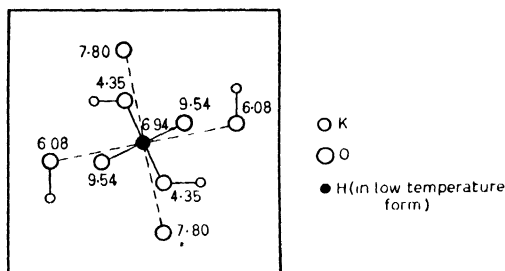


Fig. 3.2. Environment of potassium atom. Projection of central part of cell shown in Fig. 3.1; some of the atoms marked are the same as in Fig. 3.1, while others lie in the cell above. Heights of K and O above base of cell are given in Å. Full lines connect K to O of steep tetrahedron, dashed lines to O of flat tetrahedron.

All atoms of the same kind in the structure are symmetry-equivalent. The K and P atoms lie on inversion centres on the tetrad axes. The O atoms are in general positions.

2.3. It is worth considering the evidence for the location of the hydrogen atoms which follows from the facts so far mentioned. Though indirect, it led to conclusions subsequently confirmed by neutron diffraction.

The short distance of $2.49 \text{ \AA}$ between oxygen atoms not linked to the same cation is strong evidence for the existence of a hydrogen bond. The question arises, are the hydrogens at the mid-points of the bonds, or are they off-centre? Here symmetry considerations are important. The general position in the space group is sixteen-fold; since there are only eight hydrogens, they must lie in special positions. This requirement will be satisfied if they are at the mid-points of the bonds. The only alternative possibility is that they may be disordered, and randomly distributed between two off-centre

3. THE TETRAGONAL PHOSPHATES

TABLE 3.2

Bond lengths in KH_2PO_4 (Bacon and Pease, 1955)

Bond	Length in Å *		
	Room temperature	132°K	77°K
$\left. \begin{array}{l} \text{P-O} \\ \text{P-OH} \end{array} \right\}$	1.541 ± 0.005	1.541 ± 0.004	$\left\{ \begin{array}{l} 1.51 \pm 0.02 \\ 1.59 \pm 0.02 \end{array} \right.$
$\left. \begin{array}{l} \text{K-O} \\ \text{K-OH} \end{array} \right\} \text{(steep)}$	2.894 ± 0.006	2.876 ± 0.003	$\left\{ \begin{array}{l} 2.84 \pm 0.03 \\ 2.90 \pm 0.03 \end{array} \right.$
$\left. \begin{array}{l} \text{K-O} \\ \text{K-OH} \end{array} \right\} \text{(flat)}$	2.825 ± 0.004	2.808 ± 0.005	$\left\{ \begin{array}{l} 2.78 \pm 0.01 \\ 2.82 \pm 0.01 \end{array} \right.$
OH-O	2.492 ± 0.005	2.480 ± 0.004	2.491 ± 0.004
O-H	1.07 ± 0.01	1.07 ± 0.01	1.05 ± 0.014

* See footnote on p. 35.

positions. The X-ray evidence cannot decide between these two possibilities.

2.4. The results of neutron diffraction go only a little farther. They show an elongated peak at the centre of each bond (Fig. 3.3 (a)). This may represent two superposed off-centre peaks, due to statistically distributed hydrogens, or alternatively a single hydrogen at the mid-point undergoing thermal vibrations which are of larger amplitude along the bond than perpendicular to it. In the former case the separation of the two positions is about 0.35 Å. Both interpretations are equally consistent with the experimental evidence.

3 Low-temperature structure

3.1. The symmetry of the low-temperature form was established by de Quervain (1944). Detailed investigations of the atomic positions have been made by Frazer and Pepinsky (1953a) using X-rays, and by Bacon and Pease (1955) and Levy and Peterson (1954) using neutrons.

The low-temperature form is orthorhombic, with its x and y axes

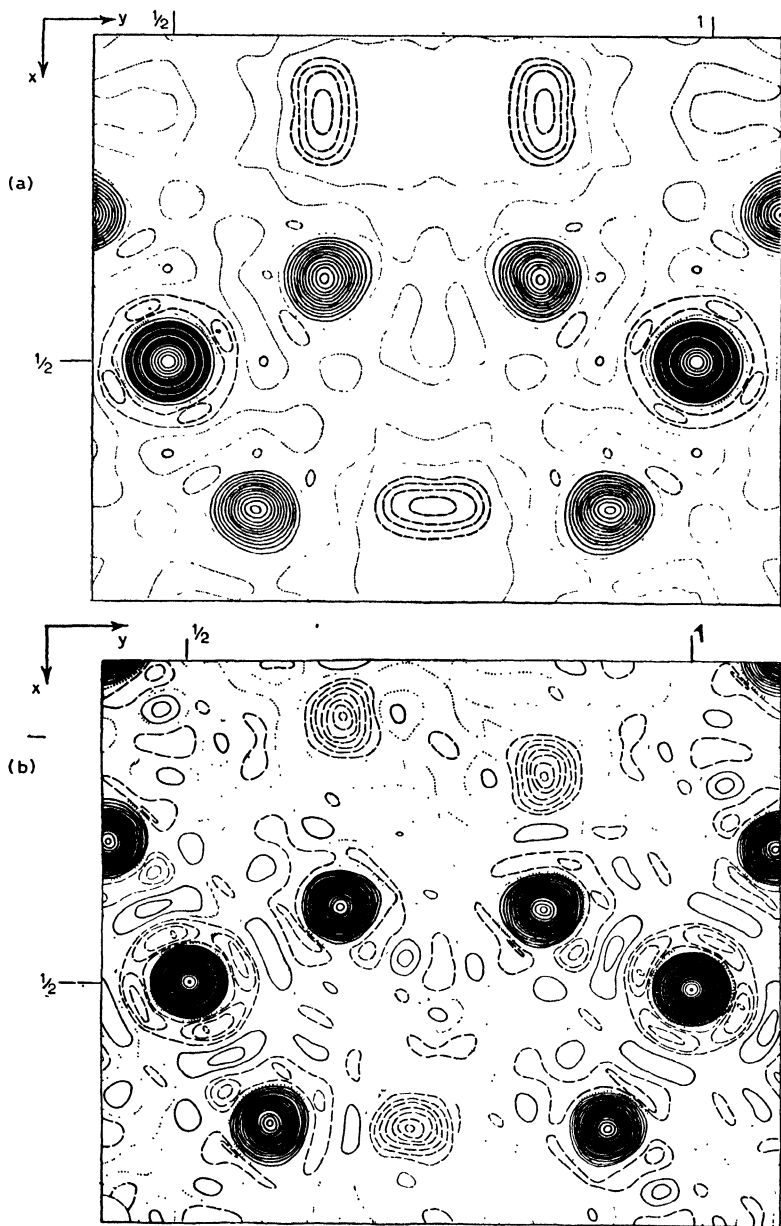


Fig. 3.3. Fourier synthesis, (001) projection, from neutron diffraction (Bacon and Pease, 1953, 1955). (a) at room temperature, (b) at 77°K.

The heaviest peaks are K + P, with O only slightly weaker; the peaks indicated by dashed contours are H. For comparison with Fig. 3.1, put the K + P peaks at $x = \frac{1}{2}$, $y = \frac{1}{2}$ and $x = \frac{1}{2}$, $y = 1$.

3. THE TETRAGONAL PHOSPHATES

approximately at 45° to the original axes of the tetragonal form (i.e. to the edges of the small tetragonal cell). The original square base of the small cell has become a rhombus, and its diagonals are the new axial directions. It is perhaps more convenient to adopt the large tetragonal cell (see § 2.1) from the beginning, to avoid having to make this change of axes. The relation of the different lattices is

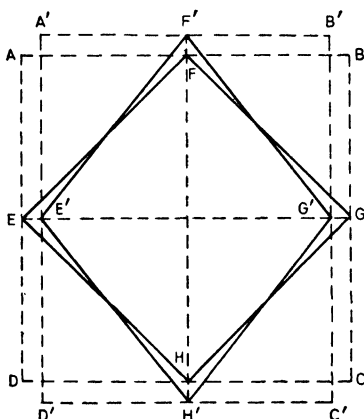


Fig. 3.4. Potassium dihydrogen phosphate: comparison of lattices of high- and low-temperature forms (distortion exaggerated) projected on 001.

ABCD—Base of large tetragonal cell

EFGH—Base of small tetragonal cell

A'B'C'D'—Base of orthorhombic cell

E'F'G'H'—Rhombus inscribed in orthorhombic cell.

shown in Fig. 3.4. The ratio of the new cell edges is 0.992, and the angles of the rhombus differ from 90° by $27'$ (de Quervain, 1944).

The orthorhombic space group * is No. 43, *Fdd2*, and the cell contains 8 formula-units. The general position is still sixteen fold.

3.2. It is important to notice that the qualitative features of the structure can be deduced directly from the symmetry of the pseudo-symmetric transition, which fixes the nature though not the magnitude of the atomic displacements. This argument will be given before considering the determination of detailed atomic coordinates.

* It should be noticed that the conventional order of symbols is different for the tetragonal and orthorhombic systems. In *F $\bar{4}$ d2* (tetragonal) the first symbol (after the lattice symbol *F*) refers to the *z* axis, the second to the *x* and *y* axes, and the third to a direction at 45° to *x*; while in *Fdd2* (orthorhombic) the three symbols refer to the directions *x*, *y*, *z* respectively. The inversion tetrad axis $\bar{4}$ includes a diad axis 2 which is retained in the orthorhombic form; the 'diamond' plane normal *d* in the *x* and *y* directions is also retained; the diad axis at 45° is destroyed.

The lowering of symmetry releases the atoms from their special positions in the high-temperature form. We postulate that displacement of any one kind of atom implies displacement of all, since loss of symmetry in the environment of one means that the others are subjected to unsymmetrically-acting forces: that is, we do not impose any further restriction on any parameter of any atom than is demanded by the symmetry and by the fact that all displacements are small. In this case, the K and P atoms are free to move in the z direction, along what are now diad axes; the O atoms are divided into two independent sets—on the upper and lower edges of the tetrahedra respectively—and the H atoms are permitted to lie in general positions, i.e. in an ordered set of positions not at the centre of the O–O bond. The particular kind of ordering consistent with the symmetry is shown by the small circles in Fig. 3.1. If every H atom is assumed to belong to its nearer O, each 'PO₄' group has two OH groups for its upper corners and two O atoms for its lower corners (where 'upper' and 'lower' are specified by an arbitrary choice of sense of the z axis). On electrostatic grounds, we should expect the sense of displacement of P to be downwards, away from the OH.

Experimental work has confirmed these deductions. The actual values of the coordinates have been found both by X-ray methods (except for the H's) and by neutron diffraction. The results are in general agreement with each other, but the neutron work probably gives more accurate values, and these are listed in Table 3.1. The choice of origin along the z axis, which is arbitrary, has been made so that the P atom has z -coordinate zero. Interatomic distances are given in Table 3.2.

3.3. The effect of the transition is as follows. The framework of O atoms changes very little, except that it suffers the small shear of the lattice as a whole. Relative to this, P moves down about 0.05 Å while K moves up 0.06 Å; H still lies on the O–O line, but is displaced by 0.20 Å from its centre (Fig. 3.3 (b)). The direction of the H displacement is towards that O atom from which P has moved away, thus making the distances P–O shorter than P–OH. Its magnitude is significantly greater than that at room temperature assuming disorder; this indicates a shortening, and therefore strengthening, of the O–H bond within an OH group, and a corresponding weakening of the force of attraction to the more distant O. Of the eight O's or OH's surrounding K, two (the OH's of the steep tetrahedron) are now at a greater distance than the other six, which are nearly equidistant; the difference is, however, small and perhaps within experimental error.

3. THE TETRAGONAL PHOSPHATES

3.4. The thermal vibrations of the atoms have also been studied. Contrary to earlier suggestions of strong anisotropy, Bacon and Pease (1953, 1955) found that there was no significant difference, either above or below the transition point, for the amplitude of vibration of any atom in different directions (assuming that the elongated H peak in Fig. 3.3 (a) is due to disordered atoms). They paid attention in their work to the fact that in the low-temperature form the z -coordinates of the atoms and the thermal amplitudes parallel to the z axis cannot be deduced completely independently of each other from the experimental data, since projections containing this axis lack a centre of symmetry; thus both sets of quantities have rather wide limits of experimental error. (The same difficulty was encountered in BaTiO_3 , Chap. 4, § 3.2.)

4 Domain texture

4.1. Investigations of the domain texture have been made by de Quervain (1944) and Ubbelohde and Woodward (1945). Twinning takes place at the transition by rotation about the normal to (110) or $(1\bar{1}0)$, which is the plane of composition. The two components of the twin have opposite polarity. There is a tendency to repeated twinning on the same plane in a given region of the crystal, forming twin lamellae. De Quervain showed that the width of the lamellae (measured where they intersect the (100) face) was between 0.05 mm. and 0.001 mm., while the size of region indicated by Barkhausen jumps was of the order of millimetres (von Arx and Bantle, 1944). It must be remembered, however, that domain texture depends on the growth of the crystal and its subsequent thermal and electrical treatment, and results obtained for a particular crystal are not universally applicable.

4.2. Some work of Jaccard, Känzig and Peter (1953) on colloidal KH_2PO_4 is of interest. Working below the Curie point, they found that in an insulating medium particles of less than about 1500 Å in size gave an X-ray pattern showing no line-splitting, i.e. no transition to orthorhombic. In a conducting medium, the smallest obtainable particles (about 500 Å) of KD_2PO_4 gave split lines. (No difference is assumed between KH_2PO_4 and KD_2PO_4 , but the latter, having a higher transition point, is ferroelectric at temperatures at which conducting media are available, while the former is not.) The authors explain this by postulating that very small crystals can only transform as a single domain, because walls between domains have a higher energy than the rest of the crystal, and this is relatively much more important in a crystal of small volume. In a non-conducting medium, the surface charges developed in a transition are not

dissipated, and thus give rise to a field opposing the transition. If the crystal is large enough to form domains, they may be of opposite polarity, and so avoid the building-up of surface charges. Känzig (1952) found the wall energy to be 40 ± 20 erg cm.⁻². From calculations of this kind Känzig and Sommerhalder (1953) estimate that the domain walls are two to three cells thick.

5 Isomorphous substances

5.1. The list of other substances isomorphous with room-temperature KH_2PO_4 which have so far been investigated is given in Table 3.3. All of them undergo a transition to a low-temperature form, but the ammonium salts differ from the others as regards the nature of the transition and the low-temperature structure. All the others appear to have forms isomorphous with low-temperature KH_2PO_4 , and are reported as ferroelectric; the ammonium salts have a different

TABLE 3.3
Substances isomorphous with KH_2PO_4

Substance	Transition temperature °K	Reference
KH_2PO_4	123	See text
KD_2PO_4	213	See text
KH_2AsO_4	92	See text
KD_2AsO_4	162	See footnote *
RbH_2PO_4	146	Matthias, Merz and Scherrer, 1947
RbD_2PO_4	218	Matthias, 1952b
RbH_2AsO_4	111	Matthias, Merz and Scherrer, 1947
RbD_2AsO_4	178	See footnote *
CsH_2PO_4	{ 159	Seidl, 1950
	{ 143	Frazer and Pepinsky, 1953b
CsH_2AsO_4	143	See footnote *
CsD_2AsO_4	212	See footnote *
$\text{NH}_4\text{H}_2\text{PO}_4$	148	See text
$\text{ND}_4\text{D}_2\text{PO}_4$	{ 242	Matthias, 1952a; Mason and Matthias, 1952
	{ 230	See footnote *
$\text{NH}_4\text{H}_2\text{AsO}_4$	216	See text
$\text{ND}_4\text{D}_2\text{AsO}_4$	304	Frazer, 1953

* These temperatures were found from cooling curves by Stephenson, Corbella and Russell (1953); electrical work is not reported.

3. THE TETRAGONAL PHOSPHATES

low-temperature structure (described below) which is antiferroelectric, and large crystals tend to shatter during the transition. The common occurrence of ferroelectricity in structures isomorphous with KH_2PO_4 is in striking contrast with its absence in structures isomorphous with Rochelle salt. Mixed crystals have also been studied (e.g. by Matthias and Merz, 1946).

5.2. Some of the substances given in Table 3.3 also possess a second form, which may in fact be the one more easily obtained. For example, KD_2PO_4 generally appears from solution as monoclinic crystals, which change after some days to the tetragonal form (Ubbelohde and Woodward, 1939). The two structures are related, as is shown by the cell dimensions ($a = 7.37$, $b = 14.73$, $c = 7.17$ Å, $\beta = 92^\circ$, for the monoclinic form) and by the continuous character of the transition (Ubbelohde and Woodward, 1942). The detailed structure of the monoclinic form is not yet known. The usual forms of RbH_2PO_4 and CsH_2PO_4 are biaxial, and are probably isomorphous with it, though this needs direct confirmation. In all cases, the tetragonal form can be grown from the solution by seeding it with a small crystal of KH_2PO_4 .

6 Ammonium salts

6.1. Though $\text{NH}_4\text{H}_2\text{PO}_4$ is isomorphous with KH_2PO_4 at room temperature, the cell dimensions are markedly different, as shown in Table 3.4. The room-temperature structure has been investigated

TABLE 3.4

Cell dimensions at room temperature (small cell), in Å *

Substance	<i>a</i>	<i>c</i>	Reference
KH_2PO_4	7.453	6.959	Ubbelohde and Woodward, 1947
KD_2PO_4	7.468	6.930	Ubbelohde, 1939
$\text{NH}_4\text{H}_2\text{PO}_4$	7.479	7.516	Ueda, 1948
$\text{ND}_4\text{D}_2\text{PO}_4$	7.510	7.535	Wood, Merz and Matthias, 1952

* See footnote on p. 35.

by Ueda (1948), who finds that the interatomic distances are very much the same as in KH_2PO_4 , except for $\text{NH}_4\text{-O}$. The distance $\text{NH}_4\text{-O}'$ (flat tetrahedron) is 2.87 Å (cf. $\text{K-O}' = 2.82$ Å), while $\text{NH}_4\text{-O}$ (steep tetrahedron) is 3.09 Å (cf. $\text{K-O} = 2.89$ Å). Thus NH_4 has 4 near neighbours and 4 rather further away, while K has

8 nearly equidistant. This difference is probably a consequence of the tetrahedral structure of the NH_4 ion and its tendency to form hydrogen bonds, though it should be remarked that the tetrahedron of nearest neighbours is very much flattened.

6.2. The structure of $\text{ND}_4\text{D}_2\text{PO}_4$ below the transition point has been determined by Wood, Merz and Matthias (1952); and it is assumed that $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{NH}_4\text{H}_2\text{AsO}_4$ are isomorphous with it. The structure is orthorhombic, but it is quite different from low-temperature KH_2PO_4 . Its axes do not lie along the base diagonals of the small tetragonal cell, as do those of low-temperature KH_2PO_4 (cf. Fig. 3.4), but along the sides. In the tetragonal (high-temperature) structure there are axes of symmetry along the cell sides and along the cell diagonals, forming two independent sets; low-temperature KH_2PO_4 retains one set, and low-temperature $\text{ND}_4\text{D}_2\text{PO}_4$ the other, neither acquiring anything new.

The cell dimensions of low-temperature $\text{ND}_4\text{D}_2\text{PO}_4$ are: $a = 7.48 \pm 0.02$ Å, $b = 7.48 \pm 0.02$ Å, $c = 7.53 \pm 0.02$ Å. The space group is No. 19, $P2_12_12_1$; and there are 4 formula-units per cell.

The essential features of the atomic arrangement are shown in Fig. 3.5. It can be seen that whereas in KH_2PO_4 all H's were attached

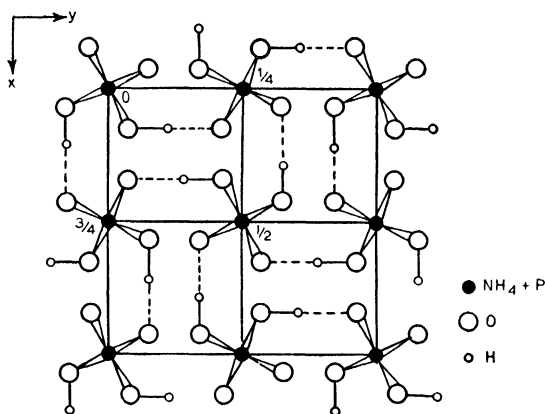


Fig. 3.5. Ammonium dihydrogen phosphate, low-symmetry form. Note: this figure has been drawn to correspond with Fig. 3.1. The H's have been arbitrarily placed so that the x axis lies near the *internal* bisector of the angle $\text{OH-NH}_4\text{-OH}$. This is only permissible as long as we have no other structural or physical means of distinguishing between the x and y axes. If any other criterion is used for this purpose, it will be necessary either to prove that the two definitions are consistent or to alter the arrangement of H's in the diagram.

3. THE TETRAGONAL PHOSPHATES

to the upper corners of PO_4 tetrahedra, here one upper and one lower corner of each tetrahedron is used. In the vertical direction as well as in the plane of the diagram every component of each vector representing an interatomic distance or displacement is balanced by an equal component in the opposite direction. This is a consequence of the space-group, and does not depend on a detailed knowledge of individual coordinates of atoms. It means that the crystal cannot possess a spontaneous polarization; this is in agreement with experimental observation. A structure possessing this symmetry was in fact predicted independently of the experimental work (Nagamiya, 1952).

An investigation of the atomic coordinates has been made by Keeling and Pepinsky (1955).

6.3. It can be seen in a general way why $\text{NH}_4\text{H}_2\text{PO}_4$ should not adopt the same low-temperature form as KH_2PO_4 . We have seen that in the high-temperature form the NH_4 group has four nearest neighbours in a rather flattened tetrahedron. In the low-temperature form, it follows from the symmetry that these four become crystallographically-independent; using the same kind of argument as for KH_2PO_4 (§ 3.2), we may distinguish two as O^{2-} and two as OH^- . On electrostatic grounds, it is likely that the nearest neighbours of NH_4 should all be O^{2-} , particularly if $\text{NH}-\text{O}$ bonds are formed, as seems probable. This is more difficult to achieve with the type of ordering adopted in KH_2PO_4 , which gives only two crystallographically-independent O or OH groups, than with that in $\text{NH}_4\text{H}_2\text{PO}_4$, which, as stated above, gives four.*

Though this seems a reasonable explanation, it cannot be taken as proved. There are 4 independent O atoms each with 3 coordinates to be determined, and neither N nor P need lie on a symmetry axis. This means that the detailed arrangement of the atoms cannot be predicted from the space-group and cell dimensions, as it can in simpler structures.

7 Lattice parameters and thermal expansion

7.1. Lattice parameters of KH_2PO_4 at different temperatures have been measured by von Arx and Bantle (1944), using optical interferometry, by de Quervain (1944) using an ionization spectrometer,

* It is an apparent paradox that low-temperature $\text{NH}_4\text{H}_2\text{PO}_4$, the most complex of the three structures, should have a cell volume about equal to that of the high-temperature structure, and half that of low-temperature KH_2PO_4 . If we compare the number of *formula-units per lattice-point*, however, the true relationship appears: low-temperature KH_2PO_4 , like the high-temperature form, has 2, while low-temperature $\text{NH}_4\text{H}_2\text{PO}_4$ has 4. The volume of the cell depends on our choice of axes, while the volume associated with each lattice-point is absolute.

and by Ubbelohde and Woodward (1947) using powder photographs. De Quervain's work was the most detailed. Above the Curie point he found expansion coefficients of 2.0×10^{-5} and 4.2×10^{-5} in the x and z directions respectively. At the transition from tetragonal to orthorhombic there was an increase in the cell dimensions c and a , and a decrease in b . The values, read from his diagram,* of the changes in spacing from 125° to 117° are as follows:

$$\delta a = +0.040 \text{ \AA}, \quad \delta b = -0.030 \text{ \AA}, \quad \delta c = +0.004 \text{ \AA}.$$

The corresponding change in volume is 0.16%. The published detail is not sufficient to show whether the change is continuous or discontinuous within this temperature interval.

The change in angle $\delta\gamma$ between (110) and ($1\bar{1}0$) can be calculated from the lengths a and b . De Quervain has investigated it at various temperatures, and his results are shown in Fig. 3.7.

7.2. It is interesting to notice that the expansion coefficients of $\text{NH}_4\text{H}_2\text{PO}_4$ are quite different (Mason, 1946). The expansion coefficient in the x direction is 3.2×10^{-5} , nearly independent of temperature. That in the z direction is about 0.3×10^{-5} at room temperature, increasing to 1.0×10^{-5} at -50°C , below which measurements were not made. (For the same temperature ranges the values for KH_2PO_4 were 2.7×10^{-5} parallel to x , 4.5×10^{-5} parallel to z , both nearly independent of temperature.)

8 Specific heat and entropy

At the Curie point, the curve of specific heat versus temperature has an anomaly of λ -shape. Fig. 3.6 shows a typical measurement.

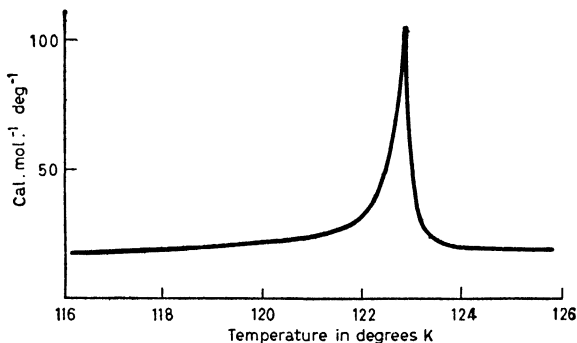


Fig. 3.6. Specific heat of KH_2PO_4 (Bantle, 1942).

* There is a mistake in the labelling of de Quervain's diagram; the text shows that his curves for (100) and (010) are drawn to half the scale of the rest.

3. THE TETRAGONAL PHOSPHATES

Different workers are not agreed about the details. Thus, for KH_2AsO_4 Bantle (1942) finds differences in the profile of the curve, but not the area under it, for specimens of different crystal texture, while Stephenson and Zettlemoyer (1944) find no such anomalies. Again, Stephenson and Hooley (1944) give for KH_2PO_4 a curve which has a lower peak, but a broader spread at the base, than that of Bantle (1942). The values of the heats of transition, and the corresponding entropies, deduced from the shape of the curve, are given in Table 3.5.

TABLE 3.5
Heat of transition, entropy, and change of entropy

Substance	Heat of transition cal. mol. ⁻¹	Entropy change cal. mol. ⁻¹ deg. ⁻¹	Entropy at 298° K cal. mol. ⁻¹ deg. ⁻¹	Author
KH_2PO_4	87 ± 6 57.3	0.74 ± 0.06 0.47	32.23 ± 0.1	S B
KD_2PO_4	100.3	0.47		B
KH_2AsO_4	84 ± 4 84.4	0.90 ± 0.05 0.87	37.08 ± 0.1	S B
$\text{NH}_4\text{H}_2\text{PO}_4$	154 ± 5	1.05 ± 0.04	36.32 ± 0.1	S
$\text{NH}_4\text{H}_2\text{AsO}_4$	220 ± 15	1.02 ± 0.07	41.12 ± 0.1	S

S = Stephenson and co-workers (1944), B = Bantle (1942)

It is possible that there may be variations of transition temperature in different parts of a crystal sample caused by local stresses and local fields. This idea has been used by Bantle to explain his results. Slater (1941) suggests that the transition is intrinsically discontinuous—associated with a true latent heat rather than an anomaly of specific heat—the observed spread being due to the local variations of transition temperature. Mason (1946) has calculated the range of transition temperatures to be expected from the measured elastic properties, and obtains a value of 2.3°, rather less than the spread observed by Stephenson and Hooley, but not very different from that of Bantle. Recent work on a similar problem in BaTiO_3 (see Chap. 4) is in support of the idea of a discontinuous transition.

9 Spontaneous polarization and coercive field

9.1. The spontaneous polarization of this group of materials has been studied chiefly by Swiss workers, in particular by Busch (1938), Bantle (1942), von Arx and Bantle (1943, 1944), Zwicker and Scherrer (1944) and Beck and Gränicher (1950).

Spontaneous polarization is measured directly from the height of the dielectric hysteresis loop when the applied field is big enough to produce saturation. If the loop is square, there is very little difference between remanent polarization (polarization at zero field) and saturation polarization (polarization at the tip of the loop); the Swiss workers generally measure the latter. Below the Curie point, it increases abruptly and reaches a nearly constant value which persists to the lowest temperatures at which saturation can be achieved

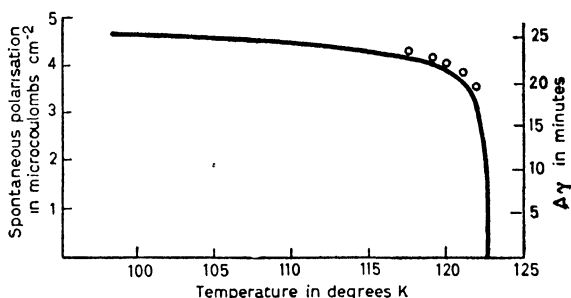


Fig. 3.7. Spontaneous polarization (full curve) and angle of shear (observations shown by open circles) in KH_2PO_4 (de Quervain, 1944).

(observations having been made down to 20°K by Barkla and Finlayson, 1953). Fig. 3.7 shows the curve of polarization versus temperature obtained by von Arx and Bantle (1943). The value for KH_2PO_4 is about 5 microcoul. cm^{-2} , and for the other isomorphous substances it is of the same order of magnitude—about 20 times the maximum value for Rochelle salt.

Von Arx and Bantle (1944) obtained very square hysteresis loops (Fig. 3.8), by use of an experimental arrangement which took 15–20 minutes to trace out a loop. The steps at the corners are due to Barkhausen jumps, in which large regions of the crystal reverse their polarity simultaneously. Similar jumps were observed by Zwicker and Scherrer in loops obtained by electro-optical methods. It is worth noting that these square loops are associated with a steeper drop of P_s at the Curie point than was obtained by earlier workers.

3. THE TETRAGONAL PHOSPHATES

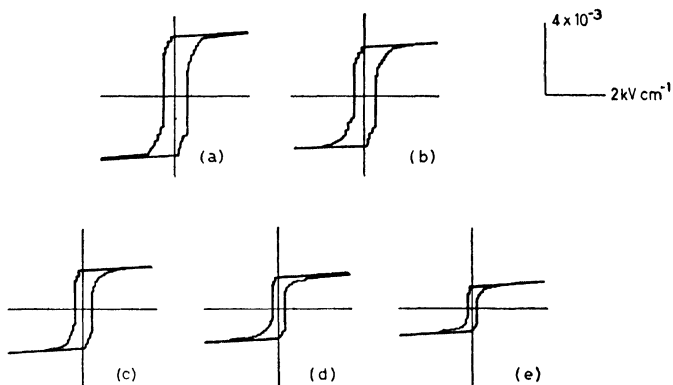


Fig. 3.8. Hysteresis loops in KH_2PO_4 , showing Barkhausen jumps (von Arx and Bantle, 1944).

(a) 116.8°K , (b) 121.5°K , (c) 122.3°K , (d) 122.7°K , (e) 122.9°K .

(Ordinates give experimentally-measured strain, which is proportional to spontaneous polarization.)

9.2. Fig. 3.7 shows a comparison by de Quervain (1944) of the spontaneous polarization with the deformation of the unit cell (measured by the change of angle of the original square). The close fit of the circles (showing change of angle) on the full curve (showing spontaneous polarization) is very striking. De Quervain goes on to show that the ratio of polarization to strain is the same above and below the Curie point, and is practically independent of temperature. Below the Curie point, the ratio of spontaneous polarization to deformation involves experimentally-observed quantities directly. Above it, the ratio of induced polarization to induced strain is equal to the ratio of two experimentally-observed quantities, the dielectric constant and the piezoelectric modulus, since

$$P_z = \epsilon_c E_z = \epsilon_c \frac{x_y}{d_{36}},$$

where x_y is the strain and d_{36} the piezoelectric modulus, both referred to the axes of the small tetragonal cell. De Quervain gives the magnitudes of the ratios in terms of the large tetragonal cell:

$$\left(\frac{P_z}{x_x + y_y} \right)_{\text{below}} = 1.85 \times 10^6 \text{ c.g.s. units}$$

$$\left(\frac{\epsilon_c}{2d_{31}} \right)_{\text{above}} = 1.95 \times 10^6 \text{ c.g.s. units.}$$

He concludes that piezoelectricity and spontaneous polarization are

connected with the same deformation of the elementary cell, and thus both depend on displacements in the structure.

9.3. At low temperatures, Bantle (1942), working with KD_2PO_4 , observed rounded loops, indicating that saturation had not been reached (see Fig. 3.9); similar loops were noted for KH_2PO_4 by Busch and Ganz (1942). This meant an increase in the coercive field so that it had become greater than the applied field. With decreasing temperature, keeping the same applied field, the loops became narrower, and eventually closed up into a straight line. The effect set in at about 80°K for KH_2PO_4 and 150°K for KD_2PO_4 , and had been

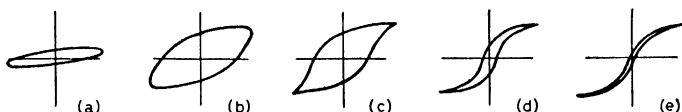


Fig. 3.9. Hysteresis loops in KD_2PO_4 , showing how coercive field increases with decreasing temperature (Bantle, 1942).

(a) 120.5°K , (b) 132.9°K , (c) 137°K , (d) 162°K , (e) 193.6°K

Maximum applied field 4 kV cm.^{-1} in all cases. In (a) and (b), saturation is not attained.

mistaken by earlier workers for a lower Curie point. Curves showing coercive field versus temperature for KD_2PO_4 have been given by Bantle and by Zwicker and Scherrer. More recent work on KH_2PO_4 has been done by Barkla and Finlayson (1953). The coercive field has an abrupt change of slope at 62°K , below which it increases linearly with decreasing temperature to the lowest temperatures observed, about 40°K . The coefficient, $\sim 0.3 \text{ kV cm.}^{-1} \text{ deg.}^{-1}$, was nearly the same for all specimens, but the constant value of the field above 62°K differed from one to another, the majority lying in the range $1\text{--}3 \text{ kV cm.}^{-1}$ (cf. Zwicker and Scherrer's value of 2.5 kV cm.^{-1} for KD_2PO_4). The effect was reproducible after the specimen had once been cooled below 62°K , and it showed no thermal hysteresis.

10 Effect of field on crystal structure

A direct study of the reversal of the structure by a field applied along the z axis has been made by Bacon and Pease (1955). They examined intensities of neutron diffraction from planes parallel to the two prism faces of their crystal, A and B , which were equal in the high-temperature form. In the low-temperature form, with a positive field, the intensity from A was very much smaller than that from B ; with a negative field, the values were reversed. From measure-

3. THE TETRAGONAL PHOSPHATES

ments of angle, it was established that in the first case the reflection from A was 400, and that from B was 040. The change of relative intensities means that there has been a movement of atoms such as to interchange the x and y axes; this is equivalent to a reversal of the sense of the z axis. A corresponding reversal of intensities was observed with the pair 16,0,0; 0,16,0.

11 Dielectric constant

11.1. Dielectric constants have been studied by many workers. For KH_2PO_4 , the constants ϵ_c and ϵ_a (referring to directions parallel to the z and x axes respectively) both have values of less than 100 at room temperature; but while ϵ_c rises at the transition point to a peak

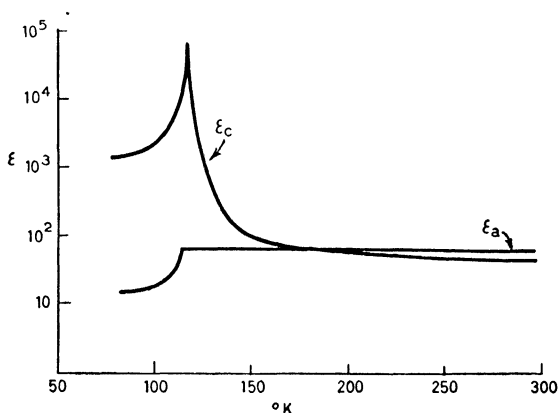


Fig. 3.10. Dielectric constant of KH_2PO_4 (Busch, 1938).

height of about 30,000, ϵ_a remains nearly constant nearly down to the transition point and then decreases very sharply. Fig. 3.10 shows the shape of the curves (Busch, 1938). Above the transition point ϵ_c satisfies a Curie-Weiss law with constants as follows (Mason, 1949):

$$\epsilon_c = 4.5 + \frac{3122}{T - 122}$$

where T is the absolute temperature.

11.2. The other ferroelectric phosphates behave similarly, but the peak values are very different. For KD_2PO_4 , ϵ_c is about 5000, while for RbH_2PO_4 and RbH_2AsO_4 , ϵ (for the powdered material) is only 80–90 at the peak (Matthias, Merz and Scherrer, 1947).

11.3. The ammonium salts behave quite differently. In $\text{NH}_4\text{H}_2\text{PO}_4$, both ϵ_a and ϵ_c rise only slightly as the temperature falls, and drop

FERROELECTRICITY IN CRYSTALS

abruptly at the transition point (Fig. 3.11). In contrast to KH_2PO_4 , ϵ_a rises more rapidly and has a higher peak value than ϵ_c , but both

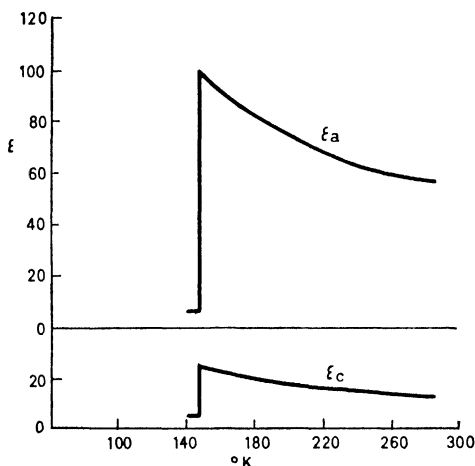


Fig. 3.11. Dielectric constant of $\text{NH}_4\text{H}_2\text{PO}_4$ (Matthias, Merz and Scherrer, 1947).

remain fairly small. They show the kind of anomaly characteristic of antiferroelectrics.

12 Discussion

12.1. We may close this chapter with a discussion of two points of theoretical importance: the mechanism of the transition, and whether it is a first- or second-order one.

12.2. Concerning the mechanism, it is clear that the ordering of the H atom in its bond plays a very important part. This is obvious from the large difference in transition temperature when D is substituted for H. We want to look further and ask whether this ordering could itself be caused by any other individual feature of the structure.

It is first worth considering whether there is any sort of internal clamping by which cross-connections between other atoms might affect the length of the O-H-O bond and hence influence the ordering. This can easily be treated rigorously, because of the simplicity of the structure. There are five independent quantities which must have their correct value: the distance P-O, the two distances K-O, the distance O-H-O, and the angle between the bonds at P. If these are all the requirements—if, for example, there is no restriction on the bond angles at K—they can be met if the structure has five variable

3. THE TETRAGONAL PHOSPHATES

parameters. This is in fact the case, since the two lattice parameters (a and c) and the three atomic parameters of O (x , y and z) are independently variable. Hence the structure can adjust itself to satisfy the five requirements. This explains the rather wide range of substitution of different atoms which is permissible in this structure. It also shows that the ordering of H's in their bonds is not forced by some sort of volume effect.

We saw that the ordering of H's implied a change in the environment of P, so that instead of having four equal neighbours it had two pairs, a pair of OH's and a pair of O's, with consequent changes in bond strength and bond length. It might be argued that it is this change in the bond system of P which forces the ordering of H. However, the rather small difference in the transition temperature (Table 3.3) when P is replaced by As is evidence against this.

It therefore seems likely, though not finally proved, that the ordering of H is spontaneous, but that it can only take place, and can only cause the transition, because the bond system of P can rearrange itself to correspond.

12.3. We also wish to know whether the transition is continuous or discontinuous. Some of the evidence on this point has already been considered—the existence of a finite change of volume inside a small temperature range; the λ -shaped curve for specific heat, with the different spreads obtained by different workers; the very sharp drop of spontaneous polarization with temperature. All these can be interpreted by assuming either that the transition is continuous over a rather small temperature range, or that it is essentially discontinuous but that the temperature at which it occurs is sensitive to variations of pressure or electric field, which may vary locally throughout the sample. Theoretical arguments by Devonshire (1954), based on experimental work by Baumgartner (1950, 1951) on the variation of dielectric constant near the transition point, suggest that the transition is thermodynamically a second-order one. The question will be discussed again in Chap. 10, but cannot be considered as finally settled.

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3. THE TETRAGONAL PHOSPHATES

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Chapter 4

BARIUM TITANATE

When Science once has reached this stage it really will be splendid,
All philosophic doubts will then be definitely ended,
And men will know exactly what they're doing.
Each individual corpuscle will then have been detected,
We'll look up in a Bradshaw and we'll find when one's expected,
And follow out the course it is pursuing.

A. A. ROBB: *Post-Prandial Proceedings of the Cavendish Society*

1 Introduction

Barium titanate, BaTiO_3 , differs from the materials discussed so far in being a ceramic, insoluble in water and melting at a very high temperature (above 1600°C). When pure it is pale yellow in colour, translucent, and with a very high refractive index. It is not easily grown in single crystals; some of the best specimens are thin plates of square outline, but twinning is very common. Most of the early work was done using polycrystalline material.

Strictly speaking the substance should be known as barium titanium oxide, since there are no discrete titanate ions, but common usage has been allowed to override this distinction.

The ferroelectric behaviour of BaTiO_3 was discovered in America during the war (von Hippel, Breckenridge, Chesley and Tisza, 1946); and independently in Russia by Wul and Goldman (1945a, b; 1946), to whom is due the first publication of it. The ferroelectric properties exist at room temperature. The Curie point is 120°C , and there is a change of structure at this temperature (Megaw, 1945). Above 120°C the structure is cubic, below it tetragonal; there are two lower transition points at about 0°C and -90°C , with further changes of structure.

2 Cubic (high-temperature) structure

Above 120°C , BaTiO_3 has the ideal perovskite structure (Megaw, 1945). This is illustrated in Fig. 4.1. It is cubic, with space group No. 221— $Pm3m$, cell edge about $4\text{ \AA}$, and cell-content one formula-unit. All the atoms are in special positions, as follows:

Ti : 000 (corners of cube)

Ba : $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ (body-centring site)

O : $\frac{1}{2}00$, $0\frac{1}{2}0$, $00\frac{1}{2}$ (mid-points of edges of cube).

4. BARIUM TITANATE

(It is legitimate, as some writers do, to take the origin at Ba and move all atoms by $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; but a description based on this makes it harder to visualize the continuity of the structure, and the practice is not recommended.)

Each Ti is at the centre of 6 O's, arranged at the corners of a regular octahedron. The octahedra are linked by their corners into a three-dimensional framework, enclosing large holes which are occupied by Ba's. Each Ba has 12 equidistant O's; each O is adjacent to 2 Ti's and 4 Ba's. The structure may alternatively be thought of as a close-packing of large atoms, one-quarter Ba and three-quarters O, with small Ti's in its octahedral interstices.

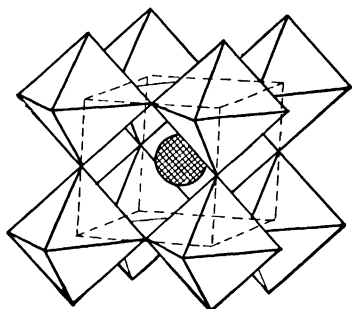


Fig. 4.1. Structure of cubic BaTiO_3 . Ti atoms are at centres of octahedra, O atoms at their corners. Ba atom is shown as hatched circle.

3 Tetragonal structure

3.1. At the Curie point, the transition only involves small changes in the structure. The new structure is tetragonal, with an axial ratio

TABLE 4.1
Atomic positions in tetragonal BaTiO_3

Atom	Coordinates	Values of z		
		(1) Frazer, Danner and Pepinsky, 1955	(2) Evans, 1953: structure with most plausible temperature factors	(3) Evans, 1953: structure with less plausible temperature factors
Ti	0, 0, 0	0	0	0
Ba	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z_{\text{Ba}}$	- 0.014	- 0.012	- 0.015
O ₁	$0, 0, \frac{1}{2} + z_1$	- 0.037	- 0.038	- 0.039
O ₂	$\left\{ \frac{1}{2}, 0, z_2 \right\}$ $\left\{ 0, \frac{1}{2}, z_2 \right\}$	- 0.028	- 0.012	- 0.035

Cell dimensions at 20° C (Rhodes, 1951):

$$a = 3.992 \text{ \AA}, \quad c = 4.036 \text{ \AA}.$$

FERROELECTRICITY IN CRYSTALS

about 1.01 (Megaw, 1945; Rooksby, 1945); the space-group is No. 99, $P4mm$ (which implies that the tetrad axis is uniterminal), and the cell-content is still one formula-unit. The atomic coordinates are given in Table 4.1.

It is easiest to visualize this structure as derived from the cubic by stretching it slightly parallel to one cube edge (see Fig. 4.2 (a)), and releasing all atoms from their special positions so that they can have

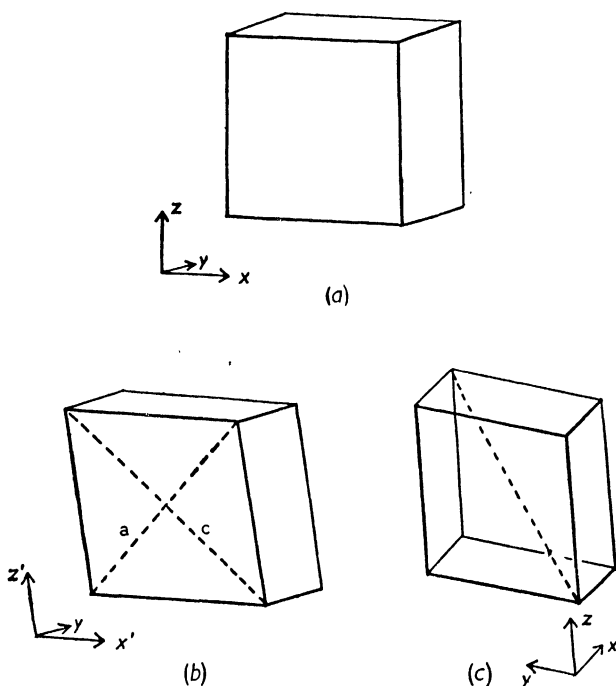


Fig. 4.2. Unit cells of different forms of BaTiO_3 .
(a) tetragonal, (b) orthorhombic, (c) rhombohedral.

small displacements in this direction (Fig. 4.3 (a)). The choice of origin is now arbitrary; it is most convenient to choose it so that Ti remains at 000.

3.2. The sequence of evidence by which this structure was established is worth considering. The tetragonal symmetry and cell dimensions were determined from the positions of lines in powder photographs. From these it follows that the space group can only be $P4mm$ or $P4/mmm$. In the latter, the atoms would retain their special positions,

4. BARIUM TITANATE

having z -coordinates fixed at 0 or $\frac{1}{2}$. But such a structure would have a centre of symmetry, and this was ruled out by the observation that the substance is piezoelectric (Kay and Rhodes, 1947; Blattner, Matthias, Merz and Scherrer, 1947).

There remained the problem of finding the z -coordinates. In principle this could have been done from a knowledge of the intensities of the powder lines; in practice, the accuracy with which these could be measured was insufficient. The coordinates have been obtained only as a result of very careful measurements of intensities given by a single crystal. A difficulty arises because the intensities depend not only on the relative positions of the atomic centres but also on the thermal vibrations which the atoms are undergoing. (A similar difficulty in KH_2PO_4 is mentioned in Chap. 3, § 3.4.) In a structure lacking a centre of symmetry—as this does—it is not easy to separate the two effects for atoms of low scattering factor. The difficulty is less serious for neutron diffraction than for X-ray diffraction, because the relative scattering factor of oxygen is much greater for the former. Table 4.1 gives the results from neutron work (Frazer, Danner and Pepinsky, 1955) and from X-ray work (Evans, 1953). For the latter, two alternative models are included, one requiring temperature factors considered less reasonable than the other, to show the limits of uncertainty. The results from neutron diffraction confirm those from X-rays and improve on their accuracy.

3.3. The bond lengths and bond angles based on the coordinates of structure (1) are given in Table 4.2.

TABLE 4.2
Bond lengths and angles in tetragonal BaTiO_3

Ti-O ₁	$\begin{cases} 1.869 \text{ \AA} \\ 2.167 \text{ \AA} \end{cases}$
Ti-O ₂	1.999 \text{ \AA}
Ba-O ₁	2.824 \text{ \AA}
Ba-O ₂	$\begin{cases} 2.800 \text{ \AA} \\ 2.886 \text{ \AA} \end{cases}$
Angle Ti-O ₂ -Ti	171° 28'

Several important points may be noticed about this tetragonal structure. First, the oxygen octahedra composing the framework are

FERROELECTRICITY IN CRYSTALS

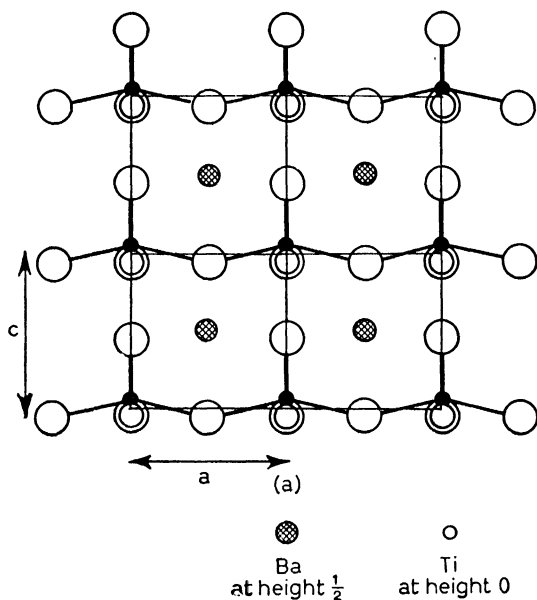


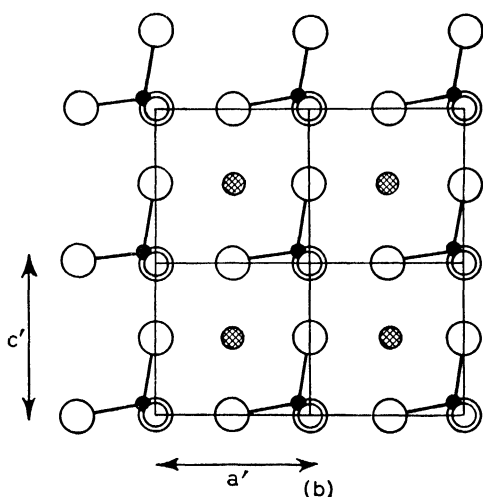
Fig. 4.3. Structure of BaTiO_3 projected on (010),
(a) tetragonal, (b) orthorhombic (referred to monoclinic axes).

very little distorted; the displacement of one set of oxygens relative to the other is small. Secondly, the Ti's are displaced relative to the centres of their octahedra by $0.13 \text{ \AA}$. Thirdly, because these displacements are parallel, the two bonds from O_2 to Ti are inclined at an angle slightly different from 180° . (It should be observed that any uncertainty in the z -coordinate of O_2 makes little difference in the bond lengths but affects very appreciably the angle $\text{Ti}-\text{O}_2-\text{Ti}$.)

4 Orthorhombic structure

4.1. Below 0° C the structure becomes orthorhombic (Rhodes, 1949; Kay and Vousden, 1949); the absolute magnitude of the change is again very small. The structure is most easily pictured as derived from the original cube by stretching it along one face diagonal and compressing it along the other, these diagonals becoming the new orthorhombic axes (see Fig. 4.2 (b)). The third axis retains its original direction but suffers a slight change of relative length. The new space group is No. 38, $Bmm2$, implying that the lattice referred to the new axes is face-centred, and that the structure has a uniterminal diad axis in the z direction. The cell-contents are 2 formula-units, that is, 1

4. BARIUM TITANATE



showing atomic displacements (exaggerated).

Origin taken so that Ba is at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ in both cases.

formula-unit per lattice point. All the atoms may have displacements relative to one another parallel to the z axis.

4.2. Again in this case the X-ray evidence needed to be supplemented by evidence of piezoelectricity before a higher space group, No. 65, $Bmmm$, could be excluded. With that, the space group is unambiguously determined, but it is still not decided whether the diad axis, and hence the direction of displacement of the atoms, is parallel to the long or short diagonal of the original cube face. Analogy with the tetragonal form suggests that the atomic displacements are in the direction of extension, i.e. of the long diagonal, and this has been chosen as the z axis; the space group symbol is accordingly written $Bmm2$. It is important to notice, however, that this evidence is indirect.

Table 4.3 gives a list of atomic coordinates compatible with the space group; the actual parameters have not yet been determined.

4.3. For some purposes it is useful to retain axes corresponding in direction to those of the original cube, and this has been done in the

FERROELECTRICITY IN CRYSTALS

TABLE 4.3

Atomic positions in orthorhombic BaTiO₃ (space-group *Bmm2*)

Atom	Coordinates
Ti	0, 0, 0; $\frac{1}{2}, 0, \frac{1}{2}$
Ba	$\frac{1}{2}, \frac{1}{2}, z_{\text{Ba}}$; $0, \frac{1}{2}, \frac{1}{2} + z_{\text{Ba}}$
O ₁	$\frac{1}{4} + x_1, 0, \frac{1}{4} + z_1$; $\frac{1}{4} - x_1, 0, \frac{3}{4} + z_1$; $\frac{3}{4} - x_1, 0, \frac{1}{4} + z_1$; $\frac{3}{4} + x_1, 0, \frac{3}{4} + z_1$
O ₂	$0, \frac{1}{2}, z_2$; $\frac{1}{2}, \frac{1}{2}, z_2$

Cell dimensions at 4° C (Rhodes, 1951):

$$'a' = 'c' = 4.017 \text{ \AA}; \quad '\beta' = 90^\circ 12'$$

$$a = 5.656 \text{ \AA}, \quad b = 3.986 \text{ \AA}, \quad c = 5.675 \text{ \AA}.$$

projection of the structure shown in Fig. 4.3 (b). The cell then has monoclinic geometry. The angle β is $90^\circ 12'$ (Rhodes, 1951). It is a useful convention to distinguish all dimensions and indices referred to such axes by enclosing them in inverted commas (Wood, 1951).

5 Rhombohedral structure

Below -90° C, yet another form is found (Rhodes, 1949; Kay and Vousden, 1949). The unit cell is the rhombohedron formed by stretch-

TABLE 4.4

Atomic positions in rhombohedral BaTiO₃ (space-group *R3m*)

Atom	Coordinates, referred to hexagonal axes
Ti	0, 0, 0; $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$; $\frac{1}{3}, \frac{2}{3}, \frac{2}{3}$
Ba	$0, 0, \frac{1}{2} + z_{\text{Ba}}$; $\frac{2}{3}, \frac{1}{3}, \frac{5}{6} + z_{\text{Ba}}$; $\frac{1}{3}, \frac{2}{3}, \frac{1}{6} + z_{\text{Ba}}$
O	$\frac{1}{3} + 2x_0, \frac{1}{6} + x_0, \frac{1}{6} + z_0$; $\frac{5}{6} - x_0, \frac{1}{6} + x_0, \frac{1}{6} + z_0$; $\frac{5}{6} - x_0, \frac{2}{3} - 2x_0, \frac{1}{6} + z_0$; $\frac{1}{2} - x_0, -2x_0, \frac{1}{2} + z_0$; $2x_0, \frac{1}{2} + x_0, \frac{1}{2} + z_0$; $\frac{1}{2} - x_0, \frac{1}{2} + x_0, \frac{1}{2} + z_0$; $\frac{1}{6} - x_0, \frac{1}{3} - 2x_0, \frac{5}{6} + z_0$; $\frac{1}{6} - x_0, \frac{5}{6} + x_0, \frac{5}{6} + z_0$; $\frac{2}{3} + 2x_0, \frac{5}{6} + x_0, \frac{5}{6} + z_0$

Cell dimensions (Kay and Vousden, 1949):

$$a_{\text{rhombohedral}} = 3.998 \text{ \AA}, \quad \alpha = 89^\circ 52'$$

$$c_{\text{hexag.}} = 6.942 \text{ \AA}, \quad a_{\text{hexag.}} = 5.649 \text{ \AA}.$$

4. BARIUM TITANATE

ing or compressing the original cube along its body diagonal (Fig. 4.2 (c)), which becomes the permissible direction for atomic displacements. The space group is No. 160, $R3m$, and the cell-content is one formula-unit. The angle between the rhombohedral axes differs from 90° by $8'$ (Kay and Vousden, 1949). It is not explicitly stated whether the angle is acute or obtuse, but by analogy with the tetragonal form one would expect an acute angle, and this has generally been taken for granted though without proof. Here again, the detailed atomic parameters have not been found. The coordinates, referred to hexagonal axes (which are easier for purposes of calculation), are given in Table 4.4.

6 Hexagonal barium titanate

When pure BaTiO_3 is quenched from high temperatures ($\sim 1600^\circ \text{C}$) a different form is obtained. It is hexagonal; its structure (worked out by Burbank and Evans, 1948) is not closely related to those with which we have been dealing, and it does not undergo any further transitions. The transition between it and the cubic form is reconstructive, not displacive, and is very sluggish (Rase and Roy, 1955). It is not ferroelectric. It will not be considered further here.

7 Cell dimensions and thermal expansion

7.1. Careful measurements over a wide temperature range have been made by Kay and Vousden (1949). Their results are shown in Fig. 4.4.

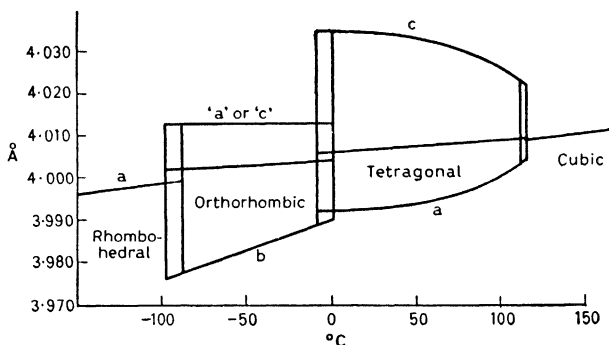


Fig. 4.4. Variation with temperature of cell edges and cube root of cell volume of BaTiO_3 (Kay and Vousden, 1949).

At the transition from cubic to tetragonal, there are discontinuous changes in the axial lengths (which earlier work by Megaw (1947) could not distinguish). The variation of axial ratio with temperature

FERROELECTRICITY IN CRYSTALS

is shown by the dotted curve in Fig. 4.5. It can be seen that below the transition there are further continuous changes of axial lengths in the same direction, but the curves gradually flatten out towards 0°C . Discontinuous changes occur again at the two lower transitions. All the transitions show thermal hysteresis—that is, a difference between the temperatures of transition according to whether the material is being heated or cooled.

It is important to notice that there is a discontinuous (though small) change of volume at the 120° transition.

7.2. The absolute values of cell dimensions and axial ratios determined by different workers do not agree exactly; those quoted in

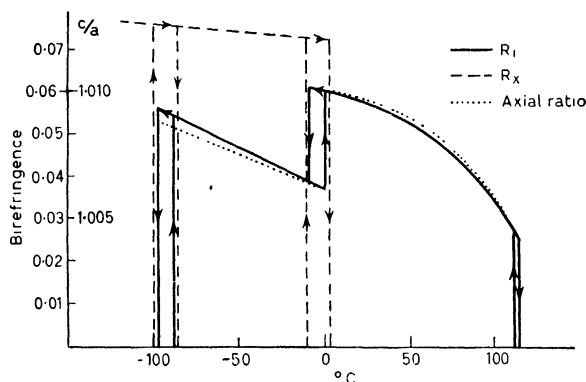


Fig. 4.5. Variation of birefringence and axial ratio with temperature (Kay and Vousden, 1949).

Tables 4.1, 4.3, 4.4 must be taken as typical only. Possibly some of the variations may be explained by impurities or non-stoichiometric composition of the material, but it seems likely that there is also an effect of crystal size, and perhaps of imperfections in the crystal. It has been shown (Harwood and Klasens, 1950) that the axial ratio depends on the temperature at which the crystal was fired, decreasing as the firing temperature decreases from about 1400°C to 900°C . Below 800°C cubic crystals are obtained, with cell volume slightly greater than the tetragonal form. Cubic single crystals of about 1 millimetre in size have been grown at 850°C (Novotsiltsev and Khodakov, 1952); they are not ferroelectric but show an anomaly at about -50°C , suggesting that they transform directly to rhombohedral. Heated above 1100°C , they revert to tetragonal on cooling.

8 Twinning and domain texture

8.1. When a single crystal undergoes transition from cubic to tetragonal, the tetrad axis may be any one of the three original cube edges, and in either direction along the edge. If the crystal is small and perfect it may transform to a single tetragonal crystal; if it is subject to local stresses, either from clamping by its neighbours or from internal imperfections, it will twin in such a way as to reduce stresses to a minimum.

Two kinds of twin are known. The first was described in detail by Kay (1948). Two individuals are related by rotation about the normal to a face of the form $\{101\}$, and this face is the composition plane common to the two. The tetrad axes are approximately at 90° ; more exactly the angle between them is given by $2 \tan^{-1} c/a$, which, for $c/a = 1.011$, is $90^\circ 38'$. Very commonly, twinning is repeated on the same plane, giving rise to a series of lamellae (Fig. 4.6 (a), (b)). With larger crystals, different regions use different planes of the same form as twin planes, giving sets of lamellae at right angles to each other (Fig. 4.6 (c), (d)). Large crystals may have even more complicated arrangements based on the same law, sometimes giving very pretty effects under the polarizing microscope (Matthias and von Hippel, 1948; Forsbergh, 1949). Extensive areas may be divided up into regions of equal size, with the same domain pattern in each, regularly repeated. This suggests some periodic regularity in the factors which give rise to twinning, whatever they may be. (It is worth remarking that periodic regularity has also been observed in the distribution of dislocations in imperfect crystals, and the two effects may perhaps spring from similar causes.)

The second kind of tetragonal twin was investigated by Merz (1952). Two individuals are related by rotation about the normal to a face of the form $\{100\}$, which is the composition plane. The tetrad axes are thus at 180° to each other. Photographs are shown in Figs. 4.6 (e) and (f); in 4.6 (f), both the 180° twinning and the 90° twinning may be seen.

Twinning also occurs in the orthorhombic and rhombohedral structures (Kay, 1948; Forsbergh, 1949). In the orthorhombic form, the individuals are related by rotation about the normal to a face of the form $\{101\}$ or $\{111\}$ (two different laws); in the rhombohedral form, by rotation about the normal to rhombohedral face (111).

The question of the movement of twin boundaries in an electric field will be dealt with in § 15, and discussion of 'boundary walls' between domains will be left till then.

8.2. The evidence for the foregoing statements about twinning comes partly from X-ray work, partly from optical studies. When a single

FERROELECTRICITY IN CRYSTALS

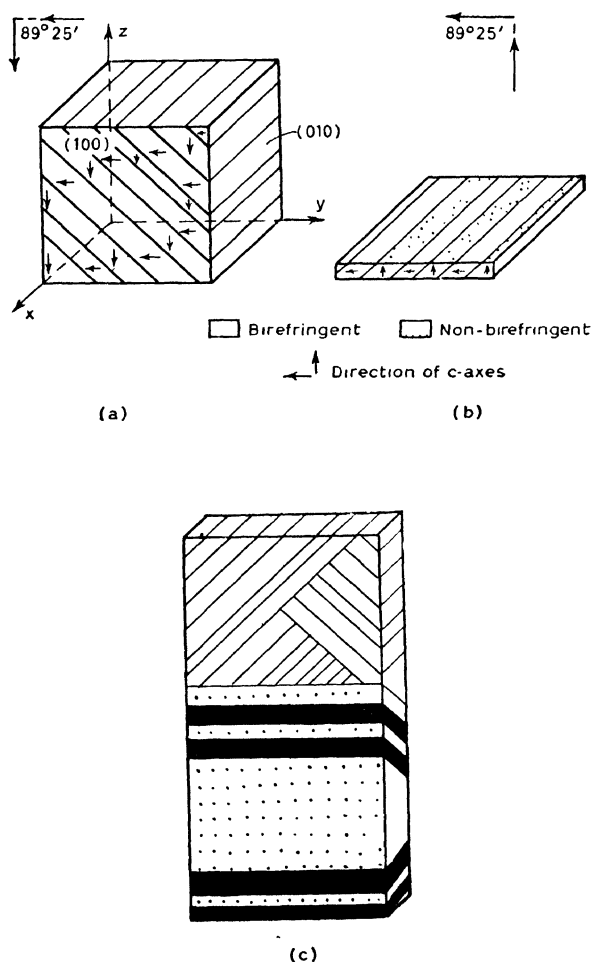
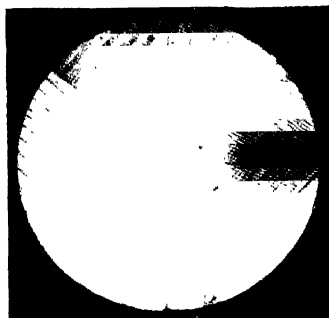
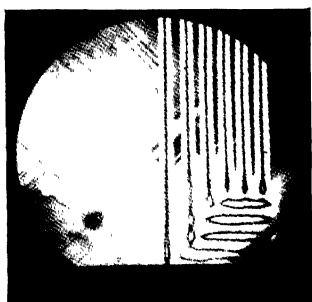
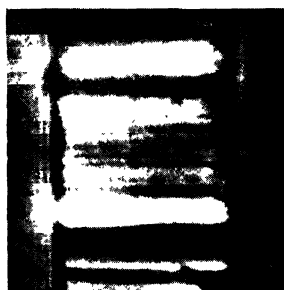
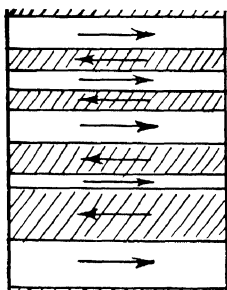


Fig. 4.6.i. Domain formation in tetragonal BaTiO_3

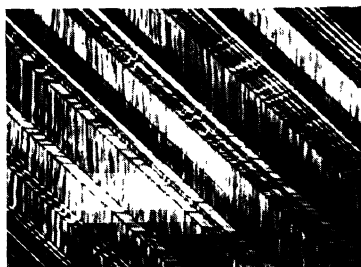
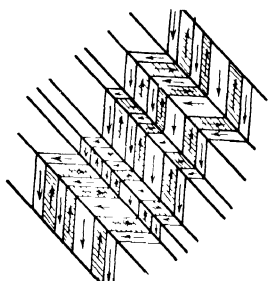
- (a) Lamellar twinning on a single plane (011) (Kay, 1948)
- (b) Lamellar twinning on $(01\bar{1})$ in a plane parallel to (001) (Kay, 1948)
- (c) Crystal with different regions showing lamellar twinning on (011), $(01\bar{1})$, (101), $(10\bar{1})$ (Kay, 1948)



(d) Complex crystals showing 90° twinning in different orientations (Blattner, Känzig, Merz and Sutter, 1948)



(e) Edge view of plate, showing 180° twinning (Hooton and Merz, 1955)



(f) Complex crystal showing both 90° and 180° twinning (Hooton and Merz, 1955)

Fig. 4.6.ii. Domain formation in tetragonal BaTiO_3

4. BARIUM TITANATE

crystal changes to a twin, single spots on an X-ray photograph are replaced by pairs or more complex groups. The relative displacement of the spots, in magnitude and direction, shows the orientation of the components of the twin, and the relative intensities their abundance. This method of studying the transition was developed by Kay (1948). It is generally not possible, however, to tell by this method how the components are arranged within the specimen—for example, whether they consist of multiple lamellae or of a pair of thick slabs—or what their composition plane is.

Optical methods give fuller information. If a doubly-refracting crystal section is examined between crossed nicols, it appears dark (extinguishes) when the direction of the polarizing or analysing nicol is parallel to a principal vibration direction—that is (for the cases considered here) to a symmetry direction or its projection on the plane of the section; if the section is perpendicular to a tetrad or triad axis it is always dark. By this means the symmetry directions in the crystal can be found. The distinction between the different symmetry directions is made by finding which has the greater and which the lesser refractive index (slow and fast vibration directions respectively); this assumes, of course, that the optical properties of a single crystal are known. These are considered in the next section.

Tetragonal twins with their tetrad axes at 180° offer more difficulty. While the 90° twins extinguish in different positions (because the angle between the axes is not exactly 90°), thus marking out a clear boundary, the 180° twins extinguish together. With careful illumination, however, the domain boundaries may be made to show as thin white lines on a dark ground, presumably because of local differences of refractive index due to boundary strains (Fig. 4.6 (e)). Another very effective method is to etch the crystals with hydrochloric acid, and examine them in reflected light (Hooton and Merz, 1955). The positive end of a domain etches rapidly, the negative end hardly at all.

8.3. For a complete knowledge of the orientation of each component in the 90° twins, it remains to establish the sense of the uniterminal axis. This cannot be done optically, but there is another line of argument. Consider a vector along the uniterminal axis. Components of this perpendicular to the twin boundary cannot change sign on crossing the boundary; otherwise, for example, if the vector represented a separation of electric charge (i.e. a dipole) there would be a piling up of charges on the boundary. In Fig. 4.6 (a), (b), (e) and (f), the permissible directions are represented by arrows. (The direction of *all* the arrows at once might of course be reversed.) The formal statement of the twin laws includes this condition about the sense of the axes.

Some interesting details of twin texture, observed experimentally

by Hooton and Merz (1955), have been explained by them in terms of this strong head-to-tail coupling across twin boundaries.

It is worth noticing that all twins actually observed are rotation twins about an axis *normal* to the composition plane. Rotation twins with a twin axis lying *in* the composition plane and reflection twins with the twin plane coinciding with the composition plane are incompatible with the head-to-tail formation, and reflection twins with the twin plane at right angles to the composition plane are less favourable geometrically. This generalization applies to all crystals with polar symmetry.

9 Optical properties

9.1. Barium titanate has a high refractive index, with a peak value of 2.46 at the Curie point (Busch, Flury and Merz, 1948). The double refraction below the Curie point depends on temperature and on wave-length. For the tetragonal form, Forsbergh (1949) found $n_c - n_a = -0.055$ for sodium light at room temperature (where n_c, n_a are the refractive indices along the z and x axes). The crystal is therefore optically negative; its indicatrix* is an ellipsoid of revolution, compressed along the z axis. The double refraction increases considerably for wave-lengths towards the violet end of the visible spectrum (Cross, Nicolson, Zlotnicki and Whiddington, 1950); its magnitude is about 0.12 at 4000 Å, suggesting that there may be an absorption band near 3800 Å. There is also an increase with decreasing temperature (Kay and Vousden, 1949; Forsbergh, 1949); this takes the form of a discontinuous jump at the Curie point, followed by a steady increase as the temperature falls (Fig. 4.5). The shape of the curve is almost exactly the same as that for the variation of axial ratio with temperature, implying that the double refraction is proportional to the difference of the axial ratio from unity.

At the 0° transition, there is another apparently discontinuous jump in the double refraction (in which, as we shall see below, the change of direction is more important than the change of magnitude); this is followed by a steady increase. Forsbergh showed, by examination of a small single crystal optically and electrically, that the smaller refractive index in the (010) plane is associated with the direction of the polar axis, i.e. the z axis. He concludes that this is the elongated axis (cf. § 4.2) because in a homogeneous isotropic solid subject to external stress the direction of extension is the direction of low refractive index. This argument is plausible but falls short of complete

* The indicatrix is the ellipsoid whose radius in any direction is proportional to the refractive index of the crystal for plane-polarized light with an electric vector parallel to that direction.

4. BARIUM TITANATE

proof; however, it is in agreement with conclusions reached from analogy with the tetragonal form.

9.2. The values of the three principal refractive indices can be derived from the observations of Kay and Vousden (1949).^{*} These authors showed that the refractive index n_b , in the direction of the y axis, is greater than n_e , in the direction of another cube edge. (The original paper does not make this quite clear, because the terms 'slow direction' and 'fast direction' are used in a sense not now generally current; the above statement was confirmed personally by Dr Vousden.) They also measured the double refraction in cases of 'symmetrical extinction' and 'straight extinction' respectively, which they called R_X and R_1 . By definition, $R_X = n_a - n_e$ and $R_1 = n_b - n_e$; to a good approximation, $n_e = n_a - \frac{1}{2}R_X$ (from the fact that the 010 section of the indicatrix is an ellipse with axes n_a and n_e). If values of R_1 and R_X read from Fig. 4.5 are substituted in these expressions, then just below the 0° transition $n_b - n_a \simeq 0$, $n_a - n_e = 0.073$; and just above the -90° transition the values are 0.019 and 0.075 respectively. Thus at the upper temperature the indicatrix is nearly an ellipsoid of revolution compressed along the new z axis; at the lower temperature the two axes of the ellipsoid perpendicular to this have become unequal.

In the rhombohedral form, magnitudes of the double refraction have not been recorded, but Forsbergh (1949) has shown that the sign is negative, i.e. that the indicatrix (here again an ellipsoid of revolution) is compressed along the triad axis.

9.3. Throughout these investigations, the identification of directions in the crystal was the vital point. This was made possible by two facts, (1) that the crystals generally showed faces of the original cube as bounding faces, (2) that application of an electric field could be used to re-orient crystal domains with their polar axes in a known direction relative to the field. This will be discussed in more detail later in the chapter.

10 Latent heat, specific heat, and change of entropy

The variation of specific heat with temperature has been studied by a number of workers. As in the other ferroelectrics, the anomaly is small and difficult to measure accurately. Harwood, Popper and Rushman (1947) found a peak at the 120°C transition with a height of $0.61 \text{ cal. deg.}^{-1} \text{ mol.}^{-1}$ and a width (at base) of several degrees.

^{*} These results are in substantial agreement with the values obtained by Jona, Shirane and Pepinsky (1955), who, however, make a different choice of axes.

FERROELECTRICITY IN CRYSTALS

Later workers confirmed this qualitatively, but found a greater peak height and widths varying from over 20°C (Sawada and Shirane, 1949) to about 3°C (Volger, 1952). An illustration is given in Fig. 4.7. Sawada and Shirane noted that their peak shape depended on the texture of their sample (a ceramic). Anomalies were also found at the two lower transitions.

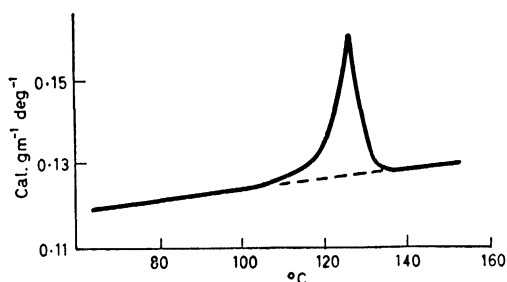


Fig. 4.7. Specific heat of BaTiO_3 (Shirane and Sawada, 1952).

The anomalous heat content is measured by the area of the peak above its background, and values obtained by different investigators are given in Table 4.5.

For the two lower transitions, the entropy changes have been measured by Todd and Lorensen (1952). Values have been deduced by Jaynes (1953) and Shirane, Danner, Pavlovic and Pepinsky (1954) from the experimental curves of the other workers quoted above. The results are recorded in Table 4.5, but in view of the unreproducibility of the peak shapes it may be questioned how far they have meaning.

TABLE 4.5
Changes in heat content and entropy of BaTiO_3

	120° C transition	0° C transition	- 90° C transition	Authors
Anomalous heat change, in cal. mol. ⁻¹	47	16	—	Blattner, Känzig and Merz, 1949
	46	15	14	Volger, 1952
	—	26	12	Todd and Lorensen, 1952
Entropy change, in cal. deg. ⁻¹ mol. ⁻¹	0.12-0.13	0.06-0.09	0.04-0.07	Shirane, Danner, Pavlovic and Pepinsky, 1953

4. BARIUM TITANATE

The experimental curves suggest that the anomalous heat changes are not abrupt, but are spread over quite a large temperature range, with a λ -shaped peak. It remains possible, however, that this spread is a secondary effect due to thermal hysteresis (which is known to exist from the study of cell dimensions, cf. Fig. 4.4) and to local stresses in the material. That this is in fact the true explanation is proved by some interesting experiments of Roberts (1952). He used the fact that an applied electric field will bring about the transition from cubic to tetragonal at temperatures near the Curie point—reversibly if the material is above the Curie point, irreversibly if it is below it in the range affected by thermal hysteresis. Above the Curie point, there was an adiabatic temperature change of 0.5°C , reversible according to whether the field was switched on or off. Below it, there was an irreversible change of 0.5°C , and no further anomaly in the heat content as the crystal was cooled to lower temperatures. This shows the existence of a true latent heat; Roberts estimated that its value was not less than 15 cal. mol.^{-1} .

11 Spontaneous polarization and coercive field

The true value of the spontaneous polarization can only be found by the use of single-domain crystals. Early investigations of the hysteresis loops in BaTiO_3 were made with ceramic materials, where the crystals are oriented in different directions, and only the component parallel to the field contributes to the hysteresis loop. A true single-domain crystal is characterized by an almost rectangular loop; it is hard to illustrate, because on the screen of the cathode-ray oscilloscope the almost-vertical sides do not show up. Only in so far as different domains reverse their polarization at different field strengths is there any rounding of the corners of the loop. If twinned crystals are used, it is difficult to be sure whether all domains have been aligned by the field; if some have not, the apparent polarization will be too low. Improved production of single-domain crystals is therefore likely to be accompanied by higher reported values of the spontaneous polarization, and a greater sharpness of jump at the Curie point. This has in fact been found with tetragonal BaTiO_3 . Early measurements (Hulm, 1947; Merz, 1949) gave values of the spontaneous polarization of about $16\text{ microcoul. cm.}^{-2}$ at room temperature. Subsequent work by Merz (1953) and Cross (1953) raised this figure to about $24\text{--}26\text{ microcoul. cm.}^{-2}$, with a discontinuous jump of about $16\text{--}18\text{ microcoul. cm.}^{-2}$ at the Curie point. Both investigators made sure that their crystals were truly single-domain by examining them under the microscope while they were traversing the hysteresis loop. Cross's curve for the variation of spontaneous polarization with temperature is shown in Fig. 4.8. That

FERROELECTRICITY IN CRYSTALS

of Merz is similar, except that his crystal had a rather lower Curie point, which he attributed to impurities not likely to affect its other properties.

With the two low-temperature forms, the directions of spontaneous polarization are not normal to the surface of the plate used, which was originally a tetragonal single crystal. In the orthorhombic form they are likely to be at 45° to the surface, whether the crystal is single

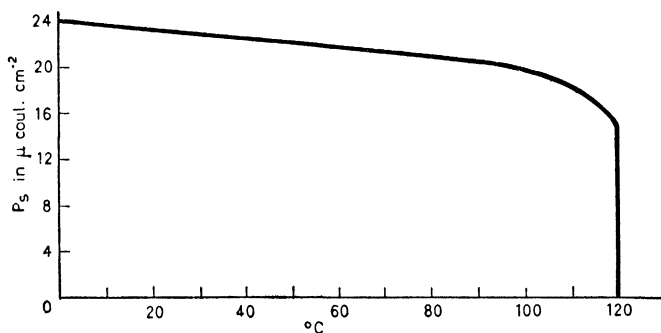


Fig. 4.8. Spontaneous polarization in tetragonal BaTiO_3 (Cross, 1953).

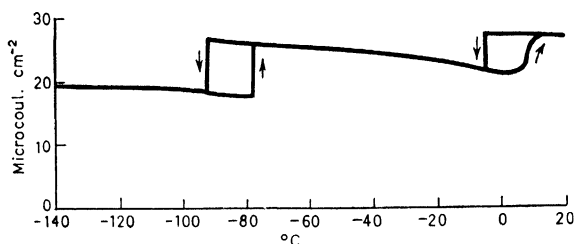


Fig. 4.9. Normal component of spontaneous polarization of BaTiO_3 in low-temperature forms (Wieder, 1955).

or twinned; in a rhombohedral single crystal they would be at $\cos^{-1}(1/\sqrt{3})$ but the twinning is likely to be such that this is not true of all domains. The quantity measured experimentally is the component of P_s normal to the surface. It is therefore not surprising to find that experimental measurements vary from one crystal to another. A representative curve obtained by Wieder is shown in Fig. 4.9. At the 0°C transition, the drop in the component of P_s is roughly in the ratio $1/\sqrt{2}$, which is what we should expect for a single crystal if the change in the magnitude of P_s were small. (The accuracy is not enough to rule out the possibility that *some* discontinuous

4. BARIUM TITANATE

change may occur.) At the -90° transition, the observed drop is considerably greater than the ratio $\sqrt{2/3}$ which would be expected for a single crystal if P_s itself remained unchanged; but, as suggested above, no conclusions can be drawn from this because of the uncertain effect of twinning. Earlier work by Merz (1949) on less perfect crystals gave similar results. Merz also showed that the value of P_s remained nearly constant in the rhombohedral form down to 4.2°K .

The coercive field at room temperature is about $500 \text{ volt. cm.}^{-1}$ for good crystals (Merz, 1953). At the approach to each transition, it shows a decrease with increasing temperature, followed by a sudden increase at the transition (Wieder, 1955). At very low temperatures it increases rapidly as the temperature falls, reaching almost $10,000 \text{ volt. cm.}^{-1}$ at 4.2°K (Merz, 1951).

12 Pyroelectric effect

An interesting application of the pyroelectric effect has been made by Chynoweth (1955). Single crystals were heated on one side by intermittent illumination from a tungsten lamp, and the pyroelectricity was detected by the currents produced in the circuit connecting the two sides.

13 Dielectric constant

13.1. The dielectric constant has a sharp peak at the Curie point; the height and exact shape of the peak depend very much on the texture of the material. Fig. 4.10 shows the curve obtained by Cross (1953),

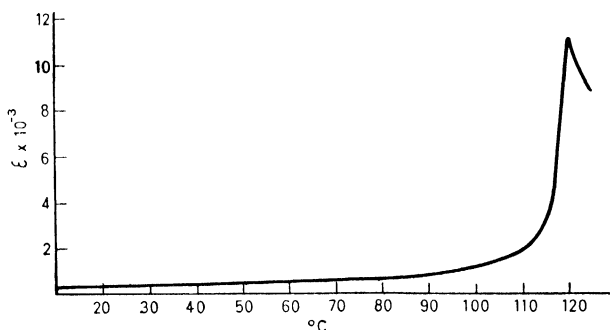


Fig. 4.10. Dielectric constant of tetragonal BaTiO_3 (Cross, 1953).

with weak fields, for the dielectric constant parallel to z . The steep drop on the low-temperature side is very marked, and it seems possible that for a perfect single crystal it may be discontinuous; Drougard and Young (1954) obtained a still more abrupt drop which

FERROELECTRICITY IN CRYSTALS

they believe to be evidence for this. The dielectric constant perpendicular to the z axis, ϵ_a , has been studied by Merz (1949) (Fig. 4.11). It too drops steeply below the Curie point but reaches a minimum of

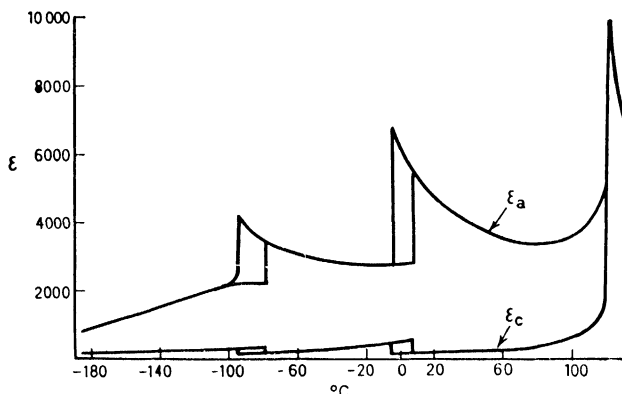


Fig. 4.11. Dielectric constant of BaTiO_3 (Merz, 1949).

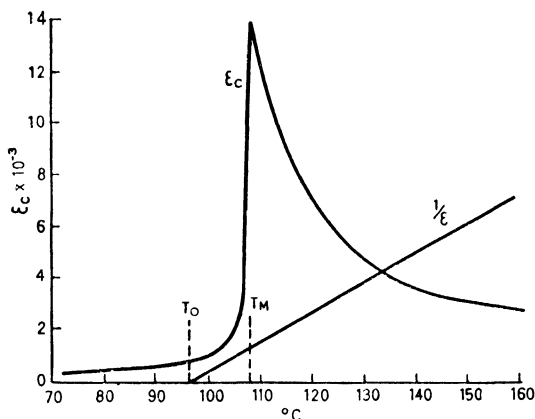


Fig. 4.12. Variation with temperature of dielectric constant and its reciprocal (illustrating Curie-Weiss Law) (Merz, 1953). (N.B. Both T_M , the temperature of the peak value, and T_0 , the point at which the $1/\epsilon$ line cuts the axis, are abnormally low because the specimen was not pure BaTiO_3 .)

about 3000 (at a temperature where ϵ_c has fallen to about 500) and thereafter climbs to a new peak near 0°C . Values measured below 0°C cannot be given any clear meaning, as the directions in the crystal to which they refer cannot be identified.

4. BARIUM TITANATE

13.2. Above the Curie point, the dielectric constant falls rapidly but not abruptly with increasing temperature (Fig. 4.12). It has been shown experimentally by many workers (for example Roberts, 1949; Gränicher, 1949; Känzig and Maikoff, 1951; Merz, 1953) that a plot of $1/\epsilon$ against T gives a very good straight line (Fig. 4.12). If the slope of the line is $1/C$, we may write

$$\frac{1}{\epsilon} = \frac{T - T_0}{C}$$

This expression is in fact the Curie-Weiss law. Here C is the Curie constant; T_0 lies in the neighbourhood of the transition temperature but about 10 or 20 degrees below it.

There is disagreement between different workers about their experimental values of C . Känzig and Maikoff suggest that it depends on the texture of the crystal, as they find values ranging from 1.5×10^5 to 6.5×10^5 deg. for crystals from different melts. Values reported by other workers lie between these extremes. The temperature T_0 is affected by thermal hysteresis, but not in the same way as the temperature T_M of the peak in the dielectric curve; Känzig and Maikoff found, for the difference between values derived from runs with increasing and decreasing temperature, $\Delta T_0 = -6^\circ\text{C}$ while $\Delta T_M = +1.5^\circ\text{C}$.

Känzig and Maikoff (1951) have also investigated the effect of a constant applied field. They find that it makes slight differences in the Curie constant, but rather large differences in T_0 . They attribute this to effects of crystal texture, suggesting that there are gaps in the crystal between the mosaic blocks, which lead to errors in the measured value of ϵ ; these will be systematic for the particular crystal in a given applied field.

14 Changes in the Curie point

14.1. *Effect of pressure*

The effect of hydrostatic pressure has been examined by Merz (1950). For the cubic-tetragonal transition, he showed that with increasing pressure the Curie point is lowered. At high pressures, the effect is influenced by the pre-history of the crystal; but if the crystal is compressed from above the Curie point, a straight-line relationship between pressure and temperature is obtained with a slope of -5.7×10^{-9} deg. cm.² dyne⁻¹. For the tetragonal-orthorhombic transition, increased pressure at first lowers the Curie point by about 3×10^{-9} deg. cm.² dyne⁻¹. The effect appears to be reversed with pressures above 500 atmospheres, but Merz suggests that this may be only the consequence of a rearrangement of domain pattern.

It was observed by Shirane and Sato (1951) that pressure applied parallel or perpendicular to the electrodes raised the Curie point of their sample. The effect of two-dimensional pressure perpendicular to the tetrad axis was studied in detail by Forsbergh (1954). He compressed a single crystal on its edges and found an increase of the Curie point with pressure satisfying a parabolic law, $\Delta T = 3.1 \times 10^{-17} p^2$, where p is in dyne cm.⁻². There was thermal hysteresis between the curves for increasing and decreasing pressures.

14.2. *Effect of solid solution*

So far, only the properties of pure (or effectively pure) BaTiO₃ have been discussed. It will be seen in the next chapter that a very great variety of solid solutions can be formed. In this section, we shall consider briefly only those near the BaTiO₃ end of the range. The effect of solid solution depends on the particular ion substituted. For (Ba,Sr)TiO₃, the Curie point decreases with increasing Sr content, while for (Ba,Pb)TiO₃, it increases with increasing Pb content (Rushman and Strivens, 1946).

It is interesting to compare the effect of solid solution with the effect of hydrostatic pressure, since both alter the lattice constants. Thus, Merz (1950) has calculated the variation of the Curie point with lattice constant in two ways, (1) from the observed change of Curie point with pressure, and the compressibility deduced from Mason's (1948) values of the elastic constants of ceramics, (2) from the observed change of Curie point with composition and of lattice spacing with composition in solid solutions of (Ba,Sr)TiO₃. He obtained values of 3.3×10^3 and 2.8×10^3 deg. Å⁻¹, which were in good agreement. This suggests that the Curie point is essentially determined by the lattice spacing. Results with other solid solutions do not bear this out, however. For example, Dungan, Kane and Bickford (1952), working on the system (Ba,Sr) (Ti,Sn)O₃, found that increasing amounts of Sn increased the lattice constant while lowering the Curie point, though they confirmed the earlier result for the effect of Sr.

14.3. *Effect of electric field*

The effect of a biasing field on the Curie point has been studied by many investigators. Känzig and Maikoff (1951) found that the maximum for the dielectric constant was shifted to higher temperatures by 1.2×10^{-3} deg. cm. volt.⁻¹. This implies that if a sufficiently large field is applied, a crystal becomes ferroelectric at temperatures above its zero-field Curie point. The effect of this on the hysteresis loops has been studied by Cross (1953) and by Merz (1953). Curious 'butterfly' loops are observed, as illustrated in Fig. 4.13. (Such loops

4. BARIUM TITANATE

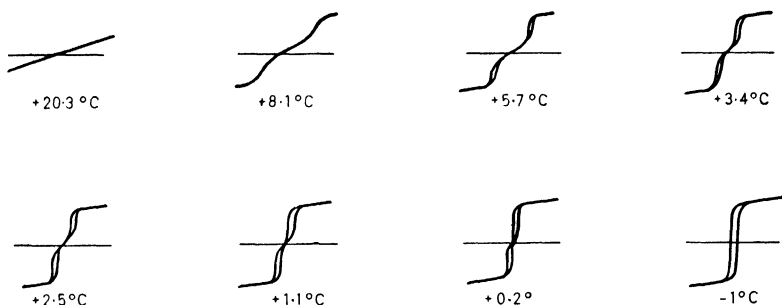


Fig. 4.13. 'Butterfly' loops for BaTiO_3 (Merz, 1953).

Temperatures indicated are differences from zero-field Curie point.

were first noticed with PbZrO_3 , which is dealt with in the next chapter.) From measurement of these loops, Merz found that the shift of Curie point is proportional to the field, and has a value of 1.43×10^{-3} deg. cm. volt. $^{-1}$, in good agreement with the work of Känzig and Maikoff.

15 Domain boundaries and effect of field

This problem has been studied in some detail by Merz (1952, 1954). As we have seen, there are two types of boundary wall, those between domains with their polar axes at right angles (90° walls) and those between domains with their polar axes antiparallel (180° walls). Both types can be moved by application of an electric field, but the latter are of greater interest. Merz observed the domains directly with a polarizing microscope, using a stroboscopic light source with a frequency close to that of the alternating field (cf. Fig. 4.6 (f)). He also made experiments sending an electric pulse through the crystal, and measuring the 'switching times' necessary for reversal of polarity. He found that the 180° walls are very thin, of the order of one unit cell thick; this differs from the state of affairs in ferromagnetic materials, where they are some hundreds of cells thick, but resembles that in Rochelle salt (Chap. 2, § 10) and potassium dihydrogen phosphate (Chap. 3, § 4.2). The wall energy (calculated from elastic constants and the axial ratio), is 7 erg. cm. $^{-2}$, about 5 times the value for ferromagnetic iron, but considerably less than that for KH_2PO_4 (Chap. 3, § 4.2). The width of the domains is about 10^{-4} cm. Merz further made the very interesting observation that, in the process of reversal of polarity by an applied field, it is easier to start new domains than to make the existing domains grow sideways. When a field acting to reverse the polarity is applied, a crop of new domains appears, starting at the surface or at internal imperfections. They

grow in a forward direction right through the crystal, but their sideways growth is practically zero. Merz explains this from the thinness of the boundary wall. Since the wall is only 1 cell thick, energy of the order of magnitude of the whole wall energy is needed to move it sideways by the width of 1 cell.

From his pulse experiments, Merz deduced the velocity of forward growth. He found, at room temperature, an average velocity of 0.5×10^4 cm. sec.⁻¹ for 2000 volt. cm.⁻¹, from which he derived a mobility of 2.5 cm.² volt.⁻¹ sec.⁻¹. This mobility increased with temperature. For fields of some 10,000 volt. cm.⁻¹, the velocity is of the same order of magnitude as the velocity of wall movements in ferromagnetics, but less than the velocity of sound in BaTiO₃. The corresponding mobility in Rochelle salt is 2×10^{-3} cm.² volt.⁻¹ sec.⁻¹.

A suggested mechanism for the forward growth of these domains has been discussed by Pulvari (1954). The experimental work has been extended to the orthorhombic form by Wieder (1955).

16 Nature of transition

The accumulation of evidence from good measurements on single-domain crystals seems to leave no doubt that the 120° C transition in BaTiO₃ is essentially discontinuous, that is, first-order. (The same is probably true of the two lower transitions.) Since, however, the transition temperature can be altered by mechanical as well as electrical stresses, it is not surprising that the behaviour of the crystal near this temperature is highly texture-sensitive. In particular, it is sensitive to stresses associated with the formation of domains. Caspari and Merz (1950) noted differences of this kind between different crystals, and explained them in this way, and Känzig (1951) examined the effect by a study of the X-ray extinction. The existence of domains is not in any way the cause of the transition, which is ideally a discontinuous single-domain process, but they influence its detailed progress and hence the value of many of the properties in the neighbourhood of the transition point.

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See also p. 149

Chapter 5

THE PEROVSKITE FAMILY

So pleas'd at first the tow'ring Alps we try,
Mount o'er the vales, and seem to tread the sky,
Th' eternal snows appear already past
And the first clouds and mountains seem the last:
But, those attain'd, we tremble to survey
The growing labours of the lengthened way,
Th' increasing prospect tires our wand'ring eyes,
Hills peep o'er hills, and Alps o'er Alps arise!

POPE: *Essay on Criticism*

1 Introduction

1.1. There are a large number of compounds possessing structures of the perovskite family—a term which is meant to include the ideal perovskite structure itself (described in Chap. 4) and all other structures which can be derived from it by small distortions and displacements of atoms or by omission of atoms not essential to the framework. Many of these compounds are ferroelectric or antiferroelectric, but by no means all; it is useful to survey the whole family and see what generalizations can be made and what differences noted.

1.2. General rules for ionic structures

Not all compounds with the formula ABO_3 have a perovskite-type structure. A criterion for the stability of the different types was put forward by V. M. Goldschmidt (1926), based on the rules which he had derived empirically for binary compounds which are ionic or predominantly so. They may be re-stated as follows:

(i) An ion has a radius which does not vary by more than a few per cent in the different structures in which the ion occurs. The sum of two such radii makes up the observed cation–anion distance. (The same radius does not necessarily hold good for anion–anion contacts.)

(ii) When a cation and the surrounding anions are given their correct radii, all the anions must touch the cation; in other words, in a model built of rigid spheres made to scale, the cation must not ‘rattle’ in the hole between the anions. The cation will be surrounded by as many anions as can touch it, but no more.

These rules are empirical, but have proved their value in all the work that has been done since they were formulated. It should be noted that they are stated for *ions*; they are based on the concept of

FERROELECTRICITY IN CRYSTALS

central forces. Homopolar forces, if they occur, are directed forces; in that case the radii will depend on direction. Nevertheless the rules represent a good starting-point for the study of all homodesmic structures—that is, structures in which all the bonds are of approximately the same strength, so that a continuous three-dimensional network is formed.

The rules allow us to predict the environment of any cation in an oxide; thus Si will be 4-coordinated, Al 6, Ti 6, Ca 8, Ba 12. The predictions are not always perfectly fulfilled; lower coordinations occur frequently, higher very rarely; but they provide a useful starting-point. Some of the common radii and coordination numbers are given in Tables 5.1 and 5.2.

TABLE 5.1

Ionic radii of some common ions. (Empirical values adopted by Goldschmidt for 6-coordination, with certain modifications by later workers.)

Radius of $O^{2-} = 1.32 \text{ \AA}$

Ion	Radius Å	Ion	Radius Å	Ion	Radius Å	Ion	Radius Å
Li ⁺	0.78	Mg ²⁺	0.78	Al ³⁺	0.57	Si ⁴⁺	0.39
Na ⁺	0.98	Ca ²⁺	1.06	Fe ³⁺	0.67	Ti ⁴⁺	0.64
K ⁺	1.33	Sr ²⁺	1.27			Zr ⁴⁺	0.77
Rb ⁺	1.49	Ba ²⁺	1.43			Hf ⁴⁺	0.74
Cs ⁺	1.65	Cd ²⁺	1.03			Sn ⁴⁺	0.74
		Pb ²⁺	1.32			Pb ⁴⁺	0.84
						Ce ⁴⁺	1.02

TABLE 5.2

Observed coordination numbers of some important cations with O as anion

Ion	Coordination number	Ion	Coordination number
Li ⁺	6	Al ³⁺	4, 6
Na ⁺	6-9		
K ⁺	8-10	Si ⁴⁺	4
Mg ²⁺	6	Ti ⁴⁺	6
Ca ²⁺	6-10		
Sr ²⁺	8-10		
Ba ²⁺	8-12		



Fig. 5.1. Powder photographs of some typical materials at room temperature (Megaw, 1946).
(CuK α radiation, 19 cm. camera low-angle end to the left).

5. THE PEROVSKITE FAMILY

It is worth noticing that coordination numbers of 4, 6, 8, or 12 are compatible with high point-group symmetry at the central cation, while other numbers are not. Hence these coordinations and these only will occur in simple high-symmetry structures. Substances with simple structures are likely to be more abundant (because more easily formed) and also better known (because more easily studied) than very complicated structures.*

1.3. *Application of rules to the perovskite structure*

It will be seen that the ideal perovskite structure (Fig. 4.1) requires one cation A to be capable of 12-coordination, the other B of 6-coordination. This means that A must be rather large. If A, like B, can only be 6-coordinated, an entirely different arrangement is taken up, for example the ilmenite structure (FeTiO_3). Another way of looking at it is to notice that the framework of linked BO_6 octahedra determines the dimensions of the structure, and hence the size of the A cation which will fit exactly into the hole between the octahedra. It can easily be seen that the ideal relation between the radii is

$$R_A + R_X = \sqrt{2}(R_B + R_X),$$

where X is the anion (in this case oxygen). However, ionic radii are not absolutely constant, but vary by a few per cent (even after making appropriate correction for the fact that radii are consistently larger for high coordination); hence we may expect a certain tolerance of fit, which may be expressed by writing

$$R_A + R_X = t\sqrt{2}(R_B + R_X),$$

where t is a 'tolerance factor', nearly but not exactly unity.

Goldschmidt showed that the perovskite structure was formed when this condition was satisfied. If t was very much less than 1, a different structure appeared, generally the ilmenite structure. Unlike the perovskite structure, this latter is specified by arbitrary parameters, and so can adapt itself easily to a range of different radii.

More recent work shows that while structures of the perovskite family occur for values of t down to about 0.8, the ideal cubic structure is found only if t is much closer to unity.

Surveys of a large number of structures in terms of their ionic radii have been made by Wood (1951) and by Keith and Roy (1954). They confirm the general principle, while showing that it is by no means the whole story.

* For a fuller account of the principles of structure building, reference may be made to R. C. Evans, *Crystal Chemistry* (Cambridge University Press, 1939), or to W. L. Bragg, *Atomic Structure of Minerals* (Cornell University Press, New York, 1937).

1.4. Classification of structure types

A useful classification of oxides with the formula ABO_3 may be made as follows.

(i) *Cubic perovskite*. A large number of compounds possess the ideal cubic structure, with cell edge a_0 about 4 Å, and cell contents one formula-unit. For many of them no other structure is known, and they are not ferroelectric. (The older records of cubic structures should be treated with reserve, as they did not always distinguish between ideal cubic and pseudo-cubic.) The tolerance factor t lies between 1.05 and 0.90. They are recognizable by a very simple pattern in their X-ray powder photographs (Fig. 5.1 (a)). Examples are given in Table 5.3.

(ii) *Distorted small-cell perovskite*. A few substances for which t is nearly unity have one or more low-temperature forms with a distorted small cell, i.e. they are no longer cubic, but if referred to the original axes the cell edges are still approximately 4 Å. Whatever the choice of axes, they have still only one formula-unit per lattice-point.

These substances are recognized in their powder photographs by patterns resembling the ideal cubic, but with each single line replaced by a group (Fig. 5.1 (b)). The detail of the splitting in each group can be used to find the shape and size of the unit cell, and the crystal system. If the change in axial ratio is small (Fig. 5.1 (b)) the splitting of the high-angle lines is most informative; if it is large (Fig. 5.1 (c)) the splitting is only recognizable as such in the low-angle lines.

The outstanding example of this class is $BaTiO_3$; others are $KNbO_3$ and $PbTiO_3$. So far as is known, all structures of this class are ferroelectric, and have a transition to the ideal cubic structure (often called the paraelectric form, cf. Chap. 1, § 13) in which the ferroelectricity disappears.

(iii) *Distorted multiple-cell perovskite*. Many substances possess a distorted structure in which adjacent units of 4 Å edge are not perfectly identical, though nearly so. The true cell is made up of a number of these sub-cells. Thus if it is referred to the original axes, its edges are all nearly multiples of $a_0 \simeq 4$ Å; but it may be more convenient to use axes on which they are nearly multiples of $\sqrt{2}a_0$.

The existence of these multiple cells is recognized by the presence of 'extra' lines on the X-ray powder photograph: that is, lines coming between those of the ideal cubic pattern, which are themselves split up into groups (Fig. 5.1 (d)). From the powder patterns alone it is difficult if not impossible to find out which one or more of the cell edges is doubled or multiplied by some higher factor. In many cases the available information does not go beyond the bare fact that the

5. THE PEROVSKITE FAMILY

unit cell is a multiple one. Only a few structures of this kind have been more fully examined.

None of these structures have been shown to be ferroelectric, though some of them are antiferroelectric. It is not impossible, however, for a multiple cell to possess polar symmetry (though it may be physically less probable); examples are the cone ferroelectrics discussed in Chap. 1, § 11.1. Thus the existence of extra lines in a powder pattern cannot be taken as proof that a substance is not ferroelectric; still less, in absence of any electrical evidence, that it is antiferroelectric.

Important examples of multiple-cell structures are CaTiO_3 , PbZrO_3 and NaNbO_3 . These will be discussed below. Other examples are given in Table 5.3.

(iv) *Other types, including ilmenite type.* These occur when the factor t falls below a limit which is about 0.75 for compounds where A has valency 1, and which increases with the valency of A.

Some important types are based on a close-packing of oxygen atoms, the 6-coordinated cations fitting into the interstices, and causing some distortion from the ideal packing. In ilmenite itself, the Fe and Ti ions occupy adjacent sites along the triad axis, so that their octahedra of surrounding O's have one face in common; successive pairs are arranged in the sequence Fe, Ti, -, Ti, Fe, -, Fe, Ti, . . . However, this is not the only way of placing cations between the O's. Each different way will lead to a different linkage of octahedra, but to very similar cell dimensions, since these are determined primarily by the oxygen packing. Thus the distinction between the different types, though it is important, may easily be overlooked experimentally. The ilmenite structure is the best known of the group, and it is possible that many of the older records in which other substances are classed as ilmenite type need to be reconsidered. An important example of wrong attribution is LiNbO_3 , a ferroelectric, which has the cation sequence Li, Nb, -, Li, Nb, -, Li, Nb, . . . It will be considered in more detail below.

Other structure types can also be adopted by ABO_3 compounds with low t values, but we shall not be concerned with them in this book. They include types related to the A and C sesquioxides, La_2O_3 and Ti_2O_3 , and the YCrO_3 type, which has some resemblance to a heavily-distorted perovskite (Keith and Roy, 1954).

1.5. This classification is used and illustrated by more examples in Table 5.3. Some of the substances listed have not been examined in very great detail, and the classification must be considered provisional. The table makes no attempt at completeness; for example, only a few compounds of the rare earths are included, though considerable work has been done on them (Naray-Szabo, 1943a, b, 1947;

FERROELECTRICITY IN CRYSTALS

Jonker and van Santen, 1950; Gränicher, 1951; Keith and Roy, 1951; Brous, Fankuchen and Banks, 1952; Yakel, 1955; Harwood, 1955). Only pure substances have been included in the table. A very great variety of solid solutions is known to occur, but it would be impossible to consider them all within the limits of this book. Only in a few cases—notably the compounds of Pb—do they show features unlike those of the end-members of the series, and discussion of them will be confined to such cases. The rest of this chapter will be devoted to individual consideration of certain important substances.

TABLE 5.3

Classification of substances related to perovskite

I. Substances occurring only in ideal cubic form	SrTiO ₃ , SrZrO ₃ , SrHfO ₃ , SrSnO ₃ , SrFeO ₃ , BaZrO ₃ , BaHfO ₃ , BaSnO ₃ , BaCeO ₃ , EuTiO ₃ , LaMnO ₃
II. Substances having at least one form with a distorted small-cell structure (C = cubic, T = tetragonal, O = orthorhombic, R = rhombohedral, ? = doubtful or not fully investigated)	BaTiO ₃ (C, T, O, R), KNbO ₃ (C, T, O, R), KTaO ₃ (C, ?), RbTaO ₃ (C, T), PbTiO ₃ (C, T)
III. Substances having distorted multiple-cell structures (a) cell size $\sqrt{2}a \times 2a \times \sqrt{2}a$ (b) cell size $\sqrt{2}a \times 4a \times \sqrt{2}a$ (c) cell size $\sqrt{2}a \times 2\sqrt{2}a \times 2a$ (d) cell size $2a \times 2a \times a$ (e) others	(a) CaTiO ₃ , (CaZrO ₃), (CdTiO ₃), (CaSnO ₃) (b) NaNbO ₃ , (NaTaO ₃) (c) PbZrO ₃ , PbHfO ₃ (d) WO ₃ (e) PbTiO ₃ (low-temp.), WO ₃ (high-temp.), NaNbO ₃ (high temp.), NaNbO ₃ (low-temp.), LaCrO ₃
IV. Substances having structures based on close-packing (a) Ilmenite type (b) LiNbO ₃ type	(a) FeTiO ₃ , CdTiO ₃ (b) LiNbO ₃ , (LiTaO ₃)

Substances in brackets have not been investigated in detail and classification is partly by analogy.

5. THE PEROVSKITE FAMILY

2 Titanates of alkaline earth metals

2.1. Barium titanate, $BaTiO_3$

This has been dealt with in Chap. 4.

2.2. Strontium titanate, $SrTiO_3$

Single crystals are colourless, with a high refractive index. They are synthesized commercially for use as ornamental gem-stones.

The structure is ideal cubic. There is no indication of a transition down to the lowest temperature examined, 1.3°K.

The dielectric constant at room temperature has a high value, about 220. Above this it falls with increasing temperature according to a Curie-Weiss law, from which a transition point at 10°K was predicted. Measurements at lower temperatures (Hulm, 1951) showed that the extrapolation did not agree with experiment. From room temperature to 50°K the observations fitted a Curie-Weiss law $\epsilon = C/(T - T_0)$ in which $T_0 = -35^\circ\text{K}$; below that, ϵ had smaller values than the law would suggest, and finally it tended to a constant value of 1300 near absolute zero. The increase was continuous, and there was no peak of any kind.

This example shows the danger of using experimental observation of a Curie-Weiss law as a criterion of ferroelectricity.

2.3. Calcium titanate, $CaTiO_3$

This occurs naturally as the mineral perovskite, which gives its name to the family. Natural crystals are dark-coloured, lustrous and much twinned. Synthetic crystals are red-brown, and also generally twinned. The twinning has been discussed by Zedlitz (1939) and by Bailey (1952).

Much work has been done on the crystal structure, but even yet our knowledge is not complete. The lattice symmetry was established by Megaw (1946), the true unit cell by Kay (1947), and the space group and some of the atomic parameters by Bailey (1952).

The structure is orthorhombic, with cell edges approximately $\sqrt{2}a_0 \times 2a_0 \times \sqrt{2}a_0$. In more detail, the values (Megaw, 1946) are:

$$a = 5.370\text{\AA}, \quad b = 3.815 \times 2\text{\AA}, \quad c = 5.432\text{\AA}$$

The lattice is primitive, the space group No.—62 $Pcmn$. The cell contains 4 formula-units. The angle $(101)_\Lambda(10\bar{1})$ differs from 90° by 40'.

2.4. Fig. 5.2 shows the relation of this structure to the ideal cubic. $ABCD$ is the base of the small sub-cell, which is distorted from a square to a rhomb of angle 90° 40' (exaggerated in the diagram). The

atoms have individual displacements which are not identical, though symmetry-related, in adjacent sub-cells. In the y direction (perpendicular to the plane of the paper), a true repeat only occurs after two sub-cells, and the same is true along the original x and z axes, where the repeat distances are AE and AJ . However, sub-cell $CFGH$ is identical with sub-cell $ABCD$, i.e., referred to the original axial directions the structure is B -face-centred. There are thus two lattice-points associated with this large cell, which contains 8 formula-units. But since the true symmetry of the atomic displacements is orthorhombic, it is better to take the unit cell with base $BFHD$, with its x and z axes parallel to the orthorhombic symmetry directions BF and BD respectively. This is the cell described in the last paragraph.

The distortion of the sub-cell in CaTiO_3 resembles that in orthorhombic BaTiO_3 (Chap. 4), where a similar change of axial directions had to be made. In BaTiO_3 , however, the orthorhombic cell was face-centred, and the sub-cell formed the true repeat unit; while in CaTiO_3 the orthorhombic cell is primitive, and eight sub-cells are needed to make up a true repeat unit referred to the original axial directions. A comparison of the symmetry elements, and of sections of the structure showing displacement of atoms, is given in Fig. 5.3.

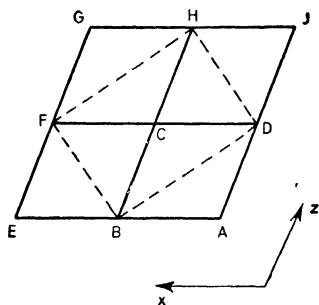


Fig. 5.2. Relation of CaTiO_3 lattice to ideal cubic. Dotted lines outline projection of true unit cell.

The space group $Pcmn$ is centrosymmetric. The Ti atoms are on centres of symmetry. The Ca atoms, and one-third of the O's, lie on the mirror planes of symmetry midway between planes of Ti, their positions in that plane being fixed by arbitrary parameters. None of the parameters are known with certainty, though plausible guesses have been made, based partly on packing considerations.

Each Ti is thus at the centre of an octahedron of O's, which is centrosymmetric but not perfectly regular. Each octahedron has the same shape, but neighbouring octahedra are differently oriented in the structure. The Ca is no longer regularly surrounded by twelve O's; it seems probable (though the experimental evidence is not conclusive) that it is nearer to six of them than to the others. This is what would be predicted from the ionic radii of Ca and O.

2.5. The fact that natural crystals of perovskite are always twinned has been interpreted by mineralogists to mean that at high tempera-

5. THE PEROVSKITE FAMILY

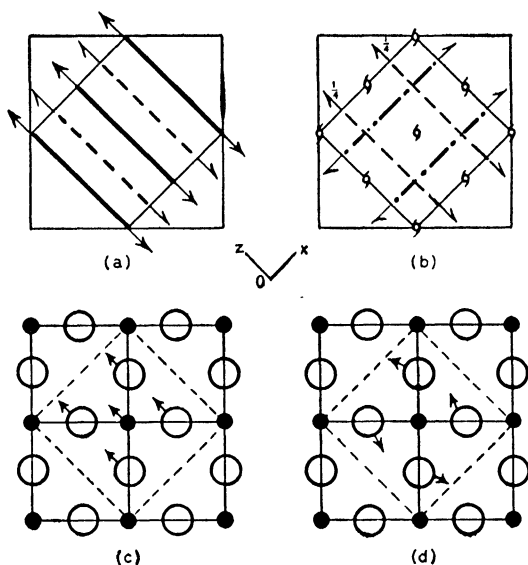


Fig. 5.3. Comparison of symmetry and atomic displacements in orthorhombic BaTiO_3 and CaTiO_3 .

(a) BaTiO_3 , space group $Bmm2$, (b) CaTiO_3 , space group $Pcmn$, (c) BaTiO_3 , section parallel to (010) , (d) CaTiO_3 , section parallel to (010) .

tures there is a stable cubic form. That there is a tendency in this direction has been shown by Bailey (1952). He found that while the structure remained orthorhombic from -150° to 700°C , the angle $(101)_\Lambda(\bar{1}01)$ changed from about $90^\circ 54'$ at the lower end of this range to about $90^\circ 18'$ at the upper end. This is shown in Fig. 5.4, together with the actual changes of length of the two cell diagonals. Other workers have obtained no evidence of any transition up to 1200°C , above which observation becomes difficult. Naylor and Cook (1946) found a small specific heat anomaly of $550 \text{ cal. mol.}^{-1}$ at 1260°C , suggesting a transition to cubic at this temperature.

2.6. The dielectric constant of CaTiO_3 does not show any marked anomalies. Gränicher (1951) found a value of 185 at room temperature, and a negative temperature coefficient of $-1.6 \times 10^{-3} \text{ deg.}^{-1}$. (The corresponding values for SrTiO_3 are 220 and $-3.7 \times 10^{-3} \text{ deg.}^{-1}$.) The increase of ϵ with decreasing temperature follows a Curie-Weiss law in which $C = 80 \times 10^3 \text{ degrees}$, $T_0 = -171^\circ\text{K}$; there is a sudden increase in both these magnitudes at -50°C , but X-ray powder photographs showed no change of structure associated

with it. Above room temperature ϵ tends to become constant, but observations above about 300°C were made difficult by the crystal becoming conducting. CaTiO_3 cannot justifiably be classed as an antiferroelectric on present evidence; its resemblance to SrTiO_3 in its electrical behaviour would rather group it with the paraelectrics.

2.7. Solid solutions of CaTiO_3 have been studied by Gränicher and Jakits (1954). They reported intermediate phases between the cubic

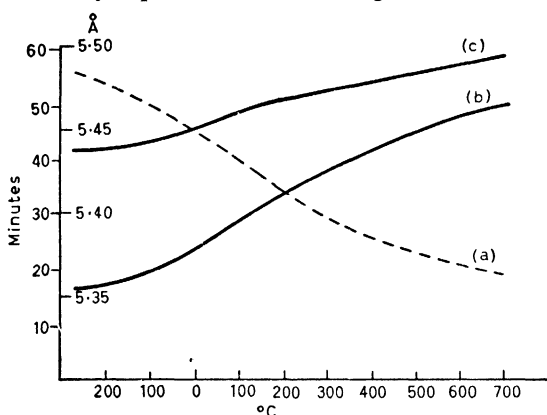


Fig. 5.4. Changes in unit cell of CaTiO_3 (Kay and Bailey, forthcoming).

- (a) Difference of angle $(101) \wedge (10\bar{1})$ from 90°
- (b) Length of short diagonal of sub-cell, a
- (c) Length of long diagonal of sub-cell, c

small-cell and orthorhombic multiple-cell end members; the high-temperature phase appears to be multiple-cell cubic.

The dielectric constant at each composition could be represented by a Curie-Weiss law, whose slope and intercept changed at certain temperatures. While the intercept—the Curie temperature T_0 —decreased continuously with increasing Ca content, the temperature of the break in the straight line increased continuously. For certain compositions, peaks in the dielectric constant were observed. It was not certain whether the breaks in the straight line could be correlated with a change of phase.

3 Zirconates and hafnates of alkaline earth metals

BaZrO_3 and SrZrO_3 are cubic, with the ideal perovskite structure (Megaw, 1946; Hoffman, 1935). So are BaHfO_3 and SrHfO_3 (Shirane and Pepinsky, 1953, quoting Gränicher unpublished). CaZrO_3 is distorted multiple-cell, probably isomorphous with CaTiO_3 (Megaw, 1946).

5. THE PEROVSKITE FAMILY

In solid solutions of $\text{Ba}(\text{Ti},\text{Zr})\text{O}_3$ increasing amounts of Zr raise the temperature of the two lower transition points, until at a composition of 15% (atomic) Zr the tetragonal and orthorhombic phases have disappeared, and there is a direct transition from cubic to rhombohedral (Sawaguchi, 1953). This may be compared with effects in the series of solid solutions $\text{Pb}(\text{Ti},\text{Zr})\text{O}_3$ and $(\text{Pb},\text{Ba})\text{ZrO}_3$ (see § 10.2, 10.9).

4 Niobates and tantalates

4.1. Many niobates and tantalates of the alkali metals, of formula ABO_3 , belong to the perovskite family. The large alkali ion is 12-coordinated, the small Nb or Ta ion is 6-coordinated. The compounds LiNbO_3 and LiTaO_3 have a rather different structure in which both kinds of cation are 6-coordinated; but they are related to the perovskite structure in a way which makes it desirable to consider them in this section.

4.2. Potassium niobate, KNbO_3

Crystals of this are translucent, yellowish in colour, and much twinned.

TABLE 5.4

Cell dimensions of KNbO_3 (Shirane, Newnham and Pepinsky, 1954; Shirane, Danner, Pavlovic and Pepinsky, 1954)

Temperature	Symmetry	Cell dimensions
425° C	Cubic	$a = 4.0214 \text{ \AA}$
220° C	Tetragonal	$a = 3.9972 \text{ \AA}$ $c = 1.0166 \text{ \AA}$
25° C	Orthorhombic *	$a = 5.6974 \text{ \AA}$ $b = 3.9711 \text{ \AA}$ $c = 5.7222 \text{ \AA}$ ' a ' = ' c ' = $4.0375 \text{ \AA}$ ' β ' = $90^\circ 15'$
- 140° C	Rhombohedral	$a = 4.016 \text{ \AA}$ $\alpha = 89^\circ 50'$

* The choice of a and c directions has been made to agree with that used for BaTiO_3 (cf. Table 4.3) and does not follow that of the original papers, which reverse them. (See appendix, 'axes of reference'.)

FERROELECTRICITY IN CRYSTALS

The structure is isomorphous with BaTiO_3 in all its forms. The lattice parameters are given in Table 5.4. At room temperature it is orthorhombic, and the temperatures of all transitions are higher than the corresponding transitions in BaTiO_3 (Table 5.5). The axial ratio ' a '/ b in the orthorhombic form is 1.017 at room temperature, dropping to 1.013 just below the transition point. The axial ratio c/a in the tetragonal form is 1.017, dropping to 1.012. The corresponding values for BaTiO_3 are about 1.011 and 1.005 at the lower and upper ends of the ranges respectively for both forms.

The changes of heat content and of entropy at the various transitions have been measured by Shirane, Danner, Pavlovic and Pepinsky (1954). Their results are recorded in Table 5.5 and compared with the

TABLE 5.5

Comparison of thermal behaviour of KNbO_3 and BaTiO_3 (Shirane, Danner, Pavlovic and Pepinsky, 1954)

Transition	Temperature		Change of energy (cal. mol. ⁻¹)		Change of entropy (cal. mol. ⁻¹ deg. ⁻¹)	
	KNbO_3	BaTiO_3	KNbO_3	BaTiO_3	KNbO_3	BaTiO_3
Cubic-tetragonal	410° C	120° C	190 ± 15	47-50	0.28	0.12-0.13
Tetragonal-orthorhombic	210° C	0° C	85 ± 10	16-26	0.17	0.06-0.09
Orthorhombic-rhombohedral	-40° C	-90° C	32 ± 5	8-14	0.12	0.04-0.07

corresponding values for BaTiO_3 . They consider that the greater values for KNbO_3 are to be explained by the greater distortion of the unit cell, as shown by its axial ratio.

A study of KNbO_3 by nuclear resonance has been made by Cotts and Knight (1954). Their work makes it clear that all three transitions are discontinuous in a given region of the crystal, though different regions often undergo the transition independently. Beyond this their detailed results were not easy to interpret; they will be referred to again in Chap. 9, § 4.8.

The ferroelectric behaviour of KNbO_3 was first reported by Matthias and Remeika (1951). They found values of the spontaneous polarization ranging from 0.9 microcoul. cm.⁻² at room temperature to 3.8 microcoul. cm.⁻² just below the Curie point. Since the measurements were made on multi-domain crystals, these values probably represent lower limits. More recent work by Triebwasser and Halpern (1955) gives a value of 26 microcoul cm.⁻² near the transition.

5. THE PEROVSKITE FAMILY

The dielectric constant has been measured by Shirane *et al.*; their results are shown in Fig. 5.5. There is very marked thermal hysteresis, especially at the lowest transition. The resemblance to the corresponding curve for BaTiO_3 (Fig. 4.11) is rather striking.

4.3. Potassium tantalate, KTaO_3

This substance is cubic at room temperature (Vousden, 1951a). The dielectric constant has been measured down to 1.3°K (Hulm, Matthias and Long, 1950). There is a peak at 13°K , of height about 5500; presumably this marks a Curie point. The presence of Na as

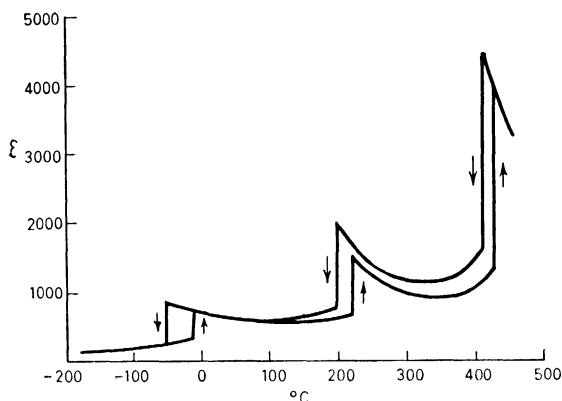


Fig. 5.5. Dielectric constant of KNbO_3 multidomain crystal (Shirane, Danner, Pavlovic and Pepinsky, 1954).

impurity displaces the peak to a higher temperature. Nothing is known experimentally about the structure of the low-temperature form.

4.4. Sodium niobate, NaNbO_3

There has been a good deal of disagreement between different workers who studied this material. It seems probably that the explanation lies in its possession of several closely-related forms which differ very little in energy, and which are sensitive to small amounts of impurity. More will be said about this below.

At room temperature the structure is orthorhombic, with a multiple cell; it has been examined in detail by Vousden (1951b), and will be described in §4.5. Early observations by Wood (1951) indicated the existence of several transitions above room temperature; these have been further studied by Shirane, Newnham and Pepinsky (1954) and by Cross and Nicholson (1955). The room-temperature phase persists up to about 360° , the 'extra lines' on the X-ray photographs

becoming weaker with increasing temperature. At $360^\circ (\pm 15^\circ)$ there is a sharp transition, marked by a sudden change in the kind of splitting of the X-ray lines and in the optical properties. The new structure is again orthorhombic, though very closely pseudotetragonal; and still has a multiple cell. The axial ratio c/a is 1.0023 at 375° and decreases at higher temperatures. The lattice parameters are shown in Fig. 5.6.

Above 430°C , the X-ray pattern cannot be distinguished from ideal cubic, but optical observations indicate transitions at about $450\text{--}470^\circ \text{C}$, 518°C and 640°C . Above this the material is certainly cubic; between 518° and 640°C it is either tetragonal or nearly so,

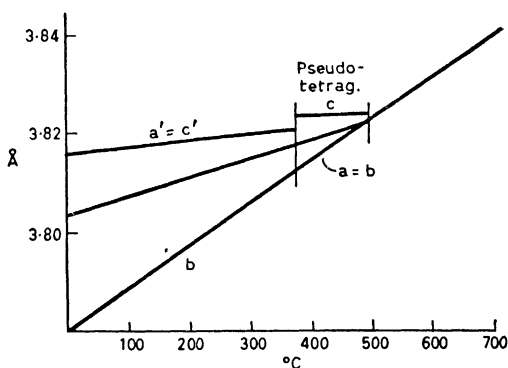


Fig. 5.6. Lattice parameters and cube root of volume of NaNbO_3 (Shirane, Newnham and Pepinsky, 1954).

with the unique axis at right angles to its direction in the pseudotetragonal form below 518° . It seems that optical methods are more sensitive than X-ray for detecting small distortions in this material.

There is a further transition below room temperature, which was detected by Cross and Nicholson (1955) by electrical evidence. Though the structure of the low-temperature form is not known*, certain features can be inferred; it will be discussed in § 4.10.

4.5. The room-temperature form (Vousden, 1951b) has cell dimensions approximately $\sqrt{2}a_0 \times 4a_0 \times \sqrt{2}a_0$; more exactly, they are

$$a = 5.568 \text{ \AA}, \quad b = 3.880 \times 4 \text{ \AA}, \quad c = 5.505 \text{ \AA}$$

The change of axial directions from the sub-cell to the true cell is exactly the same as in CaTiO_3 (see Fig. 5.2); but Vousden's choice of

* See footnote on p. 100 for a report of work which appeared while this book was being printed.

5. THE PEROVSKITE FAMILY

axes makes a the long diagonal. The detailed symmetry is however different. The space group is No. 17, $P22_12$, and there are 8 formula-units per cell. The angle $(101) \wedge (10\bar{1})$ is $90^\circ 40'$. The symmetry elements are shown in Fig. 5.7 (a).

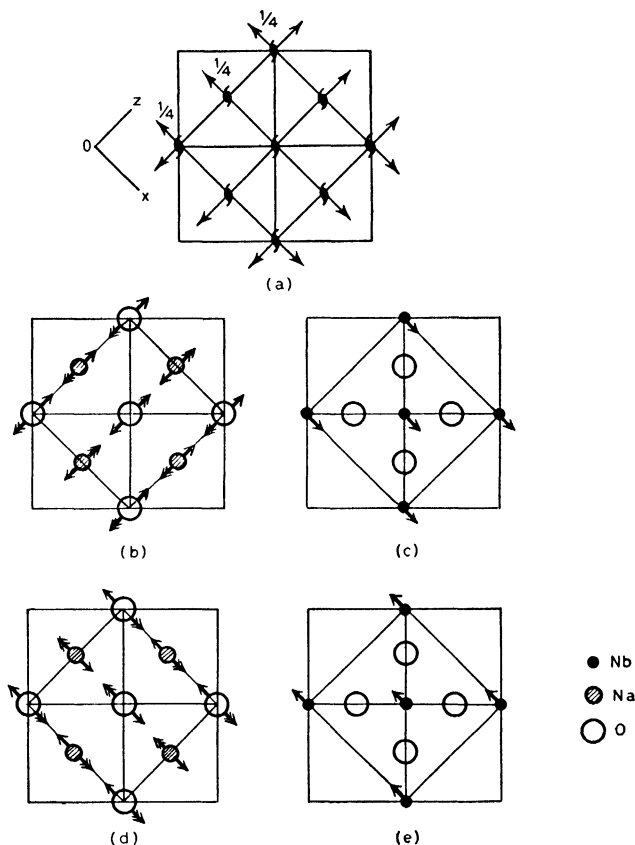


Fig. 5.7. Symmetry and structure of NaNbO_3 (orthorhombic room-temperature form).

(a) Symmetry elements, (b) Sections at $y=0$ (single arrows) and $y=\frac{1}{2}$ (double arrows), (c) Sections at $y=\frac{1}{8}$, $\frac{3}{8}$, (d) Sections at $y=\frac{1}{4}$ (single arrows) and $y=\frac{5}{8}$ (double arrows), (e) Sections at $y=\frac{3}{4}$, $\frac{7}{8}$.

It is easiest to describe the structure by considering layers of atoms parallel to (010). There are four such layers, nearly planar and very similar to each other, containing Nb and O_2 ; and four midway between them, containing Na and O_1 . These are shown in Fig. 5.7 (b)–(e), with arrows indicating direction of displacements of the

atoms. It should be noticed that the atom at the mid-point of each layer need not by the symmetry have the same size of displacement as that at the corner, but in fact it has. Similarly the displacements in (b) and (d) need not be equal to each other, but in fact they are. Displacements of Nb in (c) and (e) are necessarily equal; those of O₂ have not been determined with certainty and are therefore not marked.

The displacements from the ideal positions (fixed relative to the intersections of the symmetry axes) are all rather large, but lie very nearly in the (010) plane. Nb has a displacement of 0.11 Å in this plane, Na of 0.15 Å, O of about 0.2 Å. Components perpendicular to the plane are less than 0.05 Å. The detailed values of interatomic distances resulting from these displacements have not been worked out.

The magnitude of the distortion in this structure is fairly large. The axial ratio ' a '/ b is 1.009 at room temperature, much as in orthorhombic BaTiO₃; but the shear angle is 40' as compared with 12'. The relative displacements of individual atoms are very much greater than for BaTiO₃.

4.6. The variation of axial ratio with temperature is however rather rapid. Just below the transition at 360° C, ' a '/ b has dropped to 1.002 and the shear angle to 23' (Shirane, Newnham and Pepinsky, 1954). It is not known what changes have taken place in the atomic displacements, but the fading out of the extra lines suggests that they may be much reduced.

4.7. The optical properties show an interesting resemblance to those of orthorhombic BaTiO₃ (Jona, Shirane and Pepinsky, 1955). Both are optically negative, with the shortest axis of the indicatrix lying along the long diagonal of the rhomb and its longest axis perpendicular to the rhomb (cf. Chap. 4, § 9). The double refraction of NaNbO₃ is somewhat greater than that of BaTiO₃ at 0° C, but drops rapidly with temperature to about a quarter of its initial value just below the transition point, the orientation of the indicatrix remaining unchanged. This is in qualitative agreement with theoretical predictions treating the observed dimensional changes as strains of a homogeneous medium, but quantitatively the changes in NaNbO₃, unlike those in BaTiO₃, cannot be reconciled with reasonable values of the elasto-optical constants. A similar difficulty is encountered for PbZrO₃, which is also orthorhombic (cf. § 8.3). In each of these three crystals the shortest axis of the indicatrix lies in the direction of displacement of the small cations, but there is no very obvious correla-

5. THE PEROVSKITE FAMILY

tion between the magnitudes of the double refractions and the magnitudes of the axial ratios for the different pairs of axes.

The variation of double refraction with temperature above 360°C is shown in Fig. 5.8. Between 360° and 518°C the indicatrix is nearly an ellipsoid of revolution, with its shortest axis lying along the pseudotetrad axis. Arguments of the same kind as proved justifiable for the room-temperature form suggest that the unit cell is elongated along the pseudotetrad axis and that the atomic displacements lie in this direction. A further point of interest is the change of direction of the pseudotetrad axis from z to x or y at 518°C .

4.8. The specific heat anomaly of NaNbO_3 is 50 cal. mol.^{-1} as compared with 190 for KNbO_3 (Shirane, Newnham and Pepinsky,

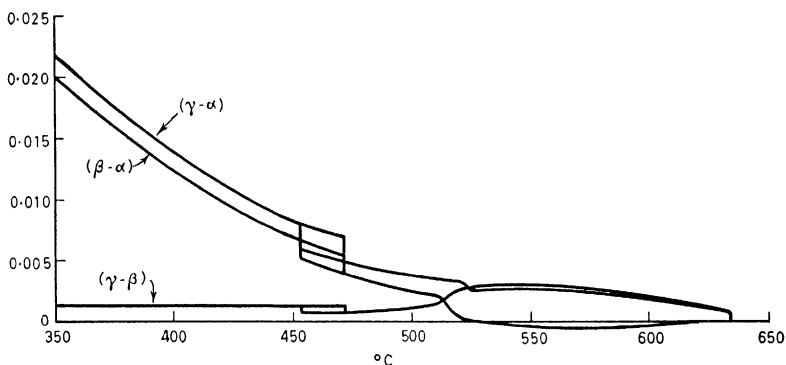


Fig. 5.8. Double refraction of NaNbO_3 (Cross and Nicholson, 1955).

(1954); it is suggested that this difference may be correlated with the smaller axial ratio for NaNbO_3 .

4.9. The space group is non-polar, and thus ferroelectricity is forbidden. It is natural to enquire whether antiferroelectricity may occur. It is compatible with the symmetry, which allows all the atoms to be grouped into pairs with antiparallel displacements; but for a definite proof of its existence we must look to the electrical evidence, which will be considered in the next paragraph.

The existence of spontaneous polarization was reported by Matthias and Remeika (1951). They also investigated the dielectric constant, and found anomalies near the two transitions. Vousden (1951b) reported movement of domain boundaries with fields of 20 kV cm.^{-1} . These facts indicate ferroelectricity, which, as we have seen, is incompatible with the symmetry of the crystal. On the other hand, Shirane, Newnham and Pepinsky (1954) could obtain no

evidence of spontaneous polarization in spite of careful search, except for movement of domain boundaries in one or two cases for fields of about 20 kV cm^{-1} . They confirmed the anomaly in the dielectric constant, but interpreted it as implying antiferroelectricity.

The difficulty was resolved by Cross and Nicholson (1954). They showed that, although for small fields there was no dielectric hysteresis at or above room temperature, for fields above 90 kV cm^{-1} applied perpendicular to the y axis a double hysteresis loop was developed. This resembled the 'butterfly loop' in BaTiO_3 above its Curie point, and had a similar explanation, namely that the material *became* ferroelectric when acted on by a sufficiently large field. This implies the existence of a ferroelectric structure of only slightly greater energy than the antiferroelectric. An earlier example of the same effect occurs in PbZrO_3 , which will be considered in § 8.6.

4.10. Below room temperature, Cross and Nicholson (1955) found a different effect. At temperatures below -120°C , the application of fields *parallel* to the y axis gave rise to normal hysteresis loops if the field exceeded a threshold value which decreased with decreasing temperature. Once hysteresis set in, it persisted for lower field strengths, and only disappeared if the material was heated above -55°C . There thus exist two slightly different structures in the same temperature range between -120°C and -55°C ; the room-temperature form is presumably metastable but is separated from the truly stable low-temperature form by an energy 'hill' which can only be surmounted with the help of the applied field.

4.11. Fig. 5.9 is a phase diagram showing the regions of different electric behaviour. It is clear that the region of double hysteresis loops corresponds to a second ferroelectric form, which is never stable in the absence of a field.

The fact that the field inducing the transition to the low-temperature form is parallel to y suggests strongly that the polar axis of this form is the y axis*, and hence that there will be relative displacements

* Work by Shirane, Johns, Jona and Pepinsky, reported at the 1956 annual meeting of the American Crystallographic Association, confirms this conclusion. The structure is monoclinic, with the unique axis y along a face diagonal of the small cube, and the direction of spontaneous polarization approximately along a cube edge, taken as the x axis. This latter is not a symmetry axis, but lies in the symmetry plane; the class is m . The sub-cell is very nearly rhombohedral. No antiparallel displacements of Nb relative to each other were observed. This does not exclude the possibility of antiparallel components of individual dipoles, since the O displacements (not known experimentally) may be antiparallel with respect to each other and to Nb. The results so far neither prove nor disprove the suggestion in Chap. 6, § 3.4, that the Nb displacements within the octahedra may be roughly parallel to triad axes of the cube.

5. THE PEROVSKITE FAMILY

of ions in the y direction. It is conceivable that these might be substituted for the x -displacements of Nb observed in the room-temperature form, but it seems more likely, as Cross and Nicholson suggest, that they are superimposed on the existing displacements. The material is then a cone ferroelectric (cf. Chap. 1, § 11.1, and Chap. 8, § 5.2), with the displacements lying roughly along the body diagonals of the original cube; this arrangement would be a multiple-cell analogue of rhombohedral KNbO_3 .

A similar argument suggests that in the unstable ferroelectric form (the form appearing only in the region of double hysteresis

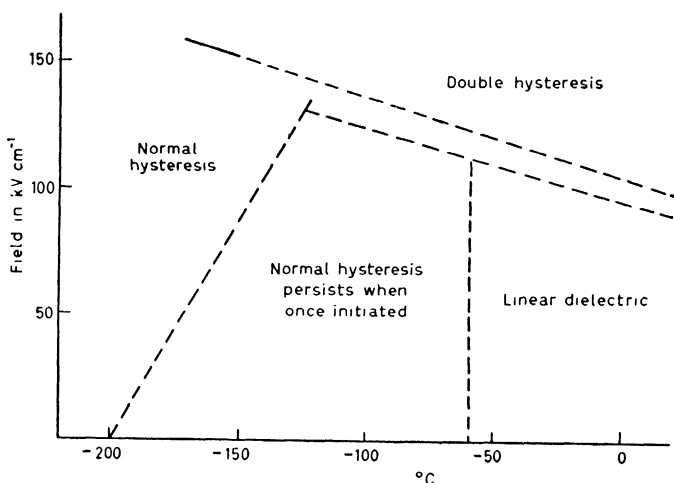


Fig. 5.9. Field-vs.-temperature phase diagram of NaNbO_3 (Cross and Nicholson, 1955).

loops) the polar displacements are perpendicular to y . Cross gives reasons for believing that the individual dipoles associated with these displacements are now divided between two directions at right angles, parallel to the original orthorhombic a and c axes. If so, the phase is cone-ferroelectric, with a structure different from either normal orthorhombic NaNbO_3 or orthorhombic BaTiO_3 .

A direct determination of these structures would be of very great interest.

4.12. Measurements of the dielectric constants have also been made by Cross and Nicholson (1955). They are shown in Fig. 5.10. It is noteworthy that in the room-temperature form the larger dielectric constant is perpendicular to the direction of cation displacement, as was true also for tetragonal BaTiO_3 . Above 360° , it was not possible

FERROELECTRICITY IN CRYSTALS

to measure the dielectric constant parallel to the pseudotetrad axis z , because of the habitual self-annealing of the crystals to give plates parallel to (001). The very small anomalies at the higher transitions in the dielectric constants parallel to x and y may be noted.

4.13. It is possible from the point of view of Chap. 6 to use the optical and electrical evidence for a guess at the structural interpretation. The 465°C transition may perhaps be due to the disappearance of the displacement of Nb relative to the oxygen framework. At higher temperatures, the individual NbO_6 octahedra would then

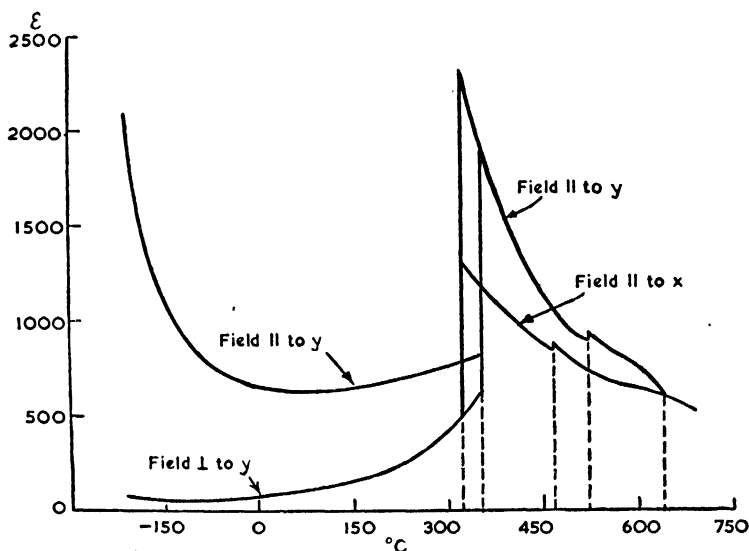


Fig. 5.10. Dielectric constants of NaNbO_3 (Cross and Nicholson, 1955).

be centrosymmetric but tilted with respect to one another, probably in the (100) and (010) planes. The 518°C and 640°C transitions would correspond to the removal of the tilt in two stages.

4.14. It is interesting to notice that solid solutions of NaNbO_3 containing as little as 10% KNbO_3 are ferroelectric and have phases corresponding to those of pure KNbO_3 (Shirane, Newnham and Pepinsky, 1954). The forced phase of NaNbO_3 (§ 4.9) occurs as a stable phase in this system (Cross, 1956); in this respect it behaves similarly to the forced phase of PbZrO_3 (see § 7.8, 7.9). The occurrence of small amounts of KNbO_3 as an impurity in NaNbO_3 may perhaps explain some of the discrepancies in the early work (cf. § 4.9).

5. THE PEROVSKITE FAMILY

4.15. *Sodium tantalate, NaTaO₃*

The structure of this substance is orthorhombic at room temperature, with cell dimensions $a = 5.524 \text{ \AA}$, $b = 3.883 \times n \text{ \AA}$, $c = 5.478 \text{ \AA}$ (Vousden, 1951a); the angle $(101)_\Lambda(10\bar{1})$ is $90^\circ 29'$.

It has been reported ferroelectric (Matthias, 1949 (*a*)) with a Curie point at 475°C , above which it becomes cubic, but no further details have been published. Cross (1956) finds certain similarities to NaNbO_3 in its high-temperature transitions, but doubts whether it is completely isomorphous.

4.16. *Rubidium tantalate, RbTaO₃*

This is tetragonal, with a transition at 245°C to ideal cubic. It is believed to be ferroelectric (Smolenskii and Kozhevnikova, 1951).

5 Lithium niobate, LiNbO_3

5.1. The room-temperature structure is related to, but significantly different from, the ilmenite structure (Bailey, 1952).

The space group is $R3c$; the unit cell is rhombohedral, with $a = 5.4920 \text{ \AA}$, $\alpha = 55^\circ 53'$, and contains 2 formula-units. (Referred to hexagonal axes, the dimensions are $a_H = 5.147 \text{ \AA}$, $c_H = 13.856 \text{ \AA}$, the cell-contents 6 formula-units.) The cations lie on the triad axis, in pairs of sites (u, u, u) and $(\frac{1}{2} + u, \frac{1}{2} + u, \frac{1}{2} + u)$. For Li, $u_1 = 0.18$; for Nb, $|u_2| = 0.02$, but the sign of u_2 relative to u_1 is not known. The oxygen atoms lie on a single set of general positions typified by $(x, \frac{1}{2} - x - \varepsilon, \frac{1}{4} + \varepsilon)$, with $x = 0.628$ and ε not distinguishably different from zero.

5.2. The structure is most easily pictured as built up from a hexagonal close-packed array of oxygens (Fig. 5.11 (*a*)). This forms octahedra with centres on the triad axes and shared faces perpendicular to the axes. Two successive octahedra are occupied by the cations Nb and Li, the third is empty, and then the sequence repeats: Nb, Li, empty . . . The oxygen parameter, 0.628, is not exactly that required for ideal close-packing, which is 0.583 or $\frac{7}{12}$; the effect is to move the atoms slightly in a plane perpendicular to the axis, as shown in Fig. 5.11 (*b*), and to enlarge the Li octahedron on the side away from Nb, while leaving the Nb octahedron small and regular. Neither Li nor Nb is centrally placed in its octahedron; Li is displaced towards the larger side.

5.3. The comparison of this structure with ilmenite (FeTiO_3) is interesting and important. Both are based on hexagonal close-packing of oxygens; both use the same octahedral sites for the cations.

FERROELECTRICITY IN CRYSTALS

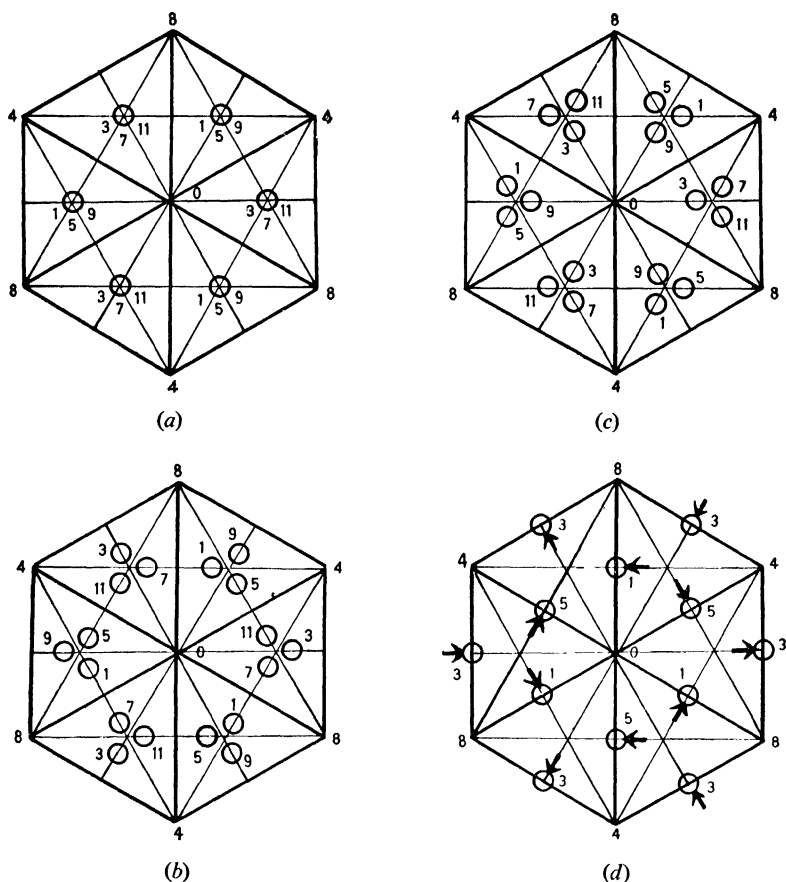


Fig. 5.11. Structures based on close packing of oxygens (Megaw, 1954).

(a) Ideal hexagonal close packing, (b) Array of oxygens with parameters as in LiNbO_3 , (c) Array of oxygens with parameters as in FeTiO_3 , (d) Array of oxygens as in ideal perovskite, with arrows showing deviation from LiNbO_3 .

In each case, contents of rhombohedral unit cell are shown projected on (111) (hexagonal (0001)) except that in (d) the upper half of the cell has been omitted. Figures give approximate heights of atoms above (0001) in twelfths of c_u .

But whereas in LiNbO_3 the sequence (representing an empty site by X) is Nb, Li, X, Nb, Li, X, Nb . . . , in FeTiO_3 it is X, Fe, Ti, X, Ti, Fe, X, Fe The oxygen parameter in FeTiO_3 is 0.550, giving the arrangement shown in Fig. 5.11 (c); the octahedra containing

5. THE PEROVSKITE FAMILY

Ti and Fe are of equal size and similarly distorted. The structure of FeTiO_3 is centrosymmetric; that of LiNbO_3 is not.

5.4. The relation of LiNbO_3 to the perovskite structure is not as immediately apparent, but is of more physical significance. If the oxygen parameter increased to 0.75, the oxygens would take up the positions shown in Fig. 5.11 (*d*) where they form a 3-dimensional network of octahedra, linked by their corners, containing Nb atoms—exactly the perovskite arrangement. The octahedra surrounding Li lose their identity, becoming merged with the empty octahedra to give a 12-coordinated site. If the Li atom moves to the centre of this site, the complete perovskite structure is formed. (In Fig. 5.11 (*d*) this is viewed in projection down the cube body diagonal.)

The perovskite structure can therefore be derived *geometrically* from LiNbO_3 by a continuous displacement of atoms—i.e. the transformation is a topological one. Whether it is *physically* possible is not known. The magnitudes of the atomic displacements involved are rather large: 1.0 Å for Li and 0.6 Å for O. A similar transition is quite impossible for the ilmenite structure, since the initial distribution of Ti is quite different, and interchange with Fe would be needed.

If LiNbO_3 is considered as a perovskite structure with very large atomic displacements, it may best be compared with rhombohedral BaTiO_3 . The sub-cell of LiNbO_3 is a rhombohedron, with $a = 3.762$ Å, and $\alpha = 93^\circ 40'$; thus the cube is compressed along the triad axis, whereas in BaTiO_3 it is believed to be extended. In BaTiO_3 the sub-cell is assumed to be the true cell; in LiNbO_3 , adjacent sub-cells differ only in the oxygen positions, an effect which might have escaped notice experimentally in BaTiO_3 .

5.5. The existence of ferroelectricity in LiNbO_3 has been reported by Matthias and Remeika (1949); the effect is said to be observed at temperatures above 200°C , and this probably implies a large coercive field, but no further details are published. At room temperature the crystals are piezoelectric.

5.6. *Lithium tantalate, LiTaO_3*

The structure of LiTaO_3 is isomorphous with that of LiNbO_3 (Bailey, 1952); the cell dimensions are $a = 5.4703$ Å, $\alpha = 56^\circ 10'$ (or on hexagonal axes, $a_H = 5.150$ Å, $c_H = 13.774$ Å). It is ferroelectric, the effect setting in at about 200°C (Matthias and Remeika, 1949).

6 Tungsten trioxide, WO_3

6.1. Tungsten trioxide is not easily obtained in good single crystals; most of the material is heavily twinned. The structure is of distorted multiple-cell perovskite type, with the large cations entirely missing. The room-temperature structure is pseudo-orthorhombic, with cell dimensions approximately $2a_0 \times 2a_0 \times a_0$. There is some doubt about the true symmetry. In the original structure determination by Bräkken (1931) it was reported as triclinic; more recent work by Ueda and Kobayashi (1953) indicates it as monoclinic. The latter authors give lattice parameters as follows:

$$a = 7.274 \pm 0.002 \text{ \AA}, \quad b = 7.501 \pm 0.001 \text{ \AA}, \\ c = 3.824 \pm 0.003 \text{ \AA}, \quad \beta = 89^\circ 56'.$$

The space group is No. 14, $P2_1/a$; there are 4 formula-units in the cell,

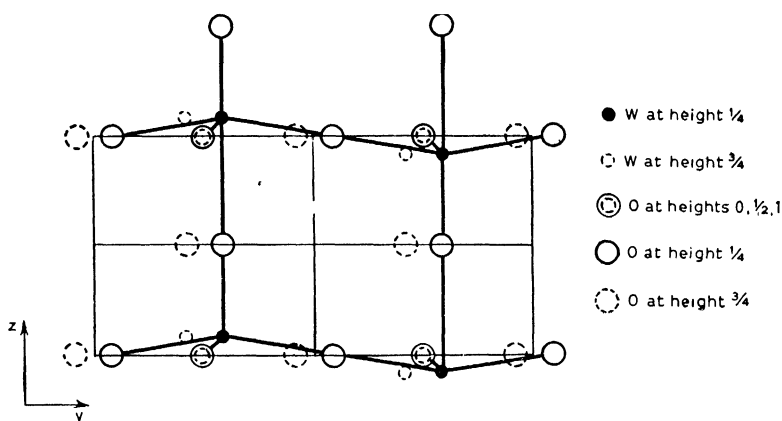


Fig. 5.12. Room-temperature structure of WO_3 : projection on (100) (with atomic displacements exaggerated).

with all atoms occupying general positions. Fig. 5.12 shows the projection on (100). Atomic parameters are given in Table 5.6. The oxygen positions were determined mainly from packing considerations, and hence interatomic distances derived from them must be treated with reserve.

6.2. The structure has a centre of symmetry, which serves as a fixed origin from which to measure atomic displacements. The displacements of W are anti-parallel in pairs related by the symmetry centre, lying nearly but not exactly in the (010) plane along the two face-diagonals of the sub-cell. Their lengths are about 0.2–0.3 Å, much larger than those in BaTiO_3 and comparable with those of Nb in

5. THE PEROVSKITE FAMILY

TABLE 5.6

Atomic parameters in WO_3 (Ueda and Kobayashi, 1953)

	x	y	z
W	0.256	0.271 *	0.053
O _I	0.250	0.030	0
O _{II}	0	0.250	0
O _{III}	0.250	0.280	0.500

General positions: x, y, z ; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2} + x, \frac{1}{2} - y, z$; $\frac{1}{2} - x, \frac{1}{2} + y, \bar{z}$.

* In the original paper, the value of $y - \frac{1}{4}$ is given as -0.021 , but this seems to be a slip, as it is inconsistent with the bond lengths and bond angles calculated by the authors.

NaNbO_3 . Considered alone, their arrangement in space also resembles that of Nb in NaNbO_3 , but relative to the neighbouring oxygens it is very different. The oxygen octahedra are distorted from regularity, and the position of W within them is such that the two W-O distances in the z direction are very unequal; their lengths are 2.11 Å and 1.71 Å, as compared with 1.83 Å and 1.87 Å in the x and y directions. These may be compared with the similar but less extreme differences of Ti-O distances in BaTiO_3 .

There is twinning on (110) (Ueda and Kobayashi, 1953) and the domain structure resembles that in BaTiO_3 (Ueda and Ichinokawa, 1950; Rhodes, 1952).

6.3. Other forms have been reported at different temperatures, but only one examined in detail.

Above 740° C there is a tetragonal structure (Kehl, Hay and Wahl, 1952) with $a \simeq \sqrt{2}a_0$, $c \simeq a_0$; more exactly, the values at 950° C are

$$a = 5.272 \pm 0.002 \text{ Å}, \quad c = 3.920 \pm 0.002 \text{ Å}$$

The space group is $P4/nmm$, the cell-contents 2 formula-units. All atoms are in special positions on tetrad or diad axes. There are two arbitrary parameters; the z -parameter of W is 0.06, while that of O₁ cannot be accurately determined.

The characteristic feature of the structure is the displacement of W from the plane of four surrounding O's by 0.23 Å. Octahedra sharing corners in this plane have W displacements which are alternately up and down; successive layers of octahedra in the z direction are identical. The structure is that shown as a hypothetical example in Fig. 6.2 (b); it is in fact the structure which might have been predicted for BaTiO_3 (see Chap. 10, § 9.3).

The thermal expansion and volume change at the transition have been studied by Ueda and Ichinokawa (1951).

Differential thermal analysis curves suggest a transition at 900°C which does not correspond to any observed change of structure.

At -50°C there is a transition below which the symmetry is increased relative to that of the room-temperature form (Matthias and Wood, 1951).

6.4. Investigation of the electrical properties is difficult, because of the tendency of the material to become conducting. The dielectric constant of the sintered ceramic is high, about 1000 at room temperature (Ueda and Ichinokawa, 1950), but no spontaneous polarization has been observed. At the transition above 700° there is an anomaly of the dielectric constant (Sawada, Ando and Nomura, 1951), indicating that the room-temperature form is antiferroelectric. The transition is also accompanied by a specific heat anomaly, a contraction of volume, and a change in the domain structure.

Hysteresis loops have been observed at -198° (Matthias, 1949), showing that the low-temperature form is ferroelectric.

7 Compounds of lead: lead titanate

7.1. At room temperature, PbTiO_3 has a small-cell tetragonal structure, isomorphous with tetragonal BaTiO_3 (Megaw 1946). The substance has been studied in detail by Shirane and Hoshino (1951) and Shirane, Pepinsky and Frazer (1955). The cell dimensions are $a = 3.904 \text{ \AA}$, $c = 4.150 \text{ \AA}$; space group No. 99, $P4mm$; cell-content 1 formula-unit. The axial ratio, c/a , is 1.063, markedly larger than for BaTiO_3 . Atomic parameters have been determined by neutron

TABLE 5.7

Atomic positions in tetragonal PbTiO_3 (Shirane, Pepinsky and Frazer, 1955, referred to origin on Ti)

Atom	Coordinates	Values of z
Ti	0, 0, 0	0
Pb	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z$	-0.041
O ₁	0, 0, z_1	$+0.069$
O ₂	$\left\{ \frac{1}{2}, 0, z_2 \right\}$ $\left\{ 0, \frac{1}{2}, z_2 \right\}$	$+0.069$

5. THE PEROVSKITE FAMILY

diffraction, and are given in Table 5.7, which may be compared with Table 4.1 for BaTiO_3 . The striking feature here is the large relative displacement of Pb. The oxygen framework remains almost undistorted, since the two independent O's have no change of parameter relative to each other. With respect to this framework, Pb moves through 0.46 Å and Ti through 0.29 Å in the same direction, as compared with displacements of 0.07 Å and 0.13 Å for Ba and Ti respectively in BaTiO_3 .

7.2. There is a transition point at 490° C, above which the substance becomes cubic. At low temperatures, a transition to a multiple-cell structure has been reported at - 100° C when the substance is cooled slowly (Kobayashi and Ueda, 1955). The new cell dimensions are $a' = 4a$, $c' = 2c$.

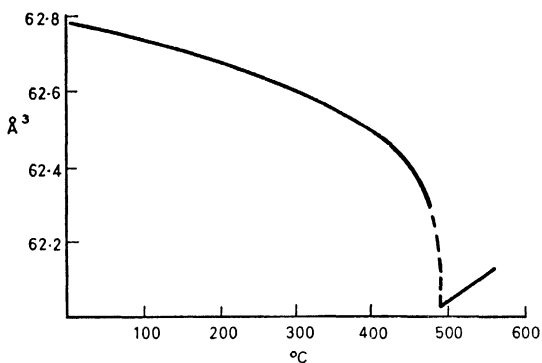


Fig. 5.13. PbTiO_3 : unit cell volume (Shirane and Hoshino, 1951).

7.3. Above room temperature, c decreases and a increases, until just below the 490° transition point c/a is 1.02. Fig. 5.13 shows the variation of volume with temperature; the negative expansion coefficient below the transition and the abrupt decrease in volume at the transition point are worthy of notice. Numerical values are given in Table 5.8.

There is also a contraction with increasing temperature at the -100° C transition. In this region, c has a negative thermal expansion coefficient.

There is a specific-heat anomaly associated with the 490° transition. The peak is sharp, and the total energy very large (see Table 5.8).

7.4. The dielectric constant (measured on a ceramic specimen) has a sharp peak at the transition point, of height 800, dropping to about

FERROELECTRICITY IN CRYSTALS

TABLE 5.8

Compound	Vol. expansion coefficient $\times 10^6$	$\frac{\Delta v}{v} \times 100$	Transition energy	Entropy	Reference
	deg. ⁻¹		cal. mol. ⁻¹	cal. mol. ⁻¹ deg. ⁻¹	
PbTiO ₃ : Tetragonal Cubic	- 16 + 25	- 0.44	1150	1.60	Shirane and Hoshino, 1951
PbZrO ₃ : Pseudo-tetrag. Cubic	+ 25 + 25	+ 0.27	440		Sawaguchi, Shirane and Takagi, 1951; Shirane, 1952
PbHfO ₃ : Pseudo-tetrag. Tetrag. Cubic	+ 20 + 27	+ 0.20 + 0.20			Shirane and Pepinsky, 1953
Pb(Ti. ₀₃ Zr. ₉₇)O ₃ : <i>A</i> α <i>A</i> β <i>F</i> α <i>P</i> α	+ 30 + 27 + 7 + 30	+ 0.07 + 0.48 - 0.10	100 35 250	0.22 0.073 0.51	Sawaguchi, 1953
Pb(Ti. ₀₅ Zr. ₉₅)O ₃ : <i>A</i> α <i>F</i> α <i>P</i> α			80 180		Shirane and Takeda, 1952
(Pb. ₉₂₅ Ba. ₀₇₅)ZrO ₃ I Rhombohedral Cubic	+ 22 + 23	+ 0.67 - 0.24	190 230		Shirane, 1952; Shirane and Hoshino, 1954
(Pb. ₉₅ Sr. ₀₅)ZrO ₃ I II Cubic	+ 24 + 32	+ 0.10 + 0.20	180 230		Shirane, 1952; Shirane and Hoshino, 1954

5. THE PEROVSKITE FAMILY

50 at room temperature. Above the transition the curve follows a Curie-Weiss law with a Curie constant $C = 1.1 \times 10^5$ deg., which is of the same order of magnitude as for BaTiO_3 (Shirane and Hoshino, 1951).

8 Lead zirconate, PbZrO_3

8.1. There has been considerable uncertainty about the symmetry of the room-temperature structure. Powder photographs suggested that it was tetragonal, with a multiple cell; the dimensions of the sub-cell are $a = 4.150$ Å, $c = 4.099$ Å, $c/a = 0.988$ (Ueda and Shirane, 1951). With a single crystal, however, optical observations showed that it was actually orthorhombic (Sawaguchi, Maniwa and Hoshino, 1951), and single-crystal X-ray photographs established the size of the unit cell as approximately $\sqrt{2}a_0 \times 2\sqrt{2}a_0 \times 2a_0$, and the space group as $Pbam$ or Pba . The cell-content is 8 formula-units. There are antiparallel displacements of the Pb atoms along the x axis (i.e. parallel to one face-diagonal of the sub-cell) of magnitude about 0.2 Å; the parameters of the other atoms are not known.

8.2. There is a transition at 230° C, above which the structure is cubic.

The expansion coefficients and the change of volume at the transition point are given in Table 5.8. The change of volume is an *increase* (Shirane, Sawaguchi and Takeda, 1950).

8.3. The optical properties have been studied (Jona, Shirane and Pepinsky, 1955). The crystal is optically negative, with the shortest axis of the indicatrix along x and the longest along y , but the double refraction is much smaller than that of NaNbO_3 or orthorhombic BaTiO_3 . The greatest refractive index has a value about 2.2.

8.4. The anomalous energy of transition is large (Shirane, 1952), and perhaps should rather be considered as a true latent heat (see Table 5.8).

8.5. The dielectric constant has a peak at the transition (Fig. 5.18), and falls off above it with increasing temperature according to a Curie-Weiss law, very similarly to BaTiO_3 with $c = 1.2 \times 10^5$ deg. and $T_0 = 185^\circ\text{C}$. In contrast with BaTiO_3 , however, it shows a lowering of the Curie point when a biasing field is applied (Shirane, Sawaguchi and Takagi, 1951). With moderate applied fields ($E < 23$ kV cm.⁻¹) no hysteresis loops are observed below the transition point. These latter properties are characteristic of an antiferroelectric.

FERROELECTRICITY IN CRYSTALS

To test this conclusion, Shirane, Sawaguchi and Takagi prepared a specimen by cooling it through the transition point in an electric field, and then shorting the faces through a galvanometer; on subsequent heating, no discharge current was observed at the transition point, as would have been expected if there had been a sudden destruction of spontaneous polarization—and as was observed when BaTiO_3 was similarly treated. PbZrO_3 is therefore not ferroelectric. In view of the dielectric constant anomaly, the low-temperature form must be regarded as antiferroelectric.

8.6. When large fields of 30 kV cm^{-1} are used at temperatures near the Curie point, hysteresis loops of a new kind appear (see Fig. 5.14). The central part of the P/E plot is linear, but at each end there is a

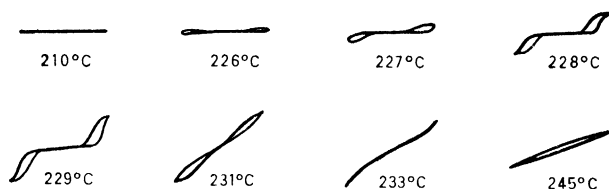


Fig. 5.14. Hysteresis loops in PbZrO_3 (Shirane, Sawaguchi and Takagi, 1951).

$$E_{\text{max}} = 30 \text{ kV cm}^{-1}.$$

loop. These can be explained by assuming that the material *becomes* ferroelectric when acted on by a sufficiently large field. This implies that there must exist a ferroelectric structure with free energy only slightly greater, in the absence of a field, than that of the stable antiferroelectric structure; in the presence of a large field, its free energy is less than that of the antiferroelectric (Shirane, Sawaguchi and Takagi, 1951). The threshold field needed to induce the ferroelectric phase can be determined from the hysteresis loops; its variation with temperature is shown in Fig. 5.19.

8.7. Though the ferroelectric phase is not stable at any temperature in the absence of a field for pure PbZrO_3 , it is stable at room temperature for solid solutions containing small amounts of PbTiO_3 or BaZrO_3 . The structure of the phase is almost certainly that of the rhombohedral phase in the system $(\text{Pb,Ba})\text{ZrO}_3$, considered in § 10.9.

9 Lead hafnate, PbHfO_3

9.1. This is isomorphous with lead zirconate, PbZrO_3 (Shirane and Pepinsky, 1953). The unit cell is slightly smaller (as is expected from

5. THE PEROVSKITE FAMILY

the smaller Hf ion). The sub-cell has dimensions $a = 4.136 \text{ \AA}$, $b = 4.099 \text{ \AA}$, $c/a = 0.991$, and the extra lines resemble those of PbZrO_3 in position and intensity.

There are two transition points, near 163°C and 215°C . Above 215°C the structure is ideal perovskite. The intermediate form is probably tetragonal multiple-cell; the sub-cell has an axial ratio of 0.997 , and the extra lines are quite different from those of the low-temperature form.

The variation of the dimensions of the sub-cell with temperature are shown in Fig. 5.15. At both transitions there is an increase of

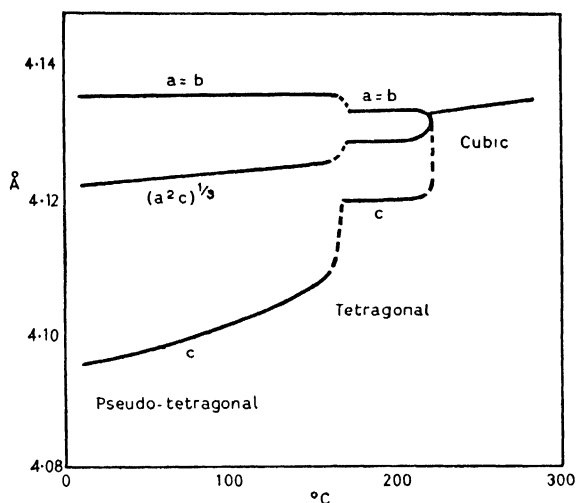


Fig. 5.15. PbHfO_3 : lattice spacing vs. temperature (Shirane and Pepinsky, 1953).

volume. Numerical values of this and the expansion coefficients are given in Table 5.8.

5.2. The dielectric constant of a ceramic specimen is about 90 at room temperature, and rises to a peak of about 550 at the upper transition. The lower transition is marked by a smaller anomaly. Above the upper point the dielectric constant follows a Curie-Weiss law with a Curie constant of the same order of magnitude as for 3BaTiO_3 and PbZrO_3 .

5.3. No dielectric hysteresis loops could be found at any temperature, with fields up to 40 kV cm^{-1} . A biasing field lowered the temperature of the peak corresponding to the upper transition. The intermediate phase, like the lower, is therefore antiferroelectric.

10 Solid solutions of PbTiO_3 and PbZrO_3 with Ba, Sr and Ca10.1. $(\text{Pb},\text{Ba})\text{TiO}_3$

There is a complete range of solid solutions between the two ends, and no new phase has been recorded. All geometrical and physical properties vary continuously, though not necessarily linearly, from one end to the other (Shirane and Suzuki, 1951; Shirane and Takeda, 1951).

10.2. $\text{Pb}(\text{Ti},\text{Zr})\text{O}_3$

Here again there is a continuous range of compositions, but a number of different phases occur (Shirane and Takeda, 1952; Shirane, Suzuki and Takeda, 1952; Shirane and Suzuki, 1952). The

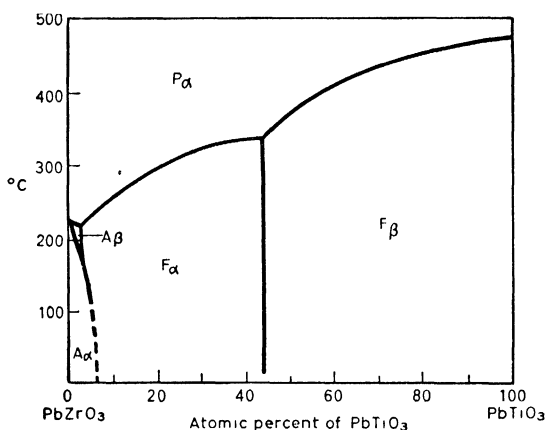


Fig. 5.16. Phase diagram of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (Sawaguchi, 1953).

phase diagram is shown in Fig. 5.16. From 100% to 45% (atomic) Ti, the structure is tetragonal, isomorphous with that of pure PbTiO_3 . Between 45% and about 5% Ti, a new phase appears, rhombohedral small-cell. Below 5% Ti, at room temperature, the phase is that of pure PbZrO_3 . The boundary between these two latter phases is temperature-dependent, the rhombohedral phase being stable for smaller amounts of Ti at higher temperatures. Near the boundary of the cubic phase, at a composition of 3% (atomic) Ti, yet another phase has been reported (Sawaguchi, 1953). This latter is easily masked by thermal hysteresis, so that it is only observed in experiments with rising temperature.

The two end phases have properties which vary continuously from

5. THE PEROVSKITE FAMILY

those of pure PbTiO_3 and pure PbZrO_3 . The lattice parameters at room temperature are shown in Fig. 5.17.

10.3. The rhombohedral phase containing 5% (atomic) Ti at 200°C has lattice parameters $a = 4.143\text{ \AA}$, $\alpha = 89^\circ 51'$ (Shirane and Hoshino, 1952). The intensities of the X-ray powder lines indicate a displacement of Pb and (Zr, Ti) atoms relative to each other along the triad axis; displacements relative to the O atoms could not be measured. This, in the small cell, is only compatible with a polar space group; the space group deduced is No. 160, $R3m$. The triad axis is the polar direction.

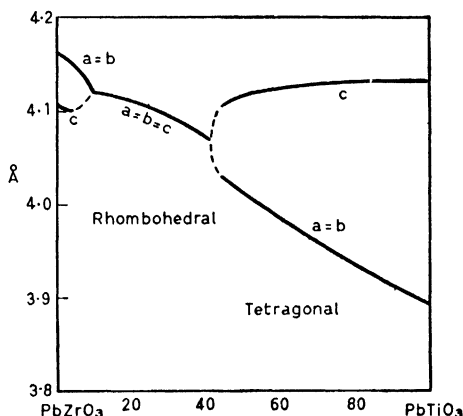


Fig. 5.17. Lattice spacing of $\text{Pb}(\text{Ti,Zr})\text{O}_3$ at room temperature (Shirane and Suzuki, 1952).

The magnitude of the relative displacement of the cations has been estimated by Sawaguchi (1953). Since there is no centre of symmetry, the same difficulty occurs as with BaTiO_3 in distinguishing between the effects of atomic parameter variations and anisotropic thermal vibrations of the atoms (see Chap. 4, § 3.1); the best agreement with experiment was obtained with a relative cation displacement of $0.14\text{ \AA}$.

This rhombohedral phase seems to be isomorphous with the rhombohedral phase of BaTiO_3 .

10.4. The intermediate phase marked $A\beta$ on the phase diagram appears to be tetragonal multiple-cell, with $c/a = 0.994$ at 190°C ; the extra lines differ from those of the $A\alpha$ phase, which is identical in structure with pure PbZrO_3 . Possibly the $A\beta$ phase may be the same as the intermediate phase in PbHfO_3 .

FERROELECTRICITY IN CRYSTALS

10.5. The thermal expansion coefficients, and the changes of volume, energy and entropy at the transition points, are given in Table 5.8.

10.6. The electrical properties show marked variations, which, in fact, gave the first evidence of the existence of different phases, and which have been used to fix the phase boundaries.

For a given composition, the dielectric constant has a peak (or shelf) at each temperature corresponding to a transition. Curves for different compositions are illustrated in Fig. 5.18.

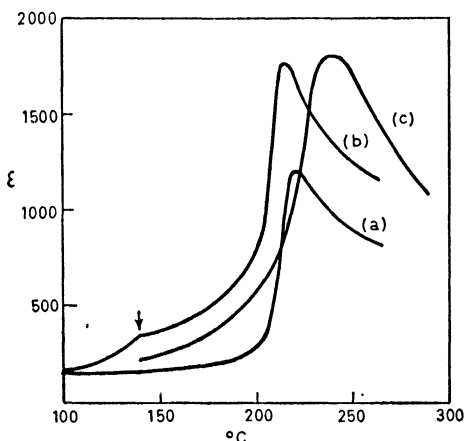


Fig. 5.18. Dielectric constant (Shirane and Takeda, 1952).

(a) PbZrO_3 , (b) $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$, (c) $\text{Pb}(\text{Zr}_{0.90}\text{Ti}_{0.10})\text{O}_3$.

The rhombohedral phase shows dielectric hysteresis loops for small fields; it is therefore ferroelectric. As expected, the upper transition temperature is raised by an applied field.

Neither of the multiple-cell phases $A\alpha$ or $A\beta$ gives loops with small fields. The upper transition temperature is lowered by an applied field. Both phases are therefore antiferroelectric.

10.7. That the lower transition point is associated with a true loss of spontaneous polarization, and not merely a freezing-in of the dipoles, was confirmed by the pyroelectric test (Shirane and Takeda, 1952). A specimen prepared by cooling from the cubic to the rhombohedral phase in an applied field, and then shorting opposite faces through a galvanometer, subsequently gave a discharge current when it was cooled through the lower transition point. This can only represent the disappearance of the bound charges associated with spontaneous polarization. A similar discharge current was observed

5. THE PEROVSKITE FAMILY

(as expected) on heating a prepared crystal through the upper transition point. This behaviour may be contrasted with that of pure PbZrO_3 (see § 8.5).

10.8. When moderately large alternating fields are applied to phases $A\alpha$ and $A\beta$ hysteresis loops of 'butterfly' type are produced. The explanation is similar to that for pure PbZrO_3 : the application of a sufficiently large field 'forces' the transition to a ferroelectric phase, which is in fact the rhombohedral phase $F\alpha$ (cf. § 10.3). The threshold field needed at different temperatures for material of composition

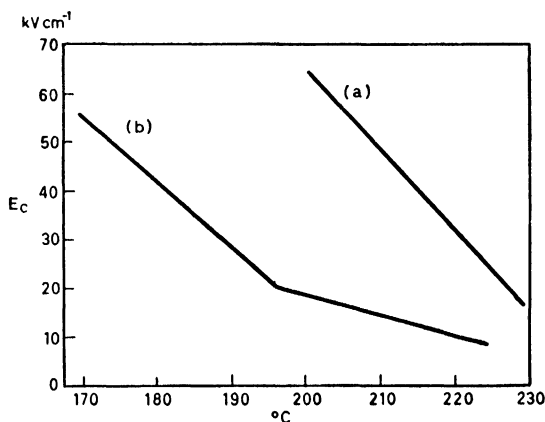


Fig. 5.19. Threshold field for transition from antiferroelectric to ferroelectric (Sawaguchi, 1953).

(a) PbZrO_3 , (b) $\text{Pb}(\text{Zr}_{0.98}\text{Ti}_{0.02})\text{O}_3$.

$\text{Pb}(\text{Zr}_{0.98}\text{Ti}_{0.02})\text{O}_3$ is shown in Fig. 5.19. The abrupt change in the slope of the curve represents the boundary between the phases $A\alpha$ and $A\beta$.

10.9. $(\text{Pb}, \text{Ba})\text{ZrO}_3$

This system has been studied by Shirane (1952) and Shirane and Hoshino (1954). It is of particular interest because, though neither of the end members BaZrO_3 and PbZrO_3 is ferroelectric, yet an intermediate phase is ferroelectric.

The phase diagram at the PbZrO_3 end is shown in Fig. 5.20. With very small amounts of Ba, the structure is pseudotetragonal multiple-cell, isomorphous with pure PbZrO_3 . With slightly larger amounts of Ba, a rhombohedral small-cell phase occurs. The lattice parameters are $a = 4.161 \text{ \AA}$, $\alpha = 89^\circ 52'$, for a composition of 7.5% (atomic) Ba

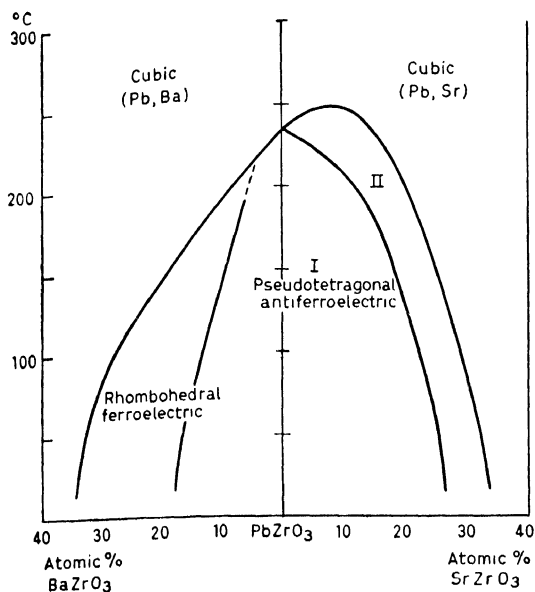


Fig. 5.20. Phase diagram of $(\text{Pb,Ba})\text{ZrO}_3$ and $(\text{Pb,Sr})\text{ZrO}_3$ (Shirane and Hoshino, 1954).

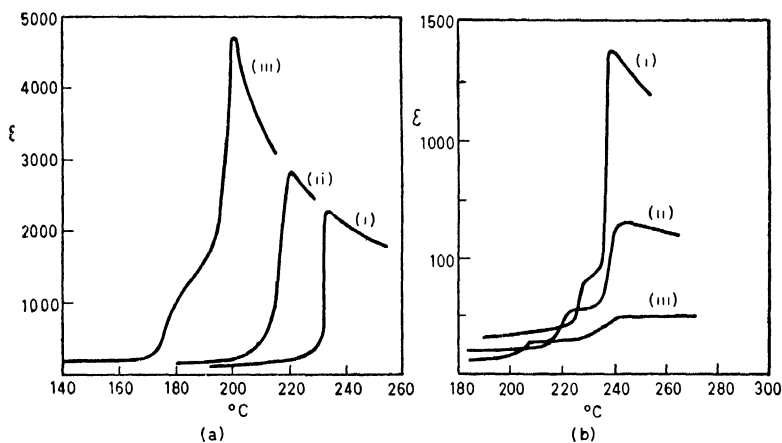


Fig. 5.21. (a) Dielectric constant of $(\text{Pb,Ba})\text{ZrO}_3$ (Shirane, 1952).

(i) Pure PbZrO_3 , (ii) 3% Ba, (iii) 7.5% Ba.

(b) Dielectric constant of $(\text{Pb,Sr})\text{ZrO}_3$ (Shirane, 1952).

(i) 2% Sr , (ii) 5% Sr, (iii) 10% Sr.

5. THE PEROVSKITE FAMILY

and a temperature of 185° C. From the intensities of the X-ray powder lines it can be deduced that there are displacements of the cations relative to each other along [111]. A similar state of affairs is true for material of composition 30% Ba at room temperature. This structure is probably isomorphous with that of the rhombohedral phase in $\text{Pb}(\text{Ti},\text{Zr})\text{O}_3$, and with rhombohedral BaTiO_3 .

10.10. The expansion coefficients and volume and energy changes at the transition points are given in Table 5.8. The increase of volume from pseudotetragonal to rhombohedral is particularly large; from rhombohedral to cubic there is a decrease.

10.11. The dielectric constant has a peak at the upper transition point, which increases in height and decreases in temperature with increasing amounts of Ba (Fig. 5.21 (a)). At the boundary of the intermediate phase, there is a small anomaly.

The rhombohedral phase is ferroelectric, showing dielectric hysteresis loops. The pseudotetragonal phase shows no hysteresis loops for small fields; like pure PbZrO_3 , it is antiferroelectric.

10.12. At compositions which are normally antiferroelectric up to the Curie point—for example, 5% (atomic) Ba—a ferroelectric phase can be induced by a moderate alternating field. The graph of threshold field against composition, at room temperature, is shown in Fig. 5.22.

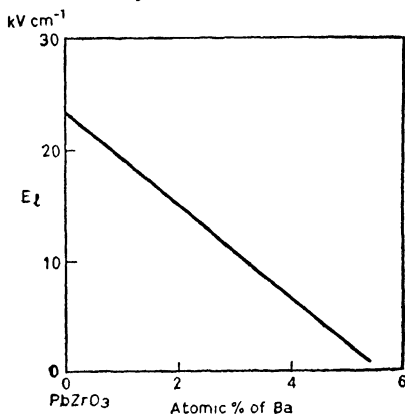


Fig. 5.22. Threshold field E_t for ferroelectric phase of $(\text{Pb},\text{Ba})\text{ZrO}_3$ at room temperature (Shirane, 1952).

It is natural to assume that this forced ferroelectric phase is identical in structure with the ferroelectric phase occurring without an applied field at slightly different temperatures or compositions. (The alternative suggestion that half the dipoles of the pseudotetragonal phase could be reversed in sign without affecting the structure as a whole is quite incompatible with any theories of crystal structure.) Direct confirmation of the identity of the two was obtained by Shirane and Hoshino, who examined the X-ray powder photograph at 202° C of a specimen containing 5% Ba, with and without a d.c. field of 15 kV cm.⁻¹, and found patterns corresponding

to the rhombohedral and pseudo-tetragonal phases respectively. The change of volume in the forced transition was about the same as that in the zero-field transition of a specimen with 7.5% Ba.

10.13. $(\text{Pb},\text{Sr})\text{ZrO}_3$

Solid solutions of SrZrO_3 in PbZrO_3 differ in certain ways from those of BaZrO_3 (Shirane, 1952; Shirane and Hoshino, 1954). The phase diagram is shown in Fig. 5.20. With small amounts of Sr, the same pseudotetragonal phase is found as for pure PbZrO_3 and solid solutions with small amounts of Ba. With slightly larger amounts of Sr, however, a second phase is found which differs from that in the $(\text{Pb},\text{Ba})\text{ZrO}_3$ system. It is tetragonal, its sub-cell having parameters $a = 4.147 \text{ kX}$ and $c/a = 0.9955$ for a composition containing 5% (atomic) Sr and a temperature of 230°C . There are very faint extra lines, of different spacing and intensity from those of the first phase; to index them, a true cell with dimensions more than double the sub-cell is required. At room temperature, for a composition containing 30% Sr, $c/a = 0.998$. At intermediate compositions, at appropriate temperatures, c/a varies continuously with composition; the pattern remains similar, but the extra lines become broader with increasing Sr concentrations. This phase appears to be isomorphous with the intermediate phase in PbHfO_3 .

Volume relations and transition energies are given in Table 5.8.

10.14. The dielectric constant shows peaks at the transition temperatures (Fig. 5.21 (b)). That at the lower transition is much more marked than in the $(\text{Pb},\text{Ba})\text{ZrO}_3$ system, but that at the upper transition decreases rapidly in height (as well as moving to higher temperatures) with increasing amounts of Sr.

No hysteresis loops were observed in either phase, even up to fields of 40 kV cm^{-1} . Both phases are therefore antiferroelectric. This was confirmed for the intermediate phase by the pyroelectric test: a prepared specimen gave no discharge current on heating through the upper transition point.

10.15. $(\text{Pb},\text{Ca})\text{ZrO}_3$

This system has not been studied in great detail, but it appears to be similar to $(\text{Pb},\text{Sr})\text{ZrO}_3$ at the PbZrO_3 end (Shirane, 1952).

11 Summary

According to present knowledge, there seem to be 5 distinct phases shown by the compounds PbTiO_3 , PbZrO_3 , PbHfO_3 and their solid solutions with each other and with corresponding compounds of alkaline earth metals. These are summarized in Table 5.9.

5. THE PEROVSKITE FAMILY

TABLE 5.9

Phases in perovskite structures containing Pb

Name of phase	Structure type	Examples
$P\alpha$	Ideal cubic	Room temperature: (Pb,Ba)ZrO ₃ above 35% Ba (Pb,Sr)ZrO ₃ above 35% Sr High temperature: all compounds
F	Tetragonal small-cell (isomorphous with tetragonal BaTiO ₃). Ferroelectric	Room temperature: Pb(Ti,Zr)O ₃ above 45% Ti (Pb,Ba)TiO ₃ , all compositions
$F\alpha$	Rhombohedral small-cell (isomorphous with rhombohedral BaTiO ₃). Ferroelectric	Room temperature: Pb(Ti,Zr)O ₃ from 7.5 to 45% Ti (Pb,Ba)ZrO ₃ from 20 to 35% Ba Near 230°: Pb(Ti,Zr)O ₃ at 5% Ti (Pb,Ba)ZrO ₃ at 7.5% Ba PbZrO ₃ with applied field of 65 kV cm. ⁻¹
$A\alpha$ or I	Pseudotetragonal multiple-cell. Antiferroelectric	Room temperature: PbZrO ₃ PbHfO ₃ Pb(Ti,Zr)O ₃ up to 7.5% Ti (Pb,Ba)ZrO ₃ up to 20% Ba (Pb,Sr)ZrO ₃ up to 27% Sr (Pb,Ca)ZrO ₃ , small amounts of Ca
$A\beta$ or II or intermediate phase	Tetragonal multiple-cell. Antiferroelectric	Room temperature: (Pb,Sr)ZrO ₃ , 27 to 35% Sr 163–215° C: PbHfO ₃ Near 230° C: Pb(Ti,Zr)O ₃ with 3% Ti (Pb,Sr)ZrO ₃ , very small amounts of Sr (Pb,Ca)ZrO ₃ , with 5% Ca

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For additional references, not dealt with in the text, see p. 149.

Chapter 6

DISCUSSION OF DISTORTED PEROVSKITE STRUCTURES

. . . we think only to find
a structur of blind atoms to their habits enslaved.

BRIDGES: *Testament of Beauty*

1 Introduction

The last two chapters gave a detailed account of the most important, or most fully-known, oxides with perovskite-type structures. We must now see whether any conclusions can be drawn as to why and in what circumstances the different structures occur.

Two different kinds of distortion from the ideal structure can be distinguished. In the first (best illustrated by CaTiO_3) the framework of oxygen octahedra crumples and becomes puckered round the large A cation, while the array of small B cations suffers only homogeneous distortion; each B remains at the centre of its octahedron, though this tilts and becomes irregular. An illustration of the effect is given in Fig. 6.1 for an imaginary structure where the tilting is in one plane only. In the second kind of distortion (for example, in tetragonal BaTiO_3) the B cation is off-centre in its octahedron; the octahedra suffer homogeneous distortion and may become irregular, but remain parallel and all alike. Both kinds of distortion may occur at once, for example in room-temperature NaNbO_3 , but it is best to consider them separately.

2 Packing distortion or crumpling

2.1. The first kind of distortion is purely a packing effect, of the kind considered at the beginning of Chap. 5. It can be explained using ionic forces only. It occurs in compounds where, if the ideal cubic structure were adopted, the cation A would be too small to make contact with its twelve oxygen neighbours. The high electrostatic valence of the B–O bond ($4/6$ in CaTiO_3 , $5/6$ in NaNbO_3), though it requires that the BO_6 group shall suffer little distortion, imposes no obstacle to its tilting relative to its neighbours. Such tilting would destroy the straight Ti–O–Ti linkage at the shared corners, and give a bond angle at O differing from 180° . But there is no reason to think that the 180° bond angle is generally the most stable

6. DISCUSSION OF DISTORTED PEROVSKITE STRUCTURES

arrangement for O, even in cases like this where the O has only two strong bonds. It would be so if the structure were purely ionic, but for homopolar bonds the expected angle is 109° . In fact, a kinked formation with some intermediate angle is commonly observed in solid oxides at room temperature (for example, about 130° in boron-oxygen groups; 142° and 150° respectively in two forms of silica, low-quartz and low cristobalite; 165° in the Si_2O_7 group in tilleyite). Thus a departure from the 180° angle is likely to add to, rather than detract from, the stability of an oxide.

2.2. We thus see that where there is a smallish A cation the B octahedra may be expected to pivot about their centres in such a way

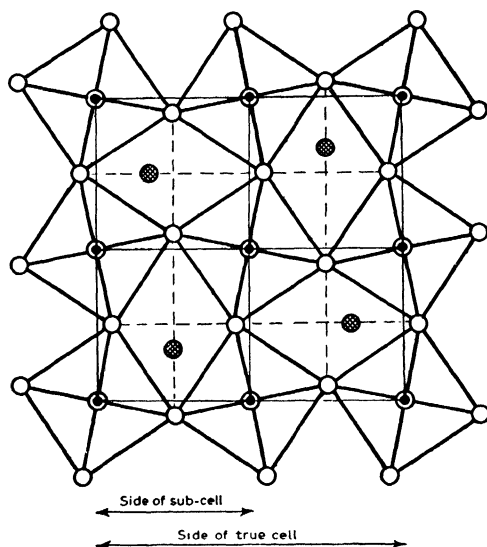


Fig. 6.1. Projection of imaginary structure, showing A displacements and BO_6 tilts in one plane.

as to bring some of their oxygens into close contact with A. The detailed way in which this is done cannot be predicted, but it is clear that it cannot be done without using at least two sub-cells for the new repeat unit.

Examining the list of structures in Table 5.3, and taking into account the ionic radii given in Table 5.1, we see that the crumpled structures are those of the moderately small A cations Ca, Na, Cd. Compounds of Pb are an exception, which will be considered separately below. It is legitimate and useful to consider LiNbO_3 as an extreme case of a crumpled perovskite.

These distortions are of the kind considered by Buerger in his discussion of displacive transitions (1951).

2.3. One point is worth noting. Some of the distorted structures with small A cations become cubic at high temperatures; CaTiO_3 is a doubtful example, but NaNbO_3 certainly does. The question arises, how is this compatible with the rules of ionic packing? Even if the whole thermal expansion of the structure were attributed to the Na ion, its radius would not become great enough to allow 12-coordination, according to the rules. Unless there are much greater changes (of opposite signs) in the separate radii of cations and anions than in their sum, the packing rules must be modified or abandoned. The ionic radii are in fact empirically-based quantities, and we rely on them because they give consistent results when used in room-temperature structures. There is little or no information to tell us what modification is needed to explain changes with temperature. We know that the atoms are undergoing thermal vibrations of considerable amplitude at room temperature, and that the amplitude increases with temperature, but not many experimental studies have been made of this 'temperature factor' at high temperatures, and its effect on the relative values of atomic radii has not been considered. The problem is an interesting one, and awaits attention.

3 'Off-centre' distortion

3.1. The second kind of distortion shown by perovskite-type structures is the 'off-centre effect'—the displacement of the small atom B within its octahedron of oxygen atoms. The best-known example is tetragonal BaTiO_3 ; here there is no tilting of the octahedra, and little distortion. The same is true of PbTiO_3 and high-temperature WO_3 , and probably of the other ferroelectric forms of BaTiO_3 and the three non-cubic forms of KNbO_3 . The off-centre effect also occurs in NaNbO_3 , LiNbO_3 , and probably in room-temperature WO_3 , though in these it is combined with various distortions and tilts of the octahedra.

Where the octahedra remain more or less regular, it is difficult or impossible to explain the distortion using only ionic forces. Ionic forces are central forces, and would be expected to hold the atom B in a symmetrical situation among its neighbours. Instead, the arrangement is very one-sided. This suggests that the bonds are to some extent *directed*, in which case they must have some covalent character. Support for this assumption comes from the actual B-O distances where they are known, namely in tetragonal BaTiO_3 and PbTiO_3 . The short Ti-O distances in these two structures are 1.87 and 1.78 Å respectively as compared with 1.96 for the radius sum. Such a

6. DISCUSSION OF DISTORTED PEROVSKITE STRUCTURES

contraction implies a considerable change in the interatomic forces. There is some rearrangement of the electron cloud which changes the balance between repulsive and attractive forces in this direction and allows closer approach. This is merely a different way of saying that some change in the homopolar bond system linking B to its neighbouring oxygens has taken place.

3.2. In arguing that an off-centre B atom can only be explained by homopolar bonding, it is not implied that a symmetrically placed B atom is necessarily wholly ionic. If, in a crystal, an atom has a regular octahedral environment, it may be explained as the effect either of ionic packing or of an octahedral system of covalent bonds; or of a combination of the two. The degree of covalent character can be estimated from the bond length, if the lengths for the two extreme cases are known (which is rarely true). Other methods of estimating it indicate that even in MgO it may make an appreciable contribution to the bond energy, and for the Ti-O bond, with its high electrostatic valence, it will be larger still.

Thus there is nothing new in supposing that the perovskites, even in the ideal cubic form, have a good deal of covalent character. The unusual feature of the 'off-centre' structures is that the covalent bond system is no longer strictly octahedral, as the ionic packing would require; there is a compromise, and the off-centre position is the result.

3.3. The covalent bond system adopted by an atom is characteristic of the atom and its state of ionization. It is rather striking that so many of the structures with off-centre B atoms are compounds of Nb^{5+} . (To the list given above we should probably add $\text{Cd}_2\text{Nb}_2\text{O}_7$ and $\text{Pb}_2\text{Nb}_2\text{O}_7$, which are dealt with in Chap. 7.) It would seem that this atom can form a bond system particularly favourable for the 'off-centre' compromise. Possibly Ta^{5+} behaves similarly, but the experimental evidence is rather scanty; if so, its transition to the symmetrical form occurs at lower temperatures.

In contrast to Nb^{5+} , the behaviour of Ti^{4+} is by no means uniform. While in BaTiO_3 and PbTiO_3 it is off-centre, in SrTiO_3 and CaTiO_3 it is symmetrically situated. The explanation seems to be that, while Ti normally has an octahedral bond system, the effect of abnormal volume conditions (to which covalent bond character is very sensitive) allows it to change to a less symmetrical arrangement. The abnormal conditions are provided in BaTiO_3 by the large Ba ion, which forces apart the oxygen framework, so that the average Ti-O distance is longer than the usual sum of the radii; this brings about the change of bond system and consequent off-centre position of Ti.

FERROELECTRICITY IN CRYSTALS

In PbTiO_3 the effect does not depend purely on the size of the Pb ion (which is smaller than Ba) but on its tendency to form covalent bonds, which will be discussed in a later paragraph.

3.4. We notice that the off-centre displacement can take place in three ways, illustrated by the three ferroelectric forms of BaTiO_3 . In order of decreasing temperature the displacements are directed towards a corner of the octahedron, towards the mid-point of an edge, and towards the mid-point of a face; referring to the corners of the octahedron towards which the cation moves, we may call them one-corner, two-corner, and three-corner displacements respectively. The same sequence of displacements occurs in KNbO_3 , but with different transition temperatures between them (Table 5.5). Again there are indications of the same sequence, with higher transition temperatures, in WO_3 .

It seems possible that the temperature ranges within which the different displacements occur are characteristic of the chemical nature of the atom. Thus in NaNbO_3 , where the detailed distortions are quite different from those of KNbO_3 , the two-corner displacement nevertheless occurs in a form stable over roughly the same range (-55°C to 360°C for NaNbO_3 , as compared with -40°C to 210°C for KNbO_3) and there are some indications that the forms existing below and above this range may have three-corner and one-corner displacements respectively (Chap. 5, § 4.10, 4.11). Again, in $\text{Cd}_2\text{Nb}_2\text{O}_7$ (Chap. 7, § 6.4), it is likely that the three-corner displacement occurs in the form stable below -88°C (the two-corner and one-corner displacements being suppressed because they are not possible derivatives of the ideal pyrochlore structure). The transition temperatures, thus interpreted, are listed in Table 6.1. LiNbO_3 is an exception, which may possibly be explained by the high polarizing power of the small Li cation.

TABLE 6.1
Transition temperatures in compounds of niobium

Compound	Centrosymmetric to 1-corner	1-corner to 2-corner	2-corner to 3-corner
KNbO_3	410°C	210°C	-40°C
NaNbO_3	$450-470^\circ \text{C}^*$	360°C^*	-55°C^*
$\text{Cd}_2\text{Nb}_2\text{O}_7$	—	—	$-88^\circ \text{C}^{\dagger*}$

* The correlation of these transitions with particular atomic displacements is tentative (see footnote on p. 100).

† Centrosymmetric to 3-corner.

6. DISCUSSION OF DISTORTED PEROVSKITE STRUCTURES

These facts suggest that the variation in off-centre effects at different temperatures is to be associated with a variation in the homopolar bond system possible to the atom concerned.

3.5. If B atoms in adjacent octahedra have parallel displacements, the two bonds at the O atom which forms the shared corner are no longer at 180° . This, we have seen, may help the stability of the structure at room temperature.

3.6. It is necessary to consider what causes the transition from the ideal structure as the temperature falls. An exact theory would consider the energy of the structure as a whole, but it can usefully be approached by considering separately the energy changes in the bond system of B and the pair of bonds at O. If each is dependent on temperature—but differently dependent—the actual transition temperature will be such that the two energy changes are equal and opposite; but without other information we cannot say which energy change is a gain and which a loss.

There is no theory of the temperature dependence of covalent bonds, and so this account of the mechanism of transition must remain qualitative only. That the bonds must be temperature-dependent can be seen from the fact that transitions *do* occur at certain temperatures*; it can also be shown from the following argument. A covalent bond can be expressed as the time-average of the wave function for all different separations of the pair of atoms concerned. The atoms are undergoing thermal vibrations, of amplitudes which depend on the temperature. Hence the time-average of the wave function depends on the temperature, and hence the bond does so.

It may be possible to distinguish empirically between the bond-changes of the different atoms from a survey of the behaviour of different compounds in which they occur. For example, we have already seen that Nb displacements generally disappear in the range $400\text{--}600^\circ\text{C}$, while W displacements persist above 900°C , and Ta displacements may perhaps normally be limited to rather low temperatures. There seems to be a tendency for the bond angle at O to become 180° somewhere in the region of $500\text{--}1000^\circ\text{C}$; this is a notable characteristic of high-temperature WO_3 , for example. Evidence is still too scanty to lay down any definite rules, but there is enough to suggest that this may be a hopeful approach.

* 'Explanations' involving entropy or free energy are only adequate when the transition is regarded as a macroscopic process. When the discussion is in terms of atomic positions and interatomic forces, the concepts of thermodynamics must be replaced by those of mechanics.

4 Pb compounds

4.1. In all the Pb compounds, the Pb is displaced relative either to its surrounding oxygens (as in PbTiO_3) or to a point fixed by the symmetry (as in PbZrO_3).

The explanation lies in the tendency of Pb^{2+} to form unsymmetrical covalent bonds, which is already known from the structure of other compounds of Pb (discussed in a paper by Byström, 1947). In tetragonal PbO, Pb lies at the apex of a flat pyramid with a square base whose corners carry the O's. In Pb_3O_4 , and in orthorhombic PbO, the pyramid has a triangular base, and is steeper—in fact, it is almost a tetrahedron.

The first of these, the square-based formation, is found in PbTiO_3 , where the pyramid height is 0.46 Å as compared with 1.16 Å in PbO. This covalent system of Pb–O bonds creates conditions which favour the development of unsymmetrical Ti–O bonds.

4.2. In PbZrO_3 , there is no evidence yet for the displacement of Zr, and it is not necessary to assume that it occurs, though it may do so. If the movements of Pb are antiparallel, each Pb can achieve an unsymmetrical Pb–O bond system without much distortion of the ZrO_6 octahedra, which may, however, be pivoted about Zr.

4.3. The same general principles, working out differently in detail in the different cases, can account for all the phases in the solid solutions of Pb compounds. In dealing with solid solutions, we have to simplify the actual state of affairs by assuming that partial replacement of one atom by another (for example, of Ti by Zr, or Pb by Ba) gives rise, if random, to a kind of average atom intermediate in size and properties between the two. All the solid solutions can be explained qualitatively in this way—the existing state of knowledge does not allow the explanation to be made quantitative.

One phase needs to be considered a little more fully—the rhombohedral small-cell phase in $(\text{Pb},\text{Ba})\text{ZrO}_3$. This is ferroelectric, and analogy with other ferroelectrics strongly suggests that the Zr atom is off-centre. If so, the conditions allowing it to form an unsymmetrical bond system must come from a combination of two factors, the large size of Ba and the tendency of Pb to form covalent bonds. Each factor independently favours such a system, as we know; we do not know how they combine, or what is the optimum balance between them.

4.4. It is also an interesting point to enquire why a rhombohedral distortion is favoured in so many of these compounds. One reason

6. DISCUSSION OF DISTORTED PEROVSKITE STRUCTURES

That immediately suggests itself is the known tendency of divalent Pb to form strong trigonal bonds in its oxides, as mentioned in § 4.1. This, however, would apply equally to the PbTiO_3 end of the series, where the rhombohedral forms do not occur. Reasons for the difference are more speculative. It may be that the larger size of Zr makes conditions more favourable for the trigonal bonding in Pb; or Zr itself may tend to form a trigonal bond system rather than a tetragonal. A third idea is that there may be some tendency to form metallic bonds Zr-Pb, where the distance of shortest approach is along the cube diagonal. In support of this is the fact that Pb-Pb bonds play a significant part in PbO (Byström, 1947), and that one would expect more tendency to similar bonds with Zr-Pb than with Ti-Pb.

5 Relation of distortion to ferroelectricity and antiferroelectricity

5.1. It appears from our survey that the recurrent feature in all perovskite-type compounds which show ferroelectricity or antiferroelectricity is a polyhedron of oxygen atoms with a strongly-bound metal atom slightly displaced from its geometrical centre. We have interpreted this in terms of an unsymmetrical homopolar bond system for the central atom. Atoms such as Na, Ca, or Ba, which are held by predominantly ionic bonds, do not contribute in any consistent way to the effects observed.

This suggests that the displacement of the atom from the centre of its polyhedron gives rise to the dipole moment of the unit cell which is characteristic of a ferroelectric, and to the mutually-balancing dipole moments within a cell which are believed to mark an antiferroelectric. For a B atom the polyhedron is an octahedron. For Pb, the polyhedron is a cuboctahedron, but it is not yet clear whether this unit is itself to be associated with a dipole moment, or whether it is better to assume that the rôle of Pb is simply to produce polarization in the octahedron round the B atom.

It is not implied that the dipole moment can be measured as the product of ionic charge and displacement from the centre of the octahedron, since the moment actually arises as a rearrangement of the electron cloud associated with the bonds. This question is taken up again in Chap. 9, § 4.7.

Distortion and tilting of the octahedra, if they occur, are not likely to affect seriously the individual dipole moments, though they may make it harder to sum them.

5.2. The question whether the displacements will be parallel or antiparallel is very much affected by the geometry of the linkage at the shared corners. It is easiest to illustrate this by considering octahedra

which are neither distorted nor tilted (Fig. 6.2). With parallel displacements, the B-O bonds form an obtuse angle at O; with antiparallel displacements, they are at 180° . Hence, of the two, that structure will be favoured which most nearly satisfies the bond angle requirements of O.

It seems likely that this is an important factor in the tetragonal structures of BaTiO_3 and PbTiO_3 , where the bond angles are 171° and 163° respectively.

In high-temperature WO_3 , the section parallel to (100) or (010) resembles Fig. 6.2 (b). The W displacements are antiparallel and the bond angle is 180° , as we should predict from the predominantly ionic

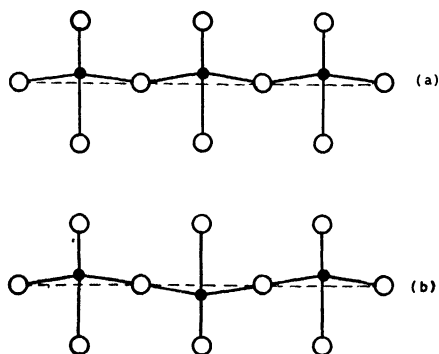


Fig. 6.2. (a) Section through line of octahedra with parallel displacements of central atom.

(b) Section through line of octahedra with antiparallel displacements of central atom.

character of O at high temperatures. In room-temperature WO_3 , the oxygens have been located mainly by packing considerations rather than direct X-ray evidence, and thus one cannot safely attempt to draw conclusions from the 180° angle.

5.3. Where the oxygen framework can crumple round a small A atom it is certainly possible to combine the 'kinked oxygen' with antiparallel displacements, as happens in NaNbO_3 . In such circumstances there is so great a variety of ways in which the oxygen framework can crumple that it is impossible to predict whether parallel or antiparallel displacements will be favoured; we have examples of the different results in LiNbO_3 and NaNbO_3 . One might perhaps wonder whether Li-Nb bonds are of significant magnitude to favour the trigonal distortion in the former.

DISCUSSION OF DISTORTED PEROVSKITE STRUCTURES

Electrical properties of multiple-cell structures

Here a word may be added about the assumption which is sometimes made that multiple-cell structures in perovskites indicate antiferroelectricity. This is not necessarily true: not all multiple-cell structures need have displacement of a covalently-bonded atom relative to the oxygen framework, which appears to be fundamentally associated with the anomalous electrical properties. Neither need the displacements within their sub-cells, where they occur, be oppositely directed; they may be equally inclined to a given direction, the polar axis, as in the cone ferroelectrics (Chap. 1, § 11.1)

On the other hand, no small-cell structure can be antiferroelectric, if we define a small-cell perovskite as one having a single formula-unit per lattice point. (This definition is more exact than one based on the number of formula-units per cell, since the cell volume depends on our choice of axes, and a non-primitive cell will contain several formula-units related by simple translation.) It is obvious that, if the displacements in an antiferroelectric are antiparallel, the individual atoms must be capable of being grouped into oppositely displaced pairs; hence the translation-repeat unit must contain at least two formula units. The existence of a multiple-cell structure in a perovskite is thus a necessary but not sufficient condition for the occurrence of antiferroelectricity. (It may be noted that a similar rule holds for structures of KH_2PO_4 type, but not for more complicated structures such as Rochelle salt, where the high-symmetry form already contains more than one formula-unit per lattice point.)

7 Conclusions

We may sum up the arguments of this chapter by saying that, from the point of view of its ferroelectric properties, an oxide is best considered as built up from Goldschmidt polyhedra of oxygens each surrounding a 'cation' which is displaced in a specific way from its geometrical centre. The formation of these units may be attributed to homopolar forces; the empirical feature of interest is the way they retain their identity from one structure to another. The individual dipole moment is associated with the polyhedron and probably remains constant, or nearly so, in different structures, for the same temperature, provided there are no other highly polarizing cations acting on the oxygens.

The polyhedra are linked by their corners so as to satisfy as well as possible both the bond-angle requirements of the oxygen and the packing requirements of any other cations. The detailed symmetry of the structure, and the multiplication of sub-cells to form a larger

true repeat unit, depend primarily on this 'hinge effect' and the packing effect.

The net dipole moment is the vector sum of the individual dipole moments of the polyhedra, whose placing in the structure is primarily determined by forces of the same kind as are operative in ordinary oxides without abnormal electrical properties.

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Chapter 7

MISCELLANEOUS STRUCTURES

Yet all experience is an arch wherethro'
Gleams that untravelled world, whose margin fades
For ever and for ever when I move.

TENNYSON: *Ulysses*

1 Introduction

Ferroelectricity has been reported in a number of other materials. Some of the early reports have not been substantiated, and about some there is still a good deal of uncertainty. This chapter includes a number of examples for which a reasonable amount of information is available, but it is necessarily very incomplete. Antiferroelectrics as well as ferroelectrics are considered, since the relationship between them is such that an understanding of one is likely to throw light on the other.

The substances are so varied chemically that very little classification is possible. As they stand, they may be divided into two broad classes, oxides and hydrogen-containing compounds, but it is not yet known whether hydrogen plays an essential part in all compounds of the second class. It is possible, for example, that $\text{Ag}_2\text{H}_3\text{IO}_6$ is more closely related to the oxides in the mechanism of its transition.

2 The double tartrates of lithium

2.1. *Lithium ammonium tartrate monohydrate*

This substance, $\text{LiNH}_4\text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$, was reported as ferroelectric by Matthias and Hulm (1951). There has been some controversy about its electrical properties, which will be discussed below.

The structure is not fully known, but some preliminary work was done on the high-temperature form by Vernon and Pepinsky (reported by Shirane, Jona and Pepinsky, 1955). It is orthorhombic, with $a = 7.86 \text{ \AA}$, $b = 14.60 \text{ \AA}$, $c = 6.47 \text{ \AA}$; space group P2_12_12 ; cell-content 4 formula-units. The NH_4 groups lie in special positions on the rotation axes. In this feature, and in the space group, there is a strong formal resemblance to Rochelle salt (see Chap. 2), but the axial ratio and chemical composition (one molecule of water as against four) are quite different, and the two structures are not isomorphous. The detailed placing of the tartrate groups is different,

and there is no reason to expect any resemblance in the general arrangement of the hydrogen bonds.

At low temperatures, about 80°K, neutron diffraction experiments show the occurrence of $h00$ reflections with h odd (Shirane, Jona and Pepinsky, 1955). This means that there is no longer a screw axis parallel to x . Only one symmetry axis can be retained, and it must be polar.

2.2. The dielectric constant in all three principal directions is small at room temperature, having a value about 8. At a temperature near 100°K there is a small sharp peak in ϵ_b , with a height of about 20, and a smaller, but rather broad, anomaly in ϵ_a . Above the transition temperature the Curie-Weiss law is obeyed only over a very short range (Jona and Pepinsky, 1953).

The existence of dielectric hysteresis loops below the transition temperature was reported by Matthias and Hulm (1951) and by Merz (1951), who agreed in finding a spontaneous polarization of 0.22 microcoul. cm.⁻² along the y axis. (This may be compared with 0.25 microcoul. cm.⁻² for Rochelle salt.)

2.3. There may be an explanation of the dielectric anomalies as follows. The displacement of NH_4 ions from their special positions in the high-temperature form has both x and y components; while the latter are parallel for all the NH_4 ions, the former are anti-parallel. It may be that the individual dipole components along x (whether resulting directly from the NH_4 displacement or indirectly from the consequent displacement of other atoms) are as large as, or larger than, the components along y . The antiferroelectric properties will then be as important as the ferroelectric. It was pointed out earlier (Chap. 1, § 11.1) that ferroelectrics may have an antiferroelectric arrangement at right angles to their polar axis; but in all substances examined in detail hitherto the ferroelectric components of the individual dipole moments are so large compared with the antiferroelectric that it has been legitimate to neglect the latter. Most treatments of ferroelectricity, theoretical or empirical, assume this. There is no fundamental reason why it should always hold good, and lithium ammonium tartrate monohydrate may be a case where it does not.

2.4. *Lithium thallium tartrate monohydrate*

This is isomorphous with the lithium ammonium salt, but its structure has not been studied in detail. The cell dimensions (Shirane, Jona and Pepinsky, 1955) are $a = 7.87 \text{ \AA}$, $b = 14.68 \text{ \AA}$, $c = 6.35 \text{ \AA}$.

The ferroelectric behaviour was reported by Matthias and Hulm

7. MISCELLANEOUS STRUCTURES

(1951). The Curie point is near 10°K , at which temperature there is a flat maximum in ϵ_a , of height about 600. Above this, the dielectric constant falls off according to a Curie-Weiss law; below, it falls off very slowly. There are dielectric hysteresis loops when the applied field is parallel to x ; at 1.3°K , the spontaneous polarization is 0.14 microcoul. cm^{-2} , and the coercive field has the low value of 0.12 kV cm^{-1} .

It is at first sight unexpected that this lithium thallium tartrate and the corresponding lithium ammonium salt, which are isomorphous in their high-temperature form, should have different directions for their polar axes. Comparison may be made, however, with KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$, which also have isomorphous high-temperature forms but quite different symmetries in their low-temperature forms. It is quite likely that the different covalent bonding requirements of NH_4 and Tl are responsible for the different atomic displacements in the two low-temperature forms.

3 The guanidine aluminium sulphate hexahydrate group

A substance recently found to be ferroelectric at room temperature is guanidine aluminium sulphate hexahydrate, $\text{CN}_3\text{H}_6\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Holden, Matthias, Merz and Remeika, 1955). The space group is No. 157, $P31m$, with three formula-units per cell, but the detailed structure is not yet known.

It appears that the Curie point is unattainable, because the material is still ferroelectric at a temperature (somewhere above 200°C) at which chemical decomposition sets in.

The direction of spontaneous polarization is along the triad axis; its magnitude is 0.35 microcoul. cm^{-2} at room temperature, where the coercive field is about 1.5 kV cm^{-1} . The dielectric constants are rather small, about 15 along the z axis and about 5 perpendicular to it.

There are a number of isomorphous substances which are also ferroelectric. Those so far known are the compounds in which Ga or Cr replaces Al, SeO_4 replaces SO_4 , and D_2O replaces H_2O .

4 Lithium niobate group

LiNbO_3 and the isomorphous LiTaO_3 have been dealt with in Chap. 5, with the perovskites. Though their structure is not itself a perovskite type, it is topologically related to it, so that they are more conveniently considered with that group.

5 The periodates

5.1. These compounds were investigated because of certain structural resemblances between $(\text{NH}_4)_2\text{H}_3\text{IO}_8$ and KH_2PO_4 , and the close

relationship which exists between the former and $\text{Ag}_2\text{H}_3\text{IO}_6$, though they may not be actually isomorphous. Both are antiferroelectric.

5.2. Ammonium periodate $(\text{NH}_4)_2\text{H}_3\text{IO}_6$

This occurs in clear colourless crystals, with a platy habit perpendicular to the triad axis.

The structure was determined by Helmholtz (1937);* it is illustrated in Fig. 7.1. It is rhombohedral, with space group No. 148, $R\bar{3}$, which is centrosymmetric. Referred to hexagonal axes, the cell dimensions are $a_H = 6.89 \text{ \AA}$, $c_H = 11.12 \text{ \AA}$; there are 3 formula-units in this

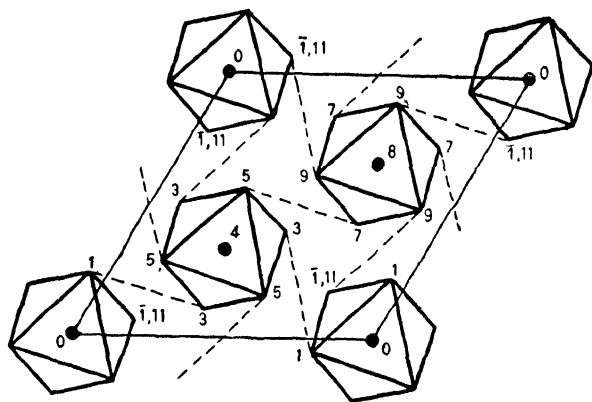


Fig. 7.1. Ammonium periodate: projection of structure on (0001). Octahedra show oxygen positions; I lie at centres of octahedra, with N vertically above and below them. Figures indicate approximate heights of centres and corners of octahedra, in twelfths of c_H . Dotted lines show hydrogen bonds.

cell, or 1 in the primitive rhombohedral cell. The coordinates of all atoms except H have been determined, and are listed in Table 7.1. The structure is composed of IO_6 octahedra lying on the centres of symmetry, with NH_4 vertically above and below them on the triad axes, so that they are 9-coordinated by O. Octahedra at successive levels are joined by hydrogen bonds of length $2.60 \text{ \AA}$.

5.3. There is a formal resemblance between the structure of $(\text{NH}_4)_2\text{H}_3\text{IO}_6$ and that of KH_2PO_4 (see Fig. 3.1). The array of octahedra on a rhombohedrally-centred hexagonal lattice in the one corresponds to an array of tetrahedra on a body-centred tetragonal

* This structure has been questioned by Aboav, Gränicher and Petter (1955), who find that $(\text{NH}_4)_2\text{H}_3\text{IO}_6$ and $(\text{ND}_4)_2\text{D}_3\text{IO}_6$ have both the space group $R\bar{3}m$, like $\text{Ag}_2\text{H}_3\text{IO}_6$.

7. MISCELLANEOUS STRUCTURES

TABLE 7.1

Atomic coordinates in $(\text{NH}_4)_2\text{H}_3\text{IO}_6$ (Helmholz, 1937)

Space group $R\bar{3}$

Kind of atom	Coordinates referred to hexagonal cell *
I	0, 0, 0
N	$\pm (0, 0, w)$ with $w = 0.34$
O	$\pm (x, y, z; \bar{y}, x - y, z; y - x, \bar{x}, z)$ with $\begin{cases} x = 0.216 \\ y = 0.232 \\ z = 0.105 \end{cases}$

* Coordinates of all atoms are derived from these by operation of lattice translations 0, 0, 0; $\frac{1}{3}, \frac{2}{3}, \frac{1}{3}$; $\frac{2}{3}, \frac{1}{3}, \frac{1}{3}$. Axes x and y have been interchanged from Helmholz's, to be consistent with International Tables.

lattice in the other. The polyhedra are linked in each case by hydrogen bonds from an upper corner of one to a lower corner of the next. In both, the symmetry is such that the H's must either lie in special positions at the mid-point of the bond or be randomly distributed between sites equidistant from this point on either side. This has not been studied in detail in $(\text{NH}_4)_2\text{H}_3\text{IO}_6$.

4. At -20°C , a transition occurs to a low-temperature form. In the unit cell of this, the hexagonal a axis is doubled and the hexagonal c axis unchanged (Busch, Känzig and Meier, 1953). It may alternatively be described in terms of a rhombohedral unit cell of the same shape as the original but body-centred, with all axes doubled, and the whole rotated through 180° about the triad axis. Since the substance was not piezoelectric at low temperatures, it is presumably centrosymmetric (Baertschi, 1945).

For $(\text{ND}_4)_2\text{D}_3\text{IO}_6$ the transition temperature is -7°C (Aboav, Gränicher and Petter, 1955).

5. Whether the mechanism of the transition resembles that in KH_2PO_4 is uncertain. In KH_2PO_4 there was an ordering of H atoms on off-centre sites in the hydrogen bonds, and off-centre displacement of P atoms in their tetrahedra; neither the high- nor the low-temperature form was centrosymmetric. In $(\text{NH}_4)_2\text{H}_3\text{IO}_6$ a similar ordering of H's could occur, and off-centre displacements of I atoms are also possible. The latter would result in trigonal IO_3 groups such as have been observed in NaIO_3 (MacGillavry and Panthaleon van

Eck, 1943); displacements of this kind probably occur also in KIO_3 , RbIO_3 , and CsIO_3 , which have multiple-cell perovskite structures (Naray-Szabo, 1947). If either H or I moves from its centre of symmetry, the structure as a whole may still be centrosymmetric, with a rhombohedral lattice, if *all* axial lengths are doubled (which does not fit the observations). Simultaneous displacement of both kinds of atom would require some more complicated distortion. It is not possible to draw definite conclusions from existing evidence; but the small difference between the transition temperatures of the hydrogen and deuterium compounds suggests that the ordering of H or D does not play as important a part as in KH_2PO_4 .

5.6. The physical properties have been studied by Baertschi (1945). There is a sharp anomaly in the specific heat curve; the energy change is $350 \text{ cal. mol.}^{-1}$, and the entropy change $1.40 \text{ cal. mol.}^{-1} \text{ deg.}^{-1}$. The dielectric constant at room temperature is about 190. It falls rather sharply at the transition to about 15. The separate values of ϵ_a and ϵ_c , measured on single crystals, are not very different from each other, except that ϵ_a falls more slowly and less smoothly at the transition. The shape of the curve, with its small peak and steep fall on the low-temperature side, is very characteristic of antiferroelectrics. No dielectric hysteresis loops were observed at any temperature.

5.7. Silver periodate, $\text{Ag}_2\text{H}_3\text{IO}_6$

This has been prepared in small single crystals of a pale yellow colour. It is rhombohedral, with space group No. 166, $R\bar{3}m$ (Gränicher, Meier and Petter, 1954). Referred to hexagonal axes, the cell dimensions are $a_H = 5.944 \text{ \AA}$, $c_H = 12.710 \text{ \AA}$, with 3 formula-units per cell. The primitive rhombohedral cell contains 1 formula unit.

It is possible to draw some conclusions about the structure from this evidence. As in $(\text{NH}_4)_2\text{H}_3\text{IO}_6$, the I atoms lie on symmetry centres, with the other cations (in this case Ag) on the triad axes vertically above and below them. The O's must lie at positions such that I is octahedrally coordinated. There are, however, two distinct possibilities, illustrated in Figs. 7.2 (a) and (b). The first, (a), resembles $(\text{NH}_4)_2\text{H}_3\text{IO}_6$ except in the azimuthal setting of the oxygen octahedra. It offers the difficulty that some O-O distances, such as 9-11, are unreasonably short, even for hydrogen bonds. Perhaps there may be a small rotation of the octahedra about the triad axes, which would lengthen these bonds; it would require space group $R\bar{3}$, not $R\bar{3}m$, but since the positions of the heavy atoms I and Ag are the same in both, the difference might have escaped experimental observation.

7. MISCELLANEOUS STRUCTURES

The second alternative, Fig. 7.2 (b), is related to the oxygen packing in perovskite (see Fig. 6.8 (d)), from which it is derived by a topological distortion similar to that suggested for LiNbO_3 (Chap. 5, § 5.4). The cation positions A and B in perovskite correspond to Ag and I respectively, but half the latter have been removed, so that the unit cell is doubled along the cube diagonal. The structure is compressed along this diagonal, and small changes in atomic parameters are allowed. The Ag atom does not remain 12-coordinated, for the distortion brings six O's, octahedrally arranged, nearer to it than the rest. This provides a more reasonable environment for it

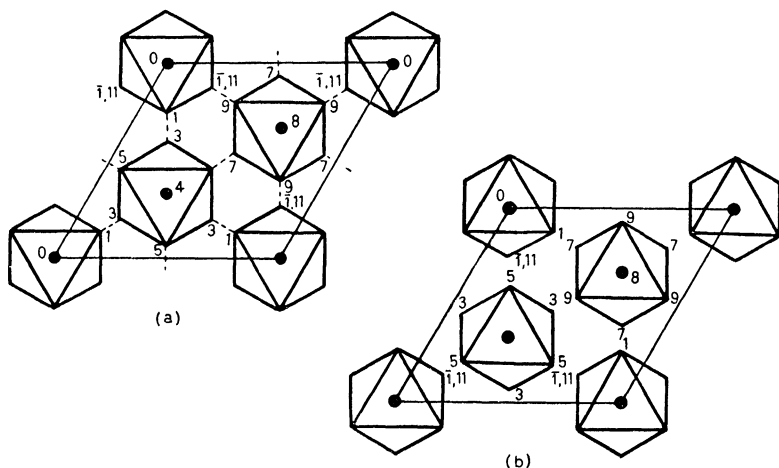


Fig. 7.2. Silver periodate: two possible arrangements, projected on (0001). Octahedra show oxygen positions; I lie at centres of octahedra, with Ag vertically above and below. Figures indicate approximate heights of centres and corners of octahedra, in twelfths of c_H .

than can be achieved in Fig. 7.2 (a). The difficulty lies in placing the H's, unless they are allocated at random to half the O's.

5.8. Below the transition, which lies at about -46°C , X-ray photographs showed extra spots, indicating a multiple cell (Gränicher, Meier and Petter, 1954). The new cell is doubled in both the x and the z directions. Optical observations show a domain texture.

5.9. The physical properties were investigated by Baertschi (1945). He found an anomaly in the specific heat curve, less sharp than for $(\text{NH}_4)_2\text{H}_3\text{IO}_6$, with an energy change of $240 \text{ cal. mol.}^{-1}$ and an entropy change of $0.96 \text{ cal. mol.}^{-1} \text{ deg.}^{-1}$.

FERROELECTRICITY IN CRYSTALS

The dielectric constant was examined with a powder specimen. In the transition region, over a range of about 20° , it fell from its room-temperature value of 55 to about 18. No dielectric hysteresis loops were obtainable. It seems certain that $\text{Ag}_2\text{H}_3\text{IO}_6$, like $(\text{NH}_4)_2\text{H}_3\text{IO}_6$, is antiferroelectric.

6 The pyrochlore group

6.1. Cadmium niobate

The ferroelectric properties of cadmium niobate, $\text{Cd}_2\text{Nb}_2\text{O}_7$, were first reported by Cook and Jaffe (1952).

Single crystals are pale yellow in colour, and grow with octahedral faces, but are generally plate-like, flattened on (111).

The substance exists in its high-symmetry form at room temperature. It belongs to a well-known structure type, named after the mineral pyrochlore, $\text{CaNaNb}_2\text{O}_6\text{F}$ (Byström, 1944). It is cubic, with

TABLE 7.2
Atomic coordinates in pyrochlore structure
Space group $Fd3m$; $Z=8$

General formula ABO_6X , where A is a large cation, B is a small cation, and X is O, OH, or F. Origin taken at a centre of symmetry.

Kind of atom	No. of atoms	Type of site*	Coordinates †
A	16	(d)	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{4}, \frac{1}{4}; \frac{1}{4}, \frac{1}{2}, \frac{1}{4}; \frac{1}{4}, \frac{1}{4}, \frac{1}{2}$
B	16	(c)	$0, 0, 0; 0, \frac{1}{4}, \frac{1}{4}; \frac{1}{4}, 0, \frac{1}{4}; \frac{1}{4}, \frac{1}{4}, 0$
X	8	(b)	$\frac{3}{8}, \frac{3}{8}, \frac{3}{8}; \frac{5}{8}, \frac{5}{8}, \frac{5}{8}$
O	48	(f)	$\therefore (u, \frac{1}{8}, \frac{1}{8}; \frac{1}{8}, u, \frac{1}{8}; \frac{1}{8}, \frac{1}{8}, u;$ $\frac{1}{4} - u, \frac{1}{8}, \frac{1}{8}; \frac{1}{8}, \frac{1}{4} - u, \frac{1}{8}; \frac{1}{8}, \frac{1}{8}, \frac{1}{4} - u)$

* Naming of sites follows notation of International Tables.

† Coordinates of other atoms derived from those quoted by the operation of the lattice translations, $0, 0, 0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0$.

For regular octahedra, $u = \frac{1}{16}$.

$a_0 = 10.372 \text{ \AA}$; the space group is $Fd3m$, and there are 8 formula-units per cell. The atomic coordinates are given in Table 7.2. There is one arbitrary parameter to be determined. A projection is shown in Fig. 7.3.

The structure may be considered as a framework of NbO_6 octahedra with shared corners throughout, built together to give large

7. MISCELLANEOUS STRUCTURES

basket-like holes each holding four Cd's grouped round a central O. Each Cd has eight neighbours, six of them corners of NbO_6 octahedra, and two, at a rather shorter distance, linked only to other Cd's. The Nb octahedra would be regular if the oxygen parameter were exactly $\frac{5}{16}$ (or 0.3125), and this is assumed as a first approximation. Its actual value * is 0.320 (Jona, Shirane and Pepinsky, 1955). The corresponding Nb-O distance is 1.97 Å, the Cd-O distances 2.61 Å and 2.24 Å. These may be compared with the distances in $\text{Cd}_2\text{Ta}_2\text{O}_7$, where Ta-O is 2.05 Å, Cd-O is 2.50 Å and 2.25 Å (Byström, 1944).

6.2. The pyrochlore structure resembles perovskite in being built up from octahedra linked by corners only, and in having large holes in its framework which are so-to-speak stuffed with atoms not strongly bonded to the framework. It differs chemically, however, in using anions as well as cations for its stuffing—there is an O surrounded by four Cd's which is not linked to any Nb. The formula should thus really be written $\text{Cd}_2\text{Nb}_2\text{O}_6 \cdot \text{O}$. Pyrochlore also differs from perovskite in its geometrical complexity. There are 8 formula-units per cell instead of 1; the Nb's, though on symmetry centres, do not lie on tetrad or diad axes, and the symmetry axes of individual octahedra are not symmetry axes for the structure as a whole. This means that the possible kinds of transition to lower symmetry will not be closely comparable with those in the perovskite family.

6.3. The transition to the low-temperature form occurs at about 185°K. The structure is not known in detail, but some information has been obtained from single-crystal X-ray studies (Jona, Shirane and Pepinsky, 1955). It is non-cubic, as is shown by the splitting of high-angle reflections, but the separations of the spots are so small that the symmetry cannot be determined unambiguously. Rather larger separations are obtained with crystals containing NaF in solid solution, and from these it can be concluded that the low-temperature lattice is not rhombohedral; all the evidence would fit the assumption of a tetragonal lattice, but the possibility that it is orthorhombic is not ruled out. If it is tetragonal, the pure crystal has an axial ratio c/a of 1.0005, the material containing NaF one of 1.0011. These are extremely small lattice distortions.

Optical investigations confirm the non-cubic character. There is a domain structure, but it is on such a fine scale that it is not easily interpreted.

* This has been recalculated to refer to an origin on the symmetry centre, in agreement with Fig. 7.3. Many of the original papers use different origins.

FERROELECTRICITY IN CRYSTALS

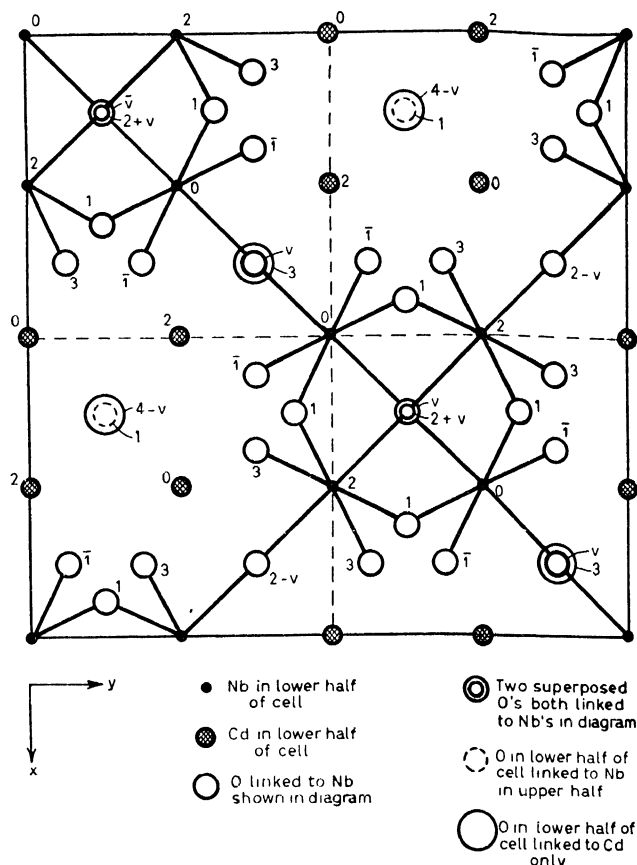


Fig. 7.3. Cadmium niobate: projection of part of unit cell on (001).

Figures indicate heights, expressed in eighths of cell side, with $v = \frac{1}{2}$ for ideal case; more generally, $(2 + v) \times \frac{1}{8} = u$. For $v > \frac{1}{2}$, the O's of each small triangular group move closer together, i.e. farther from Nb.

The intensities of the X-ray reflections show that there are displacements of Nb relative to Cd. Displacements of either kind of cation relative to O would have a much smaller effect on the intensities, and there is no evidence to say whether they occur or not.

If the low-symmetry form is tetragonal, it is likely to have the space group No. 109, $F4_1dm$, whose symmetry elements are shown in Fig. 7.4. This is more usually referred to x and y axes lying along the diagonals of the cell shown, in which case it has the symbol $I4_1md$. The crystal class is $4mm$, which is a polar class.

7. MISCELLANEOUS STRUCTURES

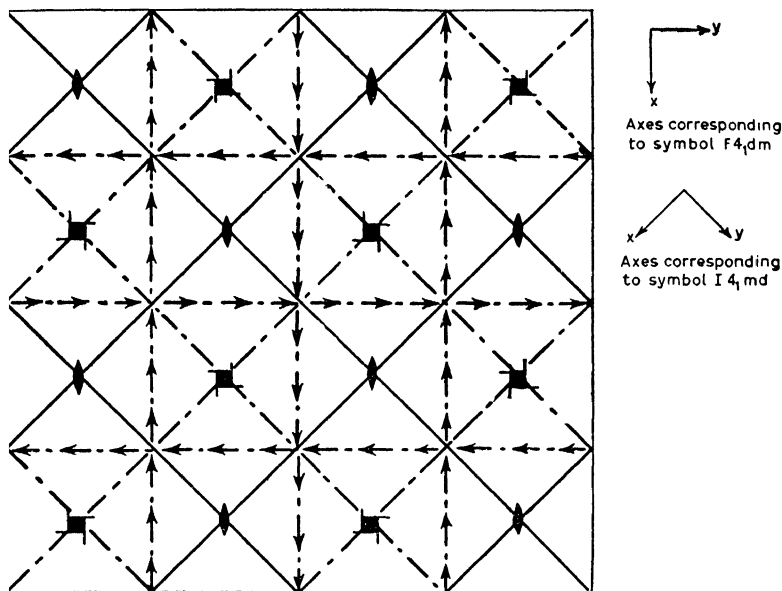


Fig. 7.4. Symmetry elements of $F4_1dm$. (Unit cell is drawn to correspond with that of Fig. 7.3.)

5.4. It is tempting to suppose, by analogy with the other niobates, that the Nb's are displaced from the centre of their surrounding octahedra. Since the lattice distortion is so small, it is unlikely that there are appreciable displacements of O's relative to one another; we may therefore take an origin fixed relative to the oxygen framework and consider cation displacements with respect to this.

The Nb's lie at some distance from the tetrad axis, an arrangement which allows their displacements to have components perpendicular to the axis though these components must add up vectorially to zero over the unit cell as a whole; the substance is in fact a cone ferroelectric. Such perpendicular displacements would, however, bring two Nb's close to one O, and leave other O's remote from any Nb for example, the two Nb's at height 2 in Fig. 7.3 would approach the O at height $2+v$, leaving behind that at $2-v$). It is difficult to see how this could take place without a much larger puckering of the O framework than the very small lattice distortion seems to suggest.

Components of the displacement parallel to the axis are also allowed, and these are uni-directional, since the axis is polar. This direction coincides roughly with the triad axis of the octahedron, which means that this kind of displacement brings each Nb into close

contact with three O's, and gives each O one close Nb neighbour only. This seems easier to reconcile with the absence of distortion in the oxygen framework. It is therefore likely that the substance, while strictly a cone ferroelectric, approximates closely to a line ferroelectric.

It is interesting to notice that the bond system of Nb then has the same form as in rhombohedral KNbO_3 . The transition temperature for rhombohedral KNbO_3 , which represents the upper limit of stability of the trigonal bond system in that structure, is -40°C (see Table 6.1), which is roughly in the same range as the transition temperature in $\text{Cd}_2\text{Nb}_2\text{O}_7$. There is presumably no small distortion of the pyrochlore structure which will allow the unsymmetrical bond systems (orthorhombic or tetragonal) possible to Nb at higher temperatures; hence the transition goes directly to the cubic form.

6.5. The energy change at the transition is $18 \pm 2 \text{ cal. mol.}^{-1}$, the entropy change $0.09 \pm 0.01 \text{ cal. deg.}^{-1} \text{ mol.}^{-1}$ (Danner and Pepinsky, 1955). These are of the same order of magnitude as the corresponding changes in the -90°C transition of BaTiO_3 (see Table 4.5).

6.6. The dielectric properties of the ceramic material have been studied by Shirane and Pepinsky (1953) and by Hulm (1953). The dielectric constant is 310 at room temperature; with decreasing temperature it rises to a sharp peak at 185°K . There is a smaller peak at about 80°K , which perhaps indicates a second transition. The 185° peak height is about 5000; above the transition, the Curie-Weiss law is obeyed.

Below the transition, dielectric hysteresis loops are observed, and they persist down to the lowest temperature investigated, 1.2°K . The spontaneous polarization of the ceramic at 100°K is reported as $10 \text{ microcoul. cm.}^{-2}$ (Jona, Shirane and Pepinsky, 1955).

6.7. Investigations of single crystals containing NaF in solid solution (Jona, Shirane and Pepinsky, 1955) give results which are somewhat different numerically from those for the ceramics. Since the crystals occurred as plates parallel to (111), all measurements were made in the direction normal to this, i.e. along the cube diagonal. The transition temperature was about 160°K , much lower than for the pure material. With a biasing field, the transition was shifted to a higher temperature, the coefficient being $1.5 \text{ deg. kV}^{-1} \text{ cm}$. The dielectric constant was 850 at room temperature and 2000 at the peak. The spontaneous polarization was about $6 \text{ microcoul. cm.}^{-2}$. If the polar axis is actually [100], the true value is about $\sqrt{3}$ times this, i.e. about $10 \text{ microcoul. cm.}^{-2}$.

7. MISCELLANEOUS STRUCTURES

The numerical values of these quantities resemble those for the perovskites rather than for the hydrogen-containing ferroelectrics.

6.8. *Lead niobate*

This has been studied by Cook and Jaffe (1952), Hulm (1953), Shirane and Pepinsky (1953), and Jona, Shirane and Pepinsky (1955).

It has a structure of the pyrochlore family, but rhombohedral rather than truly cubic at room temperature. The cell dimensions are $a = 10.675 \text{ \AA}$, $\alpha = 88^\circ 50'$.

Electrical measurements indicate a transition at a low temperature, but no structural work has been reported.

The dielectric constant at room temperature is about 150; it rises to a rather flat maximum, of height about 300, close to 15°K . Above this temperature it follows a Curie-Weiss law giving a negative value of T_0 . Below the temperature of the maximum no hysteresis loops are observed, which shows that the material does not become ferroelectric. Whether it is antiferroelectric is doubtful.

It is possible that the distortion from cubic at room temperature is due to partially covalent bonding by Pb, as in the compounds of Pb with the perovskite structure (cf. Chap. 6).

6.9. *Isomorphous compounds*

As in perovskite, there are in pyrochlore wide possibilities for isomorphous replacement by atoms whose size fits the oxygen framework; but the permissible range of sizes is rather less. This is probably a consequence of the fact that there are two different A-O distances which must lie within permissible limits. It can be expressed in a different way by writing down the relations between radii for an ideal fit (as was done for perovskite, Chap. 5, § 1.3). There are now two such relations, which cannot be satisfied simultaneously, if the condition for regular octahedra is maintained, unless different tolerance factors are introduced. The relations are then as follows:

for A-O distances where O is linked also to B,

$$R_A + R_O = t_1 \frac{\sqrt{17}}{3} (R_B + R_O) = t_1 \sqrt{1.89} (R_B + R_O);$$

for A-O distances where O is linked to A's only,

$$R_A + R_O = t_2 \frac{\sqrt{12}}{3} (R_B + R_O) = t_2 \sqrt{1.33} (R_B + R_O).$$

The first condition is best satisfied by ions very little smaller than for perovskite, the second by ions considerably smaller. Though

some adjustment can be made by allowing the O parameter to depart from the ideal value of 5/16, the net result is that the range of permissible sizes is likely to be rather narrower. For $\text{Cd}_2\text{Nb}_2\text{O}_7$, where the atoms A and B are near the lower and upper limits of size respectively for pyrochlores, the two factors t_1 and t_2 are 0.87 and 0.96.

Pyrochlores have, however, a further possibility of isomorphous substitution: oxygen atoms at site X may be wholly or partly replaced by OH or F, the electrostatic balance being maintained by appropriate substitution of other atoms for Cd or Nb. An example is pyrochlore itself, $\text{CaNaNb}_2\text{O}_6\text{F}$. In some cases the site may even be vacant or partly vacant; for example, a compound of composition $\text{Pb}_{1.5}\text{Nb}_2\text{O}_{6.5}$ has been reported by Cook and Jaffe (1953).

6.10. There are only a few compounds of the pyrochlore family whose electrical properties have been studied. Of these, $\text{Cd}_2\text{Ta}_2\text{O}_7$ and $\text{Y}_2\text{Ti}_2\text{O}_7$ are cubic, $\text{Pb}_2\text{Ta}_2\text{O}_7$ is rhombohedral; none of them show any dielectric anomalies down to 90°K. Solid solutions in which Cd is replaced by Ca or Pb, or Nb by Ta, have also been examined (Jona, Shirane and Pepinsky, 1955). Ferroelectric properties were only found towards the $\text{Cd}_2\text{Nb}_2\text{O}_7$ end of each series, and in every case the transition temperature was lowered by the substitution of the other component. The solid solution $(\text{Cd,Pb})_2\text{Nb}_2\text{O}_7$ was cubic at room temperature up to 90% Pb.

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Chapter 8

THEORIES OF FERROELECTRICITY: THE PHENOMENOLOGICAL APPROACH

'Gin a body meet a body
Flyin' through the air,
'Gin a body hit a body,
Will it fly?—and where? . . .
Ilka problem has its method
By analytics high;
For me, I ken na ane of them,
But what the waur am I?

J. CLERK MAXWELL: *Rigid Body Sings*

1 Introduction

It is clear from what has been said in the foregoing chapters that experimental facts about ferroelectricity have been accumulating rapidly in the last fifteen or twenty years. It is not surprising to find that theory has not been able to keep up with them: a theory devised to account for one set of facts is faced, almost before it is published, with a new set of facts which requires a new set of postulates. The discussion in these three chapters will therefore be chiefly directed to examining the postulates of the various theories and seeing how they are related to each other. For the detailed treatment, reference should be made to the original papers.

Two kinds of theory may be distinguished, the phenomenological theory and the model theory. Their approaches and their purposes are rather different.

A phenomenological theory takes as its starting point a formal expression connecting all the properties of the material which are relevant to the particular purpose of the moment. Such an expression can always be constructed; where judgment comes in is in the decision which properties *are* relevant. Next, assumptions are made as to which of the coefficients change significantly during the process considered, and which are to be taken as constant. These are partly based on experimental evidence, but again are partly a matter of judgment. Then with the help of fundamental laws, such as the laws of thermodynamics, mathematical relations are established between the various quantities. If some of the quantities are known experimentally, others can be calculated. There is thus a wide variety of relations which can be submitted to experimental test. A 'good'

8. THEORIES OF FERROELECTRICITY

theory (i.e. a useful theory) is one in which many of the coefficients are constants; but it does not provide any mechanism to explain why this should be so, or to account in detail for the variation of the others.

Phenomenological theories are very general in their scope, and can give extremely useful results. They serve to pick out those relationships which follow from fundamental laws and are independent of any particular model, and to distinguish them from others which are likely to give more insight into the actual mechanism. They provide a mathematical framework which can be used in connection with any particular model.

A model theory, on the other hand, begins by postulating certain particular arrangements of charges or forces in the structure. The model is devised to account quantitatively for some features of the structure or of the changes undergone by it, and then it should be possible to predict other consequences which can be tested experimentally. For a model theory to be satisfying, it must either give good quantitative agreement with observation over a wide range of properties in one particular case, or it must use the same kind of mechanism to give reasonably good agreement in a large number of different cases. Most of the model theories of ferroelectricity apply to a single case, and have not been used to predict experimental behaviour outside the range of properties they were devised to fit. They will be considered in Chaps. 9 and 10. The rest of this chapter will be devoted to phenomenological theories.

2 Devonshire's theory of barium titanate

2.1. A phenomenological theory of BaTiO_3 has been put forward by Devonshire (1949, 1951, 1954). He assumes that it is legitimate to treat the material, in all its forms, as a strained cubic crystal, and considers an expression for its free energy as a function of temperature, stress and polarization. If the stresses are taken as zero, the expression can be written as a series involving powers of the polarization, P , the coefficients being functions of temperature applying only to the stress-free condition. These are distinguished by the superscript X . In its most general form, the expression must have separate terms and separate coefficients for the components of polarization along each of the axial directions x, y, z , but to begin with we shall consider the case where only one direction of polarization is concerned in a transition. Devonshire found that it was necessary to consider terms in P^6 . The particular free energy for the variables considered is the elastic Gibbs function G_1 . Devonshire wrote:

$$G_1 - G_{10} = \frac{1}{2}\chi^X P^2 + \frac{1}{4}\xi^X P^4 + \frac{1}{6}\zeta^X P^6 \quad (8.01)$$

where G_{10} is the value of G_1 for the unpolarized, unstressed crystal.

The meaning of χ^x can be seen by differentiating $G_1 - G_{10}$ with respect to P .

$$E = \frac{\partial G}{\partial P} = \chi^x P + \xi^x P^3 + \zeta^x P^5 \quad (8.02)$$

$$\frac{\partial E}{\partial P} = \frac{\partial^2 G}{\partial P^2} = \chi^x + 3\xi^x P^2 + 5\zeta^x P^4 \quad (8.03)$$

$$\left(\frac{\partial E}{\partial P}\right)_{P=0} = \chi^x \quad (8.04)$$

Thus χ^x is the dielectric stiffness (or reciprocal susceptibility) for zero polarization; since the susceptibility is large, it is effectively equal to $\epsilon/(4\pi)$, whence $\chi^x = 4\pi/\epsilon$ for the unpolarized crystal. For the polarized crystal, the dielectric stiffness is given by 8.03, and thus the dielectric constant depends on ξ^x and ζ^x .

The magnitudes and signs of the constants χ^x , ξ^x and ζ^x have an important bearing on the nature of the transition. Consider a graph of $G_1 - G_{10}$ against P . Since stable states are those with a minimum free energy, this curve must have either a minimum at $P = 0$ or (since the form of (8.01) is symmetrical in $\pm P$) a pair of minima symmetrically on either side. It can be seen from 8.03 that if χ^x is positive there will be a minimum at $P = 0$, if it is negative, a maximum, which implies a pair of minima on either side. The former condition corresponds to a state of zero polarization, the latter to a pair of oppositely polarized states. This is true whatever the magnitudes and signs of ξ^x and ζ^x . But if either of these is negative and fairly large, it is possible to have a pair of minima on either side *as well as* a central minimum at $P = 0$. Then the relative stabilities of the unpolarized and polarized states will depend on the relative depths of the central and outer minima.

So far, we have considered the shape of the curve at a single temperature. But the constants may be temperature-dependent, and hence we expect the shape to change with temperature. Here two important cases must be considered.

If ξ^x and ζ^x are positive throughout, and χ^x changes continuously from positive to negative, we get the situation illustrated in Fig. 8.1(a), where the family of curves represent the plots of $G_1 - G_{10}$ against P at successive temperatures. Below the temperature for which $\chi^x = 0$ the single minimum splits into a pair, whose separation $2P_s$ increases as T decreases. There is no discontinuity in P . This state of affairs represents a second-order transition. Since $\chi^x = 0$ at the transition the dielectric constant becomes infinite.

Alternatively, if ξ^x is negative and ζ^x positive (Fig. 8.1 (b)), there will be a certain temperature range in which there are three minima,

8. THEORIES OF FERROELECTRICITY

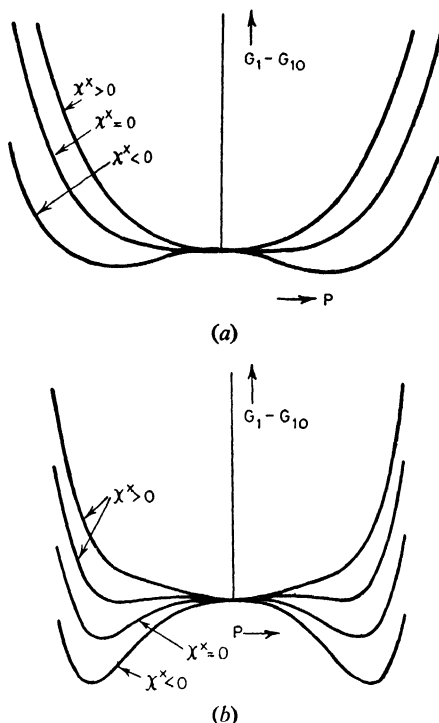


Fig. 8.1. Variation of elastic Gibbs function with polarization at different temperatures (schematic): (a) for a second-order transition, (b) for a first-order transition (Devonshire, 1954).

and one particular temperature at which they are all of equal depth. This is the transition temperature. Since $G_1 - G_{10} = 0$ for $P = 0$, and therefore in this case also for $P = P_s$, and since $\partial G / \partial P = 0$ at a minimum, we have:

$$\frac{1}{2}\chi^X P_s^2 + \frac{1}{4}\xi^X P_s^4 + \frac{1}{6}\zeta^X P_s^6 = 0 \quad (8.05)$$

$$\text{and} \quad \chi^X P_s + \xi^X P_s^3 + \zeta^X P_s^5 = 0 \quad (8.06)$$

$$\text{Hence} \quad P_s^2 = -\frac{3}{4} \frac{\xi^X}{\zeta^X} \quad (8.07)$$

$$\text{and} \quad \chi^X = \frac{3}{16} \frac{(\xi^X)^2}{\zeta^X} \quad (8.08)$$

On one side of the transition, P is zero, on the other it jumps suddenly to the finite value P_s — i.e., it changes discontinuously. At the transition χ^X is not zero but positive. Its zero value, found by extrapolation, occurs at a lower temperature T_0 . The dielectric stiffness, given by

8.03, changes discontinuously because the polarization does so; hence the dielectric constant changes discontinuously also.

Devonshire assumed that χ^X decreased linearly with temperature, and that ξ^X and ζ^X were effectively constant. The experimental evidence about χ^X comes from the Curie-Weiss law, that a graph of $1/\epsilon$ against T gives a straight line; the same graph establishes the value of T_0 .

2.2. Using these same assumptions, Merz (1953) has expressed Devonshire's relations in rather convenient form. He writes

$$\left. \begin{aligned} \chi^X &= 2A(T - T_0) \\ \xi^X &= -4B \\ \zeta^X &= 6C \end{aligned} \right\} \quad (8.09)$$

and then defines new 'dimensionless' units:

$$\left. \begin{aligned} p &= \left(\frac{3C}{B}\right)^{\frac{1}{2}} P \\ e &= \frac{1}{B} \left(\frac{3C}{B}\right)^{\frac{3}{2}} E \\ t &= \frac{A}{B} \left(\frac{3C}{B}\right) (T - T_0) \end{aligned} \right\} \quad (8.10)$$

Then (8.02) becomes

$$e = 2pt - 4p^3 + 2p^5 \quad (8.11)$$

This allows convenient plotting of e against p for a succession of values of t , as shown in Fig. 8.2. The curves are identical with those of E against P at different values of T if the scale is multiplied by the factors in equation (8.10).

It is at once possible from this figure to explain the existence of dielectric hysteresis loops, since regions in which $\partial e/\partial p$ are negative represent unstable states, and the crystal switches over to a state with positive $\partial e/\partial p$ and the same e , as shown in Fig. 8.2 by the vertical dashed lines. The figure also indicates how forced dielectric hysteresis is brought about by large fields at a temperature above the normal transition point, for example at $t = 1.5$. Here there is only one stable state for $e = 0$, but for a narrow region near $e = 1$ there are two states with p having values of roughly 0.4 and 1.0. Dielectric hysteresis loops are formed in this region, and in the corresponding region near $e = -1$, the curve joining them being nearly a straight line. Curves obtained experimentally are shown in Figs. 4.13, 5.14.

It should be noted that the existence of these forced loops is dependent on the negative value of ξ^X . If ξ^X is positive and constant, $\partial^2 e/\partial p^2$ has always the same sign as p (as can be seen from equation

8. THEORIES OF FERROELECTRICITY

8.03), and therefore $\partial e/\partial p$ cannot change sign twice in a region where p does not change sign, as would be needed to make the forced loop. Thus forced loops can only be found in connection with a first-order transition. (This assumes that $|\zeta^X| \ll |\xi^X|$; table 8.1 shows this to be legitimate.)

The experimental curves of P versus E can be compared with the theoretical curves of p versus e by finding the scaling constants P/p and E/e from a few points on the curves (ideally two points on the curve for $t = 0$ or $T = T_0$) and the scaling constant $(T - T_0)/t$

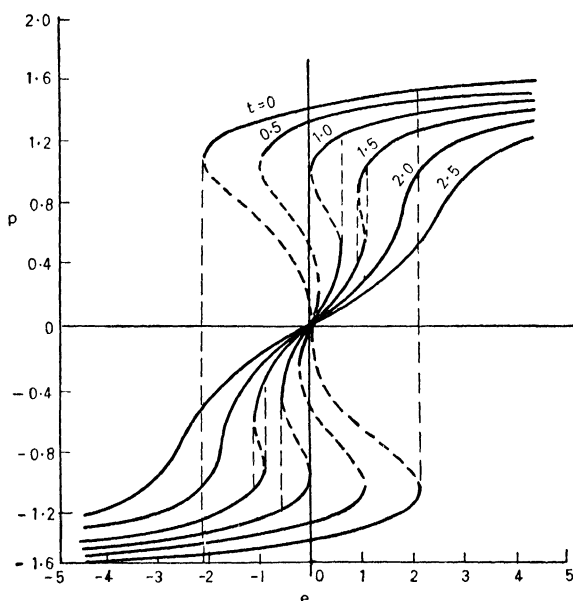


Fig. 8.2. Reduced curves of polarization versus field at different temperatures (Merz, 1953).

from these and the directly-measured values of A and T_0 . (It will be remembered that T_0 is the temperature of zero dielectric stiffness for the unpolarized state, found by extrapolation, and not the transition temperature.) It is then possible to check whether the curves match for other values of P , E , and T . Merz found very satisfactory agreement. This confirms the assumptions made in drawing the theoretical curves, namely that ξ^X is negative, χ^X linear with temperature and with a positive temperature coefficient, and ξ^X and ζ^X effectively independent of temperature. The scaling factors allow these constants to be calculated. Merz's values are given in Table 8.1.

FERROELECTRICITY IN CRYSTALS

TABLE 8.1

Constants in Devonshire's expression for the free energy of BaTiO₃
(quoted in c.g.s. units)

Author	$\frac{\beta(\text{or } 2A)}{= \chi^X/(T - T_0)}$	ξ^X	ζ^X
Merz (1953)	7.4×10^{-5}	-0.68×10^{-12}	2.3×10^{-22}
Devonshire (1949)	10×10^{-5}	-4.4×10^{-12}	37×10^{-22}
Recalculated by Merz (1953) from Devonshire's paper, using newer data	10×10^{-5}	-1.1×10^{-12} to -1.2×10^{-12}	2.8×10^{-22} to 3.5×10^{-22}

2.3. Devonshire (1949) also considered the more general equation which can be used when the spontaneous polarization has components in more than one axial direction. The equation corresponding to (8.01) is

$$G_1 - G_{10} = \frac{1}{2}\chi^X(P_x^2 + P_y^2 + P_z^2) + \frac{1}{4}\xi^X(P_x^4 + P_y^4 + P_z^4) + \frac{1}{6}\zeta^X(P_x^6 + P_y^6 + P_z^6) + \frac{1}{2}\lambda(P_y^2P_z^2 + P_z^2P_x^2 + P_x^2P_y^2) \quad (8.12)$$

The last term corresponds to an interaction between the components of polarization along the different axes. Its coefficient λ may be positive or negative; if positive, it means that polarization along one axis tends to prohibit polarization along an axis at right angles. (The values of all the coefficients will of course change if a different set of axes is chosen.) This expression has a series of minima for zero field, satisfying the conditions:

$$\left. \begin{aligned} P_x = P_y = P_z = 0 & \quad (a) \\ P_x = P_y = 0, \quad P_z \neq 0 & \quad (b) \\ P_y = 0, \quad P_x = P_z \neq 0 & \quad (c) \\ P_x = P_y = P_z \neq 0 & \quad (d) \end{aligned} \right\} \quad (8.13)$$

These represent respectively the cubic, tetragonal, orthorhombic (referred to monoclinic axes) and rhombohedral forms. The relative depths of the minima change with χ^X . If this decreases steadily with decreasing temperature, and suitable constant values are chosen for ξ^X, ζ^X and λ , the sequence in which they occur is that actually observed in BaTiO₃.

Devonshire evaluated the constants ξ^X and ζ^X from the experimental values of the slope and intercept on the temperature axis of

8. THEORIES OF FERROELECTRICITY

the graph of $1/\epsilon$ versus T , and the spontaneous polarization at room temperature. By putting the ratio λ/ξ^x equal to 1.2, which gave the temperature of the second transition correctly, he found he was able also to give a correct prediction of the third. The experimental data available in 1949 were rather rough; by substituting better later data, Merz (1953) obtained values which agreed with those deduced from his own work (see Table 8.1).

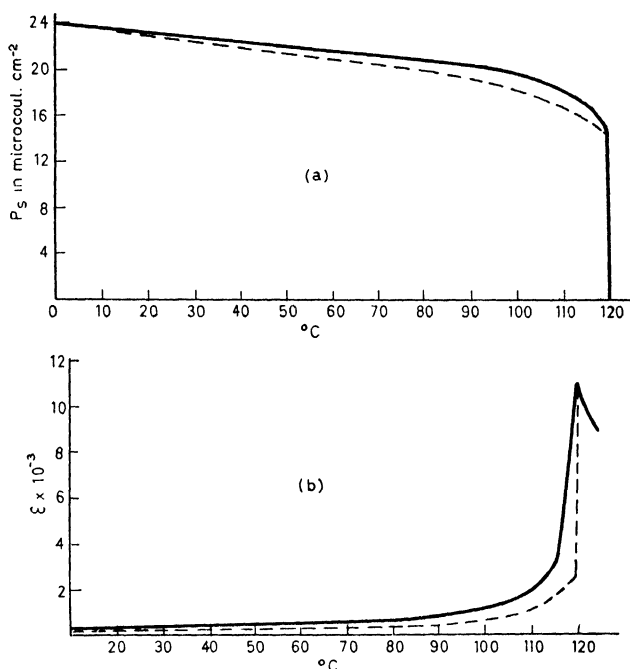


Fig. 8.3. Comparison of observed (full lines) and calculated (dotted lines) values of (a) spontaneous polarization, (b) small-signal dielectric constant, for BaTiO₃. Theoretical curves from Devonshire's theory with constants evaluated by Cross (1953).

The constants being known, Devonshire (1949) was able to draw theoretical curves for the free energy, the spontaneous polarization, and the principal dielectric constants, over a range of temperature which included the stability ranges of all four forms. The agreement with the experimental curves for P_s and ϵ was qualitatively good, but not quantitatively exact. Fig. 8.3 (a) and (b) illustrate this; here the constants for the theoretical curves were evaluated by Cross (1953) from yet another set of experimental data.

2.4. Devonshire also considered the effect of stress on the crystal. For a clamped crystal, where the strain is zero, the Helmholtz free energy A is the relevant function. It cannot be taken for granted that the coefficients χ , ξ etc. will be the same for the stress-free crystal and for the strain-free crystal, because in a piezoelectric crystal the polarization depends on the stress. Using the appropriate strain-free coefficients, distinguished by the superscript x , we have for the clamped crystal

$$A - A_0 = \frac{1}{2}\chi^x(P_x^2 + P_y^2 + P_z^2) + \frac{1}{4}\xi^x(P_x^4 + P_y^4 + P_z^4) + \dots \quad (8.14)$$

If the crystal is now allowed to change shape, and the strains are measured as differences in dimensions from those of the clamped crystal, terms have to be added involving the strains, the elastic coefficients, and certain piezoelectric coefficients. The equation then is

$$A - A_0 = \frac{1}{2}\chi^x(P_x^2 + P_y^2 + P_z^2) + \frac{1}{4}\xi^x(P_x^4 + P_y^4 + P_z^4) + \frac{1}{2}\lambda'(P_y^2P_z^2 + P_z^2P_x^2 + P_x^2P_y^2) + \dots + \text{terms in } (c_i, x_i) + \text{terms in } (g_j, x_j, P_j) + \dots' \quad (8.15)$$

where the c_i 's are elastic coefficients, the g_j 's piezoelectric coefficients, the x_i 's and x_j 's components of the linear strains, and the P_j 's components of the polarization. Differentiation of A with respect to each kind of strain gives the corresponding stress. If the stresses are zero, the equations which involve them give the strains in terms of the polarization. It turns out that the strains are proportional to the square of the polarization. The numerical factors bring in the elastic constants. These can be evaluated by calculating the theoretical value of each kind of strain at a single temperature (in the range where it can be manifested in a stable form of the material) and equating it to a value derived from observations of cell dimensions at that temperature. Once the numerical factors are known, the variation of the strains with temperature over the whole range can be deduced. This has been done by Devonshire (1949). Again the agreement between theory and experiment is good qualitatively, but not exact.

In a later paper, Devonshire (1954) discusses the effect of clamping on the nature of the transition. We have seen that the magnitudes and signs of the coefficients χ^x , ξ^x , ζ^x are important for the stress-free transition; similarly it is χ^x , ξ^x , ζ^x , which are important for the strain-free transition. The relation between them can be found. It turns out for BaTiO_3 that $\chi^x = \chi^x$ (as expected, because the unpolarized form is not piezoelectric) but that whereas ξ^x was negative, ξ^x is positive. Higher powers were not considered, but it is probable that they too have positive coefficients. If so, it means that the transition in clamped BaTiO_3 is a second-order one. The point is of more theoretical than practical importance, since it would be extremely

8. THEORIES OF FERROELECTRICITY

difficult to devise experimental conditions in which a crystal of BaTiO_3 could not deform at all during its transition.

2.5. From the theory as a whole it was possible to calculate various other quantities, which agreed reasonably well with observation.

Two results in particular may be noted, which are quite general and do not apply only to BaTiO_3 . Firstly, the entropy change at the transition is given by the expression

$$S - S_0 = \frac{1}{2} P^2 \frac{\partial \chi^x}{\partial T} = \frac{2\pi P^2}{C}$$

where C is the Curie constant. This result was also shown to be a general one by Jaynes (1953). Devonshire (1954) tabulates the experimental data for several compounds and shows that the equation holds good; the relation has also been confirmed for KNbO_3 by Triebwasser and Halpern (1955) and for $\text{Cd}_2\text{Nb}_2\text{O}_7$ by Danner and Pepinsky (1955). Secondly, it can be shown that for an antiferroelectric the presence of a biasing field lowers the transition temperature. This is in accordance with experimental observation.

There is no *a priori* assumption made in the theory about the nature of the transition, and Devonshire (1954) has in fact applied it to the transition of KH_2PO_4 , which he considers is second-order. The conclusion that it is first-order in BaTiO_3 follows from the particular values of the constants, which are derived experimentally.

2.6. Direct measurement of the coefficients ξ^x and ζ^x has been attempted by Drougard, Landauer and Young (1955). They find that ξ^x is by no means temperature-independent; it decreases by 50% over a range of 30° above the Curie point. It is also sensitive to clamping (as would be expected); this makes experimental work difficult. No reliable results have been obtained for ζ^x .

2.7. It is possible to criticize Devonshire's theory on logical grounds, as has been done by Jaynes (1953). He argues that the use of a single expression for the free energy above and below the transition implies a continuity of the constants across the transition-point, while a first-order transition is essentially discontinuous. This argument is valid, but is met by the empirical answer that the same set of constants *does* predict with reasonable accuracy the numerical values observed experimentally in the two ranges. The objection could have been stated in other terms as a criticism of Devonshire's initial assumption, namely that it is permissible to treat the substance in all its forms as a strained cubic crystal. We know that the low-temperature forms are not cubic; to say that they are derived from cubic by a

system of internal stresses or 'spontaneous strains' is so artificial that it may be misleading, since it glosses over the question of the structural origin of stress and deformation. Nevertheless the difference from the cubic form is so small that we may reasonably expect many constants to remain the same for both, within our accuracy of measurement. It is a matter of judgment, requiring experimental verification, to decide which of them may be taken as invariant. The success of Devonshire's theory shows that the expression for the free energy is at least very nearly continuous, or in other words that any discontinuities are not important to the present degree of approximation. Perhaps the argument can best be treated as an illustration of the difficulty of achieving a satisfactory definition of first- and second-order transitions where displacive or pseudosymmetric rather than reconstructive transitions are concerned.

3 Mueller's theory of Rochelle salt

3.1. Mueller, in a series of papers (1940a, b, c, d), put forward two phenomenological treatments of Rochelle salt which have proved very successful in correlating its properties and have contributed much to subsequent theories of ferroelectricity. A full account and discussion of this work can be found in Cady's *Piezoelectricity* (1946); what follows here is only a very brief outline of the postulates and conclusions, to show their relation to the other theories.

In his first approach, Mueller postulated an internal field related to the polarization by a polarizability which is the sum of two terms, one due to distortion and one to orientation (see Chap. 9, §§ 2, 4.2 and 4.3). From these the dielectric constant, the Curie-Weiss law, and other properties of the crystal outside the Curie range can be correlated fairly successfully. Though phenomenological, this treatment is so closely linked with model theories that it is better considered with these in Chap. 9.

In his interaction theory, developed later, Mueller assumed that piezoelectric stresses were proportional to the polarization rather than the field, and that the expression for the field as a function of polarization was not linear but contained a term in P^3 . If the two free energies are expressed in powers of P (cf. equations (8.12), (8.15)) they go as far as P^4 ; they include terms which involve the piezoelectric coefficients because they result from the interaction of polarization with stress. Different but related expressions are obtained according to the choice made for the reference state (the strain-free crystal) in the ferroelectric range—whether this is 'rhombsically clamped' to maintain the orthorhombic symmetry, or 'normal', i.e. monoclinic and stress-free. The dielectric constants under various defined conditions can be expressed in terms of each other and of the

8. THEORIES OF FERROELECTRICITY

spontaneous polarization, using only coefficients which are experimentally derived and which have been found temperature-independent. Thus for example if the variation with temperature of P , χ^x or χ^y is known, that of the others can be found.

Values of the same quantity calculated by different sets of equations do not agree perfectly, but the discrepancies are probably within the limits of experimental error of the observed data.

2. This is as far as the phenomenological theory can take the matter. We may ask which of the temperature-dependent quantities is most significant for the explanation of the transition. Mueller put the emphasis on χ^y , because it, for normal Rochelle salt, when plotted against temperature gave a minimum with a value very close to zero. If it were exactly at zero, it would imply that the clamped crystal just voided becoming polarized at any temperature, and this might perhaps have some physical interpretation. On the other hand, it is now known that for deuterium-substituted Rochelle salt the curve of χ^y cuts the axis at two well-separated points, giving a minimum below zero, and no disappearance of the ferroelectric region. This suggests that the zero value of the minimum for the normal salt is simply coincidence.

The temperature where spontaneous polarization sets in is fixed, in the unstressed crystal, by the point where χ^x (not χ^y) becomes zero, as was shown in Devonshire's treatment of a second-order transition (§ 2.1). The peculiarity of Rochelle salt lies in the opposite signs of the temperature coefficients of χ^x for temperatures above and below the Curie region, and this is not explained.

Comment on the phenomenological theories

1. The theories outlined above have had considerable success in achieving their first aim, the derivation of useful relations between the various properties of the substances concerned. In their second aim, the isolation of particular features which are likely to provide critical tests for the model theories, their achievements are more doubtful. They have focussed attention on χ , the dielectric stiffness or zero polarization, and its variation with temperature. Experimentally we know that in many substances it is linear, as shown by the existence of a Curie-Weiss law. But a large number of laws of temperature dependence will give a linear law as a first approximation for small temperature differences. Hence we may expect to find a linear law derivable from a large number of different models, and we cannot use it as a test by which to recognize the correct one: also, cases are known where the graph of χ versus T shows a curvature just above the Curie point (see Chap. 2, § 8), or has a discontinuous

change of slope in a non-polar crystal without any obvious transition (Chap. 5, § 2.7), or has hardly any linear range at all (Chap. 7, § 2.2). If the approach which emphasizes the dielectric stiffness is to account for the wide range of experimental facts, it loses its apparent advantage of simplicity.

4.2. It is of course true that every model theory can be expressed in terms of a phenomenological theory, though it may need the introduction of more non-negligible constants than have yet been considered. It does not follow that the thermodynamical relations always give the quickest or most accurate ways of calculating numerical values of any properties. The more constants that have to be introduced, the more cumbrous do the theories become, and the less direct their connection with experimentally observable quantities.

5 Phenomenological theory of antiferroelectricity

5.1. A theory of antiferroelectricity was first put forward by Kittel (1951). He used a model in which the repeat unit associated with the lattice consisted of a pair of oppositely directed dipoles, contributing polarizations P_a and P_b respectively, and having an interaction between them. He showed that there would be two possible stable states, with $P_a = \pm P_b$. Though the model is rather unreal, as the forces holding the dipoles fixed in position with respect to the lattice would not be independent of their interaction, it has served as a useful approach. For the case with $P_a = -P_b$ the resultant polarization is zero, and the material is antiferroelectric.

5.2. Devonshire (1954) has expressed the theory in a form which does away with the need of a particular model. He supposes that there are two polarizations P_a and P_b , which may be rewritten to give a resultant ferroelectric polarization P and a quantity p which is formally equivalent to an antiferroelectric polarization:

$$\begin{aligned} P &= P_a + P_b \\ p &= P_a - P_b \end{aligned} \quad (8.16)$$

If P_a and P_b are not in the same direction, these equations may still be used if all the quantities in them are defined as vectors. The free energy is then

$$\begin{aligned} G_1 - G_{10} &= \frac{1}{2}\chi^x P^2 + \frac{1}{4}\xi^x P^4 + \frac{1}{6}\zeta^x P^6 + \dots \\ &\quad + \frac{1}{2}\chi'^x p^2 + \frac{1}{4}\xi'^x p^4 + \frac{1}{6}\zeta'^x p^6 + \dots \\ &\quad + \frac{1}{2}\lambda p^2 P^2 + \dots \end{aligned} \quad (8.17)$$

It depends on the particular values of the coefficients whether this can possess a simple ferroelectric state (a minimum of $G_1 - G_{10}$ with P

8. THEORIES OF FERROELECTRICITY

non-zero and p zero) or an antiferroelectric state (a minimum with p non-zero and P zero) or both states in turn at successive temperatures, or a 'mixed state' in which both p and P are non-zero. This 'mixed state' (which is a ferroelectric state according to the definition of Chap. 1, § 9) is prohibited if the cross terms such as $\frac{1}{2}\lambda p^2 P^2$ are positive and sufficiently large.

In terms of a model, Devonshire's postulate implies that there are two dipoles per lattice point; the 'mixed state' is an equilibrium state such that neither the sum nor the difference of the vectors representing the dipoles is zero. If the *magnitudes* of the vectors are different they must be attributed to crystallographically non-equivalent units of the structure, and therefore their mechanisms need separate consideration from a physical point of view; the formal theory which takes them together may not be very useful. If the two vectors differ only in *direction* we have a special case of the cone ferroelectrics discussed in Chap. 1, § 11.1. In these, the polarization of the unit cell is the vector sum of polarizations of identical sub-units oriented differently in space but all inclined at the same angle to the polar axis. Devonshire's theory applies formally to two dipoles only, whereas a cone ferroelectric is not restricted to two dipoles in the symmetry-equivalent set; possibly the theory could be restated for the more general case.

Though earlier experimental and theoretical work dealt only with line ferroelectrics with a single dipole per lattice point, possible examples of cone ferroelectrics are now known (see Chap. 5, § 4.11, and Chap. 7, § 2.3 and § 6.4) and are likely to increase in number. An application of Devonshire's theory to one such compound, NaNbO_3 , has been made by Cross (1956). It is also quite possible that complex structures may contain more than one set of crystallographically-independent dipoles; indeed, some of the known ferroelectrics, such as KH_2PO_4 , may be cases in point. Devonshire's treatment shows in a general way how a phenomenological theory can be extended to such cases, but does not provide any way of relating the coefficients of the theory with any properties of the separate dipoles.

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Chapter 9

MODEL THEORIES: GENERAL BACKGROUND

... Turns them to shapes, and gives to airy nothing
A local habitation and a name.

SHAKESPEARE: *A Midsummer Night's Dream*

Introductory ideas

1. Model theories begin by postulating some mechanism in the structure which is likely to explain some of the properties; from this they go on to deduce various other properties. Historically, most theories have used the idea of electrostatic dipoles, and it will be simplest and most useful to consider this approach rather fully, even though later on we shall see that it needs to be widened.

2. Suppose a structure consists of, or contains, a set of small poles held at fixed points in a regular array. There will be thermal motions tending to destroy the regularity; we suppose that they will not seriously affect the *positions* of the dipoles * (an assumption which is often taken for granted, but needs to be explicitly stated) but may change either their *orientations* or their *magnitudes*. In the former case we have *permanent dipoles*, which retain their individual dipole moments unchanged, though the net dipole moment of the whole array is lowered or destroyed because of their different orientations—which may be at random over all directions in space, or distributed between a limited number of fixed directions. The other type are the *induced-direction dipoles*, where the formal separation of charge is always in a given direction, but varies in magnitude because of the thermal motion. They include induced dipoles, which are always parallel to the field inducing them.

3. Forces tending to keep the array of dipoles in ordered formation parallel or antiparallel—are of two kinds: the long-range forces, electrostatic in character, arising from the fields of the dipoles themselves, and the short-range or structural forces due to interaction between near neighbours.

* They will of course give rise to a thermal expansion, but this effect is small and may be neglected in a preliminary discussion.

Earlier theories dealing with induced polarization in ionic non-polar crystals* (see for example Mott and Gurney, 1940) used only electrostatic forces. The assumption that only such forces were important was carried over into some of the theories of ferroelectricity and applied to polar crystals.* In the following sections, therefore, we shall have to consider it rather fully.

If, in such a theory, the dipoles are of fixed-direction type, it means that the whole separation of charges which constitutes the dipole is caused by the action of an internal field which is itself caused by the dipoles. This particular type of theory has been given the nickname of 'Bootstraps Theory', because 'it leads to the situation experienced by Munchausen's soldier who lifted himself out of the swamp by his own bootstraps' (von Hippel, 1950). It is a paradoxical situation, but the arguments have been widely accepted. An example is Slater's theory of BaTiO_3 (1950) (Chap. 10, § 9).

When the dipoles are permanent, and the internal field serves to orient rather than to create them, the same kind of paradox does not arise. An example is Mason and Matthias's theory of BaTiO_3 (1948) (Chap. 10, § 7), which however has been strongly criticized on other grounds.

It is, however, by no means obvious that short-range forces, not electrostatic in origin, never contribute to the restoring forces. Such forces certainly exist—if only to provide for the finite separation of the array of atoms carrying the dipoles, or in other words for the finite compressibility—and we cannot assume that their interaction with the other forces is negligible. A theory in which short-range forces provide the whole restoring force (or where long-range forces are only included as a small correcting term) is Slater's theory of KH_2PO_4 (1941) (Chap. 10, § 4).

2 Polarization and susceptibility in terms of long-range forces

2.1. Before we consider any detailed model, we must deal with some phenomenological arguments (resembling those of Mueller for Rochelle salt, cf. Chap. 8, § 3.1) which will be needed in handling it.

Consider an array of dipoles of net polarization P (total dipole moment Pv , where v is the volume) acted on by an external field E . If each individual dipole has a moment μ (or, if they are permanent dipoles, a moment with average component μ parallel to P) and if there are n dipoles per unit volume,

$$P = n\mu \quad (9.01)$$

There is a local field acting on every dipole due to the whole array of

* Here and throughout this book the term 'polar crystal' is used in its macroscopic sense to mean a crystal of polar symmetry (see appendix).

9. MODEL THEORIES: GENERAL BACKGROUND

other dipoles. This can be expressed as a power series in odd powers of P ,

$$E_{\text{loc.}} = \beta P - \xi^X P^3 - \zeta^X P^5 \quad (9.02)$$

The restriction to odd powers ensures that $E_{\text{loc.}}$ changes sign but not magnitude when P changes sign. For small fields, only the term in P need be considered. Then if the effective field acting on the dipoles is F ,

$$F = E + \beta P \quad (9.03)$$

2.2. We next assume that the net dipole moment is proportional to the effective field inducing it, and define their ratio as the (macroscopic) polarizability, α_M . It is at this point we postulate the absence of any short-range forces which could affect the magnitude (or in the case of a permanent dipole, the orientation) of the individual dipole. Then since the polarization is the dipole moment per unit volume,

$$P = \frac{\alpha_M}{v} F \quad (9.04)$$

Combining equations (9.03) and (9.04), we have

$$P = E / \left(\frac{v}{\alpha_M} - \beta \right) \quad (9.05)$$

By definition, the susceptibility η is $\frac{dP}{dE}$; hence

$$\eta = 1 / \left(\frac{v}{\alpha_M} - \beta \right) = \frac{\alpha_M/v}{1 - \beta\alpha_M/v} \quad (9.06)$$

In this, β is constant, but v/α_M is temperature-dependent; the variation in v (the thermal expansion) is small, but that in α_M may be larger. If at some temperature v/α_M becomes equal to β , the susceptibility (and hence the dielectric constant) becomes infinite. We may call this temperature T_0 .

2.3. The approximation made in (9.03) does not hold good if spontaneous polarization has set in, because the higher terms in (9.02) are now not negligible. Instead of (9.05) we have:

$$E = \left(\frac{v}{\alpha_M} - \beta \right) P + \xi^X P^3 + \zeta^X P^5 \quad (9.07)$$

(Comparison with (8.02) justifies the use of these particular coefficients for the higher terms.) For the susceptibility near the Curie point this gives (cf. (8.03))

$$\frac{1}{\eta} = \left(\frac{\partial E}{\partial P} \right)_{E=0} = \left(\frac{v}{\alpha_M} - \beta \right) + 3\xi^X P_s^2 + 5\zeta^X P_s^4 \quad (9.08)$$

P_s may be evaluated from (9.07) by putting $E = 0$, and is then eliminated from (9.08). There are two different cases (discussed in detail by Kittel (1953)) corresponding to first- and second-order transitions (cf. Chap. 8, § 2.1). For a second-order transition ξ^x is positive, ζ^x negligible, and $(v/\alpha_M - \beta)$ negative below the Curie point, at which it is zero. For a first-order transition, ξ^x is negative, ζ^x positive, and $(v/\alpha_M - \beta)$ positive even below the Curie point. The expressions for η just below the Curie point are as follows:

$$\left. \begin{array}{l} \text{Second order: } \frac{1}{\eta} = -2 \left(\frac{v}{\alpha_M} - \beta \right) \\ \text{First order: } \frac{1}{\eta} = 4 \left(\frac{v}{\alpha_M} - \beta \right) \end{array} \right\} \quad (9.09)$$

We shall use T_0 to mean the temperature at which $v/\alpha_M = \beta$, as distinguished from T_M , the temperature where the susceptibility has its maximum, i.e. the transition temperature.

3 The internal field

3.1. An early treatment of the internal field was due to Lorentz (1916). He showed that a randomly-placed array of point dipoles in parallel orientation in an uninsulated body gave a field of $4\pi P/3$. An array of similar dipoles on a simple cubic lattice also gave this value, $4\pi P/3$, for the field acting at each dipole.

The condition of parallel orientation does not hold for models with permanent dipoles, where misorientation follows as a consequence of thermal motions. An alternative theory was put forward by Onsager (1936), whose postulates implied that the neighbours of any mis-oriented dipole at a given instant were in equilibrium with it—that they followed its movements with no time-lag. In the Lorentz theory, they remained completely unaffected by it. Devonshire (1954) suggested that something between the two extremes was likely to be a better representation of any actual system, but it is convenient to consider the ideal cases. Onsager's theory gives the value of the internal field as βP , where β is not constant but dependent on ϵ .

For dipoles of fixed direction, it would seem that the Lorentz field is applicable, provided the further condition is satisfied that their array is either random or on special positions on the triad axes of a cubic structure. The cubic condition is fulfilled for all atoms in certain simple structures, such as those of the alkali halides, but not in BaTiO_3 . In rather complicated structures such as Rochelle salt, where all or most of the atoms are in general positions, it is reasonable to consider the array of atomic dipoles as random.

Where more than one kind of dipole is postulated, the Lorentz condition may be applicable to one and not to the other. Thus each

9. MODEL THEORIES: GENERAL BACKGROUND

model must be examined separately, and particular assumptions made. Sometimes an empirical factor β is used instead of the Lorentz $4\pi/3$, and it is later evaluated by comparison of the theory with experimental results. It is interesting to notice that it is often found to be not very different from $4\pi/3$.

In other cases, notably BaTiO_3 , the variation of the field from point to point inside the unit cell has been taken into account. Here there are several independent dipoles in the unit cell, each repeated by the lattice translations to give a set characterized by its own internal field. The field due to a set i acting in a given direction at a given vector distance $\mathbf{r}_i$ from the dipole in the same unit cell can be calculated, and expressed in terms of a (scalar) constant $\beta_{\mathbf{r}}$. If the polarization of this set of dipoles is P_i , its contribution to the internal field is $\beta_{\mathbf{r}}P_i$, and the total internal field at any point is the sum of such contributions, where the $\beta_{\mathbf{r}}$'s are worked out for the vector distances of the various dipoles from the point. This treatment is used in Slater's theory of BaTiO_3 (1950) (Chap. 10, § 9.2). For details of the calculation of the β 's, see Jaynes (1953).

3.2. We must next consider whether an internal field of any of these types is adequate to explain the existence of a Curie point. Equation (9.06) shows that the requirement is

$$\frac{1}{\beta} = \frac{\alpha_M}{v} \quad (9.10)$$

We have therefore to find the polarizability, α_M , from independent data as a function of temperature, and see if it gives a reasonable prediction of the Curie point. This can easily be done (cf. § 4.3) for polar liquids with permanent dipoles, such as water. It turns out that the Lorentz theory gives a Curie temperature so high that water would be ferroelectric at 100°C ! The difficulty using this theory is to explain, not why some substances are ferroelectric, but why others are not. This was called by Van Vleck (1940) 'the $4\pi/3$ catastrophe' or 'the Lorentz catastrophe'. It has since been met by the realization that Onsager's theory is more appropriate than Lorentz's to such a case.

It was originally thought that Onsager's theory denied altogether the possibility of a polarized state in a substance with permanent dipoles. However, Pirene (1949) has shown that, while the unpolarized state always represents a minimum in the free energy, there may be lower minima corresponding to polarized states—that is, a first-order transition is possible though not a second-order one.

The more important type of model with fixed-direction dipoles

cannot be dealt with till we have given some further consideration to the interpretation of polarizability.

4 Polarizability

4.1. In equation (9.04) we defined α_M , the dielectric polarizability of the crystal structure. Its relation to the experimentally-observed susceptibility, η , was derived in equation (9.06) in terms of an internal field having a field constant β . This equation may be rewritten

$$\frac{\alpha_M}{v} = \frac{\eta}{1 + \beta\eta} \quad (9.11)$$

If β has the Lorentz value $4\pi/3$, this can conveniently be expressed in terms of the dielectric constant, $\epsilon = 1 + 4\pi\eta$,

$$\frac{4\pi}{3} \frac{\alpha_M}{v} = \frac{\epsilon - 1}{\epsilon + 2} \quad (9.12)$$

This is known as the Clausius-Mosotti relation; it serves to define α_M in terms of the observable ϵ . It holds strictly only for crystals where the Lorentz theory applies, namely those with a random arrangement of dipoles or cubic crystals where all ions are in special positions on triad axes. Equation (9.11) is more generally applicable.

If the polarizability is to be of any use in a model theory, it will need to be expressed in terms of the dipole moments of individual dipoles. Before going into details, it will be useful to obtain some general relations showing what happens when more than one kind of dipole is present.

4.2. Suppose the structure contains two different kinds of dipoles giving rise to polarizations P_1 and P_2 . These are additive, and their sum gives the resultant polarization P . Both will give contributions to the internal field at any given point, but they will not necessarily have the same field factor. The equation corresponding to (9.03) is then

$$F = E + \beta_1 P_1 + \beta_2 P_2 \quad (9.13)$$

Let the first set of dipoles have a polarizability $\gamma_1 v$, where γ_1 is defined by

$$P_1 = \gamma_1 F \quad (9.14)$$

$$\text{Then} \quad F = \frac{E + \beta_2 P_2}{1 - \beta_1 \gamma_1} \quad (9.15)$$

$$\text{and} \quad P = \frac{\gamma_1 E}{1 - \beta_1 \gamma_1} + P_2 \left\{ 1 + \frac{\beta_2 \gamma_1}{1 - \beta_1 \gamma_1} \right\} \quad (9.16)$$

9. MODEL THEORIES: GENERAL BACKGROUND

hence
$$\varepsilon = 1 + \frac{4\pi\gamma_1}{1 - \beta_1\gamma_1} + \frac{4\pi P_2}{E} \left\{ 1 + \frac{\beta_2\gamma_1}{1 - \beta_1\gamma_1} \right\} \quad (9.17)$$

In this context ε is the overall dielectric constant $1 + 4\pi P/E$, not the differential dielectric constant $1 + 4\pi\partial P/\partial E$. Outside the ferroelectric range the difference is negligible.)

Suppose it is in any way possible to measure ε under conditions such that $P_2 = 0$; let its value then be ε_1 . Then

$$\varepsilon = \varepsilon_1 + \frac{4\pi P_2}{E} \left(1 + \frac{\beta_2\gamma_1}{1 - \beta_1\gamma_1} \right) \quad (9.18)$$

Some of these relations will be useful for the theories considered in Chap. 10.

3. The first important case to be considered is that of a set of permanent dipoles of fixed magnitude, subject to thermal agitation and oriented by a field F . These are the postulates of the Langevin-Weiss theory of ferromagnetism; they lead to an expression for P in terms of F as follows (assuming F small, so that it is far from saturation):

$$P = \frac{n\mu^2}{3kT} F \quad (9.19)$$

where μ is the dipole moment of an individual dipole, n the number per unit volume, k Boltzmann's constant, and T the absolute temperature. If the polarizability is α_{or} , we have

$$\frac{\alpha_{or}}{v} = \frac{n\mu^2}{3kT} \quad (9.20)$$

We notice that this orientation polarizability per unit volume is inversely proportional to the absolute temperature. The susceptibility follows from equation (9.06):

$$\eta = 1 / \left(\frac{3kT}{n\mu^2} - \beta \right) = \frac{n\mu^2}{3k} / \left(T - \frac{\beta n\mu^2}{3k} \right) \quad (9.21)$$

This is the Curie-Weiss law. It may be written

$$\eta = \frac{C}{4\pi(T - T_0)} \quad (9.22)$$

here
$$\frac{C}{4\pi} = \frac{n\mu^2}{3k} = \frac{\alpha_{or}T}{v} \quad (9.23)$$

and
$$T_0 = \frac{\beta n\mu^2}{3k} = \frac{\beta \alpha_{or}T}{v} \quad (9.24)$$

4. For larger fields, we cannot expect the magnitude of the dipoles to be independent of the field. A dipole consisting of a pair of nuclei

embedded in an electron cloud will be affected in two ways by a strong field: the distance between the nuclei will change, and the electron cloud will be altered in shape. This distortion introduces new terms into the expression for the polarization. It is nearly always assumed that, to a first order of approximation, individual ions can each be represented by a point charge plus a point dipole at the same position. This will be accepted for the present, though it may need reconsideration later.

In some of the models with which we shall be concerned, the orientation and distortion terms are of very unequal magnitude. We can in fact isolate the two extreme cases, and treat them separately (and have done so to some extent earlier in the chapter): the fixed-magnitude dipoles, where the effects of distortion are very small, and the fixed-direction dipoles, where thermal agitation cannot appreciably alter the direction (or balance of directions), and only the distortion terms need be considered. The latter case is a very important one, and must be examined in some detail.

It is not difficult, if necessary, to include terms for both types of polarization at once, as is shown formally in § 4.2. We may notice that, if one type of polarization is independent of temperature, the expression for the dielectric constant will include a constant term. For example, if in equation (9.14) P_1 (and therefore γ_1) does not vary with temperature, equation (9.18) becomes

$$\epsilon = \epsilon_0 + \frac{cP_2}{E} \quad (9.25)$$

where c is constant. If P_2/E has an inverse linear relation to T , the law takes the form

$$\epsilon = \epsilon_0 + \frac{C}{T - T_0} \quad (9.26)$$

If the graph of $1/\epsilon$ versus T is to be a straight line within experimental error (the Curie-Weiss law), ϵ_0 must be small.

4.5. We must now distinguish between the two factors which together make up the distortion: the relative displacement of the cores (the nuclei with their most tightly-held electrons) and the distortion of the looser parts of the electron cloud. The former can only be observed in an applied field which is static or of rather low frequency. If the field frequency is greater than the natural frequency of the atomic vibrations (which generally lies somewhere in the infra-red) only the electrons will follow it, and the consequent polarization is known as *electronic polarization*. We define an *electronic polarizability*, α_e , by an equation comparable to (9.12), but with the ordinary

9. MODEL THEORIES: GENERAL BACKGROUND

(low frequency) dielectric constant replaced by the 'optical dielectric constant', the square of the refractive index n . Thus

$$\frac{4\pi\alpha_e}{3v} = \frac{n^2 - 1}{n^2 + 2} \quad (9.27)$$

Like (9.12), this is only valid if the field at each ion is a Lorentz one. A more general equation, comparable to (9.11), can be used when β has a known value different from $4\pi/3$.

4.6. It is next necessary to see how the polarizabilities α_M and α_e can be expressed in terms of individual atoms. Recent writers do not rely on measurements of polarizabilities of free ions, but start with the experimental values for crystals defined by (9.12) and (9.27). The problem then is: can we allot a polarizability to each kind of atom such that the sum will in all cases represent the observed polarizability α_M or α_e ? It is of the same type as the problem, solved by Goldschmidt, of allotting a radius to each kind of atom such that the sum always represents the observed interatomic distance.

This problem has been tackled by Roberts (1949, 1951) for the total polarizability α_M , and by Tessman, Kahn and Shockley (1953) for the electronic polarizability α_e . Both sets of authors show that for the alkali halides the additivity law is very well satisfied; in doing so they confirm the correctness of the Lorentz field for this problem, which had earlier been questioned (Mott and Gurney, 1940; but see below, § 4.7). Both also extend their studies to other cubic crystals, to obtain polarizabilities for a wide range of atoms. They find that for many non-cubic crystals there is still a reasonable agreement between α_M and $v \sum \alpha'_j$ (where the α'_j are the separate polarizabilities per unit volume). Further, Roberts (1951) modifies the theory to cover cases where the Clausius-Mosotti law does not hold, and β is not the same at all points, by writing

$$\gamma_j = \alpha'_j \beta_j, \quad \alpha_M = v \sum \gamma_j \quad (9.28)$$

For ions of the same valency, Roberts finds that the total polarizability per ion varies linearly with the cube of the ionic radius, i.e. with the ionic volume, a result which may be physically significant.

Tessman, Kahn and Shockley obtain a very considerable spread in values of the electronic polarizability derived from compounds which have some homopolar character. This is particularly marked for O^{2-} , where the polarizability seems to depend on the volume per oxygen ion.

Some particular values of polarizabilities are given in Table 9.1. They are only intended as illustration; there is a good deal of uncertainty still about the best values to use, and the original papers should be consulted.

FERROELECTRICITY IN CRYSTALS

TABLE 9.1

Some atomic polarizabilities

Atom	Polarizability in Å ³		
	Total polarizability (Roberts, 1951)	Electronic polarizability (Tessman, Kahn and Shockley, 1953)	Electronic polarizability used by Slater (1950)
Ti	0.87	—	0.19
Ba	5.94	2.5	1.95
Sr	3.74	—	—
Ca	2.55	—	—
O	2.70	0.5 to 3.2	2.4

4.7. It would be possible to use the difference of the observable quantities α_M and α_e to define an ionic polarizability α_i ,

$$\alpha_i = \alpha_M - \alpha_e \quad (9.29)$$

(This has not been done with the actual experimental values; in view of their present experimental limits of error, it might not be very informative.) Then the dipole moment associated with ionic polarization could be expressed in terms of the number of ions N , the ionic charge ze , and a displacement δ :

$$F\alpha_i = F(\alpha_M - \alpha_e) = Nze\delta \quad (9.30)$$

In this, δ represents a separation between positive and negative charges of magnitude ze . The question now is, can such charges be found in the structure with such a separation? Can δ be identified, for example, in terms of the structure as determined by X-rays?

One treatment is due to Roberts (1950). He assumes a model in which the whole distortion of the atom takes place without affecting its outer boundary. Then δ is the distance between the nucleus of the atom in its distorted and its undistorted positions. His arguments are restricted to non-polar crystals*, and hence to the case of induced polarization.

For a polar crystal*, it is very far from clear what physical meaning can be given to the displacement in equation (9.30). A displaced atom does not constitute a dipole, and since the displaced position is the equilibrium position there is no necessary concentration of negative charge in the central site from which it has been removed, even if that

* See footnote on p. 166.

9. MODEL THEORIES: GENERAL BACKGROUND

could be defined with respect to all the other atoms which may also suffer displacements.

Takagi (1953) has faced this difficulty. He has shown that while no meaning can be given to the ionic polarization of a single set of translation-equivalent ions, the mutual polarization of a pair of sets can be expressed in terms of their displacement relative to each other, which is uniquely defined. The total ionic polarization of the structure is the sum of the polarizations of all the pairs.

There is another fundamental difficulty involved in equation (9.30). The difference between α_M and α_e is not wholly due to displacements of the cores in a static or slowly varying field. It was pointed out by Eucken and Büchner (1934) that a change of internuclear distance *necessarily* involved a rearrangement of the electron cloud. There is in fact a short-range interaction between the true ionic polarization and the true electronic polarization, so that what is measured depends on both. We may express it otherwise by saying that α_i as defined by (9.29) contains a contribution from the outer electron cloud, which could be rather large, and that neither z nor δ has an independent meaning.

An attempt has been made by Szigeti (1949) to deal with polarizabilities in an entirely different way. He defines them, for each atom, in terms of natural frequencies in the crystal for applied fields of different frequency. He does not use the concept of the internal field, nor divide the polarizabilities into ionic and electronic parts. This treatment, however, has only been applied to non-polar crystals*.

It is thus clear that 'ionic polarization' is a concept which cannot very easily be given a physical meaning, because of the difficulty of finding the effective charge. In particular, the individual dipoles in a ferroelectric or antiferroelectric cannot be identified with the products of the charges corresponding to the valency and the observable 'displacements' of selected atoms.

4.8. The difficulty in giving a physical meaning to the ionic polarizability brings us back to the doubtful validity of our original assumption (§ 2.1), namely that all the restoring forces were long-range, and that short-range forces were negligible. We may put this another way by saying that it is not a good enough approximation to represent each atom (or rigid group of atoms) by a point charge plus a point dipole. The way out of the difficulty is not merely to add a quadrupole term to the atom (as Szigeti (1950) has pointed out), but to consider the actual ways in which the electron cloud becomes non-spherical. From the quantum point of view we see that the effects of overlap at

* See footnote on p. 166.

the contact between an atom and its neighbours will give rise on the one hand to repulsive forces, on the other to attractive forces of covalent character (see for example the treatment of the Si-O bond by Fyfe, 1954). From the electrostatic point of view, we recognize that it is necessary to place dipoles on the atomic bonds instead of, or as well as, at the atomic centres. In this way, by either approach, we have to take into account the short-range forces.

There is evidence from nuclear resonance experiments on KNbO_3 (Cotts and Knight, 1954) that a treatment of this kind is necessary. The direction and magnitude of the field gradient at the Nb atom cannot be predicted, even qualitatively, by the use of simple models based on point charges, and the authors conclude that their results can only be explained by covalent bonding, where the field gradient 'is generated by valence electrons which penetrate the ion core'.

It seems clear from these arguments that only quantum-theory treatment can give an exact description; but that a reasonable electrostatic model might perhaps be devised if the concept of point atoms were abandoned. Meanwhile, it might be fair to say of the model theories outlined in Chap. 10 that the most successful quantitatively are those which have been least specific in interpreting 'polarizability' in terms of particular dipoles in the structure.

5 Construction of a model theory

5.1. We can now re-state the method of constructing a theory in a rather more general way. It is first necessary to pick out some feature of the unit of structure which can exist in different states having slightly different energies. Then the states corresponding to each possible value of the energy must be enumerated.

Here the treatment for long-range and short-range forces differs. For long-range forces, the state of each unit is independent of its neighbours except through the effect of the internal field. Hence it is easy to enumerate the possible states of the unit. The calculation of the energy of each state involves an assumption about the field-factor of the internal field; if the model postulates different kinds of dipoles, there may be a separate factor for each.

With short-range forces, the state of each unit is affected so strongly by the state of its neighbours that we cannot consider them in isolation, but have to derive from the separate units the possible states of the crystal as a whole. The energy of each unit, however, is not dependent on the state of the whole, and enters into the energy of the whole as a constant factor.

When the possible energy states of the independent units (the unit cell or the whole crystal, according to the circumstances) have been enumerated in terms of their energies, a partition function is con-

9. MODEL THEORIES: GENERAL BACKGROUND

structed, and the Helmholtz free energy obtained from it. From this in turn various other quantities are directly derived, notably the maximum polarization, the dielectric constant of the unpolarized substance and its temperature variation (generally expressed in terms of the constants C and T_0 of the Curie-Weiss law), the changes of energy and of entropy at the transition. These can be compared with experimental observation. Further assumptions introducing the piezoelectric coefficients are needed if the detailed rate of rise of the spontaneous polarization or the dielectric constants below the Curie point are to be explained.

This is, in outline, the pattern followed by most of the theories described in Chap. 10.

It is worth noting the warning given by Devonshire (1954), that the quantities most easily calculated from a model theory are usually not those most easily observed. For example, theoretical calculations usually give isothermal susceptibility at constant strain, and the transition temperature of the clamped crystal, whereas experimental observations usually give adiabatic susceptibility at constant stress, and the transition temperature of the free crystal. The differences must be taken into account if a critical comparison of theory and experiment is being made.

5.2. It should be noticed that the model theory has to begin by postulating the nature of the low-temperature structure. In the theories using short-range forces, this is done by specifying the type of interaction between units; in those using long-range forces, by specifying the direction of the dipole and the size of the repeat unit. In both, this amounts to an acceptance of the particular kind of low-temperature structure actually observed. For example, the assumptions made in Slater's theory of KH_2PO_4 (Chap. 10, § 4) do not hold for $\text{NH}_4\text{H}_2\text{PO}_4$, and there is nothing in the theory to show why it applies to one structure and not to the other.

It is thus not true to say that ferroelectricity can be adequately explained in terms of electrostatic dipoles, since this must always include an empirical assumption about the kind of low-temperature structure adopted. Further, it would seem that such theories cannot explain antiferroelectricity without again introducing an arbitrary assumption about the nature of the new lattice (which is formed, as we have seen, from some multiple of the original unit cell). For example, though Takagi (1952) has studied a model which could show ferroelectricity or antiferroelectricity, the unit cell of the antiferroelectric structure was a postulate for the theory, not a deduction from it.

The type of theory we have considered so far must therefore be

prefaced by other ideas which will serve to give a qualitative explanation of the low-temperature structure. The failure of the long-range forces to do so means that they cannot be considered as the cause of ferroelectricity, whatever their contribution to the effect when it does set in. It would in any case seem arbitrary to explain ferroelectricity, which we have seen to be so closely dependent on crystal structure, without reference to our knowledge of structure-building principles in other low-symmetry compounds. This again focusses attention on the short-range homopolar forces. Some suggestions for an approach along these lines are made at the end of Chap. 10.

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Chapter 10

MODEL THEORIES: PARTICULAR APPLICATIONS

The mind, that ocean where each kind
Does straight its own resemblance find;—
Yet it creates, transcending these,
Far other worlds, and other seas.

MARVELL: *The Garden*

1 Introduction

The account of the individual theories which follows does not include very much of their detailed mathematical treatment. Emphasis has been given to the assumptions put into the theories and the conclusions drawn from them, and an attempt has been made to state them in terms which will allow comparison of one with another.

The theories are grouped according to the substance with which they deal, and within each group are in chronological order. The last section gives an account of the structural approach which is applicable to all substances.

2 Rochelle salt: theories of Kurchatov and of Fowler

The first theoretical treatment of ferroelectricity in Rochelle salt was put forward in 1930 by Kobeko and Kurchatov. It assumed rotatable dipoles, and was closely related to the Langevin-Weiss theory of ferromagnetism. Fowler's theory (1935) postulated the existence of certain preferred directions in the low-temperature structure, and a cooperative transition between this ordered state and the disordered state of complete rotation. In both theories, the water molecules were supposed to constitute the dipoles.

Later work on the crystal structure failed to provide evidence that the water molecules were freely rotating in the high-temperature form. The theories were also criticized on the ground that they took no account of the piezoelectric effects. Nevertheless they provide the starting-point from which a good deal of the more modern work has developed.

3 Mason's theory of Rochelle salt

3.1. The theory of Rochelle salt put forward by Mason (1947a, b;

1949) postulates fixed-magnitude dipoles with two possible orientations of different energy.

The dipoles are associated with the short hydrogen bond O(10)–O(1) (see Chap. 2, § 1.2), which lies nearly parallel to the polar axis. On the bond are two potential wells in one of which the hydrogen will lie (see Fig. 10.1); they are of unequal depth because of the different environments of the oxygen atom at either end. The potential barrier separating them is not very high, and for equilibrium at a given temperature both wells will be occupied, though to unequal extents.

If the separation of the wells along the bond is δ , and the bond

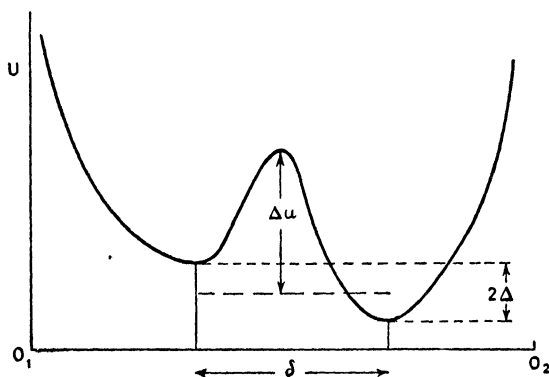


Fig. 10.1. Potential wells of unequal depth in a hydrogen bond.

makes an angle of θ with the polar axis, the dipole moment of each bond is taken as

$$\mu = \frac{1}{2}\delta e \cos \theta \quad (10.01)$$

where e is the charge on an electron. The effect of any polarization of the oxygen atoms is here explicitly neglected. The net contribution to the dipole moment of the structure depends on the numbers of dipoles pointing in each direction, i.e. on the numbers of atoms in each kind of well.

There is a second hydrogen bond O(1)–O(10) related to the first by a symmetry axis (see Fig. 2.1) and if there is no field it will have an equal and opposite dipole moment. The effect of a field is to change the balance between the numbers of atoms occupying the two kinds of wells, and this effect is different for the two oppositely-directed bonds.

The height of the potential barrier, measured from the mean level of the two wells, is Δu , the difference in depth of the two wells 2Δ . The internal field includes contributions from the dipole polarization,

10. MODEL THEORIES: PARTICULAR APPLICATIONS

P_d , and from the polarization due to distortion (electronic and ionic taken together), P_a ; it may be written

$$F = E + \beta_d P_d + \beta_a P_a \quad (10.02)$$

where E is the applied field. For β_a the Lorentz value of $4\pi/3$ is assumed, and β_d is written as β . The distortion polarization P_a is expressed in terms of a polarizability γv . To define it, we consider the state of affairs at absolute zero, where P_d must be zero, because all hydrogen atoms are then fully ordered in the deeper wells. Thus the limiting value ϵ_0 which the dielectric constant ϵ approaches at low temperatures can be used to define γ , by using equation (9.17) with $P_2 = 0$ (compare equation 9.12).

$$\frac{4\pi}{3}\gamma = \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \quad (10.03)$$

Since the internal field is now known, it is possible to calculate the potential energy μF due to the dipoles. If this is added to the energy differences shown in Fig. 10.1, a partition function can be constructed giving the distribution between the two wells. From this an expression is found for $P_d/(n\mu)$ (which we may write P' for short) in terms of $\Delta/(kT)$ and a quantity a defined by the equation

$$a = \frac{n\mu^2\beta}{kT(1 - 4\pi\gamma/3)} \quad (10.04)$$

Comparison with equation (9.20), for freely rotating dipoles, shows that a is related to a polarizability.

Outside the ferroelectric range, P' is zero, and within it, very close to the transition, it must be small. Expansion in powers of P' then gives:

$$P' = \left(1 - \tanh^2 \frac{\Delta}{kT}\right) a P' + \text{terms in higher powers of } a P' \quad (10.05)$$

The condition for spontaneous polarization is that this equation should have non-zero solutions for P' ; this happens if the coefficient of the term in P' on the right-hand side is greater than 1.

Thus the temperature at which ferroelectricity sets in is the value of T satisfying the equation

$$a \left(1 - \tanh^2 \frac{\Delta}{kT}\right) = 1 \quad (10.06)$$

where a is defined by (10.04).

3.2. We must now relate this to the experimental data. Of the quantities concerned in the left-hand side of (10.06), all are defined in terms of observables except Δ , μ and β . Of these, Δ can be estimated from

the rate of falling off of the dielectric constant at low temperatures, from which it is taken to be $2kT_0/3$. To obtain μ as the product $ze\delta$, an estimate of δ is needed. It can be taken as the difference of two quantities: the actual O(10)–O(1) distance in Rochelle salt, found by X-ray structure analysis, and twice the O–H distance in water, found by infra-red measurements. With these assumptions, β can be estimated from (10.06). It comes out as 4.4—not very different from the Lorentz value of $4\pi/3$.

Equation (10.06) can be used to predict the existence of a lower Curie point. We multiply the left-hand side by T above and below. The factor $(1/T)[1 - \tanh^2 \Delta/(kT)]$ can be plotted as a function of T for any given value of Δ ; for the range of T with which we are concerned, and $\Delta = 2kT_0/3$, it increases slowly as the temperature decreases. The factor aT or

$$\frac{n\mu^2\beta}{k(1 - 4\pi\gamma/3)}$$

is also temperature-dependent, because there is variation in n due to thermal expansion, and also variation in μ through its proportionality to δ . If we assume (as Mason does) that the O–H distance remains constant while the O–O distance is subject to the overall thermal expansion of the crystal, we find a decrease in δ (with decreasing temperature) which is more important than the increase in n , and causes a net decrease in aT . Since this factor decreases while the other increases, there may be some lower temperature where the product is again 1. This is the lower Curie point. Numerical values of the quantities involved can be chosen so as to predict the temperature actually observed.

The differences between the Curie points of normal and deuterium-substituted Rochelle salt are explained in terms of a factor which brings in the zero-point energy. The signs of the observed temperature differences agree with those expected for $\Delta \simeq 2kT_0/3$.

The dielectric constants inside and outside the Curie range can be calculated from the theory, and agree reasonably well with experiment. On the other hand, the theory would predict fairly large entropy and energy changes at the transition, which are not observed, and this is a serious objection.

3.3. Other criticisms of Mason's theory may be directed towards his model. For this, we must first consider the chemical implications of the two-well theory. If the hydrogen is in the deeper well, it is attached to a water molecule, O(10) (see Fig. 2.1), while the oxygen at the other end, O(1), forms part of a carboxyl ion belonging to a tartrate group. If the hydrogen is in the shallower well, it is attached to O(1)

10. MODEL THEORIES: PARTICULAR APPLICATIONS

and forms part of an electrically-neutral acid group, leaving O(10) as a hydroxyl ion. There is no chemical evidence for this latter arrangement; even if we could suppose it to be in tautomeric equilibrium with the former, the balance-point could be nothing like as nearly central as Mason's theory requires.

A second difficulty is one common to many of these theories—the nature of the dipole. An isolated proton does not constitute a dipole; it is the OH group which does so. The O–H bond undoubtedly has a good deal of homopolar character, as is made obvious by the fact that the internuclear distance is roughly 1.0 Å while the O radius is 1.32 Å—that is, the H nucleus lies within the electron cloud of O. Further, the very fact that the H atom can be detected by X-rays by means of its electron concentration shows that it is not fully ionized. Thus we are not likely to get a good approximation to the actual dipole moment by considering the displacement of a proton relative to a fixed set of negative charges. Mason recognized that the polarization of the oxygen atoms would be altered, but he did not consider the difficulty serious. From any chemical point of view, however, it is a vital matter.

Even if we consider the proton displacement to be significant, the indirect method of estimating it cannot be taken as very reliable. Neither the O–O distance nor its temperature coefficient is accurately known; the latter need not be the overall expansion coefficient of the structure (as has been shown experimentally by Candlin, 1956). The O–H distance in many compounds seems to be sensitive to the O–O bond length. Thus predictions of the lower Curie point based on our present knowledge of the temperature variation of δ do not carry great conviction.

The interest of Mason's theory is that it does provide a single mechanism to explain the two Curie points by explaining the reversal in sign of the temperature coefficient of ϵ , even though the experimental data used for fixing the numerical values are not good enough. On the other hand, we do not yet know whether the structure below the Curie range is the same as that above it; if not, the fact that the theory uses the same mechanism to explain the two transitions does not tell in its favour.

4 Slater's theory of potassium dihydrogen phosphate

4.1. Slater's theory of KH_2PO_4 (1941) differs from most other theories of ferroelectrics in putting the emphasis on short-range forces and neglecting long-range forces.

Slater begins by assuming that on every hydrogen bond there are two equal and symmetrically-placed potential wells. The distribution of H's between them is subject to two conditions, (i) that there is one

FERROELECTRICITY IN CRYSTALS

and only one H on each bond, (ii) that there are two H's attached to each PO_4 group (cf. Fig. 3.3). From (ii) it follows that there are 6 possible configurations for each PO_4 group, illustrated in Fig. 10.2. Of these, (a) and (b) give a net O-H component parallel to z (the tetrad axis) pointing up and down respectively; the other four give a net O-H component in the plane of the paper (perpendicular to z). Slater attributes a dipole moment to the displacement of H in the bond; hence the direction of the net O-H component gives the direction of the dipole moment of the PO_4 group. He further postulates—to explain the electrical properties—that a group or unit whose dipole lies parallel to z has a lower energy than one perpendicular to it. The energy difference of the two units may be called ϵ_u .

Conditions (i) and (ii) mentioned in the last paragraph imply that the orientation of any unit cannot be independent of the orientation of its neighbours. Starting with a unit of given configuration, there

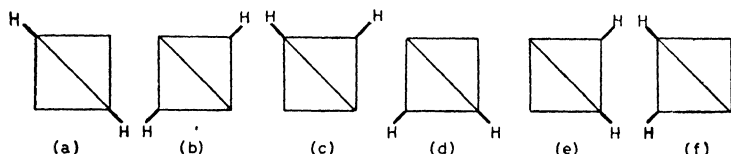


Fig. 10.2. Possible orientations of PO_4H_2 tetrahedra (z axis perpendicular to paper).

are a limited number of ways in which another unit can be built on to it. Slater enumerates all the ways in which a structure of n units per unit volume can be built up to give any chosen energy. This was a difficult piece of work. When complete, it gives the partition function. From this are derived the Helmholtz free energy A in terms of the dipole moment μ , the energy difference ϵ_u , and a quantity x which is the difference in the numbers of dipoles pointing in the positive and negative directions. The polarization is then $n\mu x$, and from the free-energy equation it is found that

$$x = \frac{\mu E}{2kT(q - \frac{1}{2})} \quad (10.07)$$

where

$$q = \exp \left[-\frac{\epsilon_u}{kT} \right] \quad (10.08)$$

Hence we obtain the susceptibility:

$$\eta = \frac{P}{E} = \frac{n\mu x}{E} = \frac{n\mu^2}{2kT(q - \frac{1}{2})} \quad (10.09)$$

This becomes infinite at $q = \frac{1}{2}$, or

$$\epsilon_u = kT_0 \ln 2 \quad (10.10)$$

10. MODEL THEORIES: PARTICULAR APPLICATIONS

Expanding the denominator of (10.09) in powers of $T - T_0$ gives, near the Curie point,

$$\eta = \frac{n\mu^2}{T - T_0} \cdot \frac{1}{k \ln 2} \quad (10.11)$$

This is the Curie-Weiss law, with

$$\frac{C}{4\pi} = \frac{n\mu^2}{k \ln 2}, \quad T_0 = \frac{\varepsilon_u}{n\mu^2} \cdot \frac{C}{4\pi} \quad (10.12)$$

These expressions may be compared with equations (9.23) and (9.24).

4.2. The entropy difference between the polarized and unpolarized states can be calculated from the number of possible configurations, which can be deduced directly from conditions (i) and (ii) (§ 4.1). The discontinuous change at the Curie point is thus $(R/2) \ln 2$ or 0.69 cal. mol.⁻¹ deg.⁻¹. There is a further continuous increase above that temperature, making a total change $R \ln (3/2)$ or 0.805 cal. mol.⁻¹ deg.⁻¹. These changes are of the right order of magnitude to agree with experiment (cf. Table 3.5).

The theory predicts a first-order transition. The phenomenological argument from the constants in the free-energy expression (Devonshire, 1954) suggests that it is second-order, and this has been used as a criticism of Slater's theory. There is no doubt, however, that the observed transition is a very sharp one, and the question whether it is discontinuous cannot be considered as finally settled.

Slater introduced modifications to allow for the polarizabilities of the atoms other than H and their long-range interaction with the H dipoles. Though their effect was not negligible it could be dealt with by including a correcting term in the theory as originally developed.

4.3. A serious difficulty in accepting the theory in its original form concerns the direction of the dipoles. Slater attributed them to the displacements of H's in the bonds, which are very nearly perpendicular to z , yet the dipole moment of the crystal must be parallel to z .

This difficulty disappears if we realize that the movements of H make the PO_4H_2 groups as a whole into dipoles; the P-OH bonds and the P-O bonds will not be of equal strength, and thus P will be displaced with respect to its neighbours. There may also be displacement of K. Both P and K displacements lie along the z axis and are likely to contribute more to the dipole moment than the H displacements.

Another objection to the theory is that it fails to predict the very large change of Curie point when H is replaced by D.

It may also be noted that the theory does not predict the *kind* of transition undergone by KH_2PO_4 , namely to the tetragonal structure of point-group $mm2$. As we saw, it accepts without explaining the

empirical fact that dipoles are oriented along the z axis. The subsequent discovery that low-temperature $\text{NH}_4\text{H}_2\text{PO}_4$ was orthorhombic, with point-group 222 and dipoles oriented perpendicular to z , makes it desirable to have a theory which would show why one structure rather than the other was preferred.

In spite of these difficulties, it remains true that Slater's theory has proved extremely useful in the study of KH_2PO_4 . The underlying assumption that the transition involved order-disorder relations in the hydrogen bonds has been directly verified by the neutron-diffraction work described in Chap. 3.

5 Mason's treatment of potassium dihydrogen phosphate

5.1. Mason (1949) applied to KH_2PO_4 the same theory he had used for Rochelle salt (see § 3) by putting $\Delta = 0$, that is, by making the two wells in the hydrogen bond of equal depth. This assumption is the same as Slater's, but thereafter the two theories differ, for Mason uses only the long-range electrostatic forces and does not introduce the condition that there should only be two H's on each PO_4 group. The same treatment as for Rochelle salt shows that at the Curie point $a = 1$, where a is defined by equation (10.04). The clamped dielectric constant above the Curie point, ϵ , is given by the relation

$$\epsilon - \epsilon_0 = \frac{C}{T - aT} \quad (10.13)$$

(cf. equations (9.18), (9.25)) where ϵ_0 is no longer the dielectric constant at absolute zero, because 'the positions of the hydrogen nuclei do not freeze out at low temperatures', but a constant to be determined empirically. The experimental observations follow the Curie-Weiss law; hence aT is constant and may be put equal to T_0 . The only temperature-dependent factors in aT are n and μ ; since the changes in n due to thermal expansion are negligible, μ must remain effectively constant.

5.2. Comparison with the observed values of C and T_0 enables μ and β to be calculated, and hence the maximum spontaneous polarization. The values so found are $\mu = 0.81 \times 10^{-18}$ c.g.s. units, $\beta = 0.567$. The calculated spontaneous polarization is much larger than that observed; Mason considers that the observed value is too low because the applied fields are not big enough to overcome the large coercive field at low temperatures (cf. Chap. 3, § 9.3).

There is no explanation why the dipole moment μ should be constant in KH_2PO_4 if it is temperature-dependent in Rochelle salt, since the same method for evaluating δ would apply to both cases.

The very low value of β required by this theory may also be noted.

5.3. A rather more general treatment of a two-position dipole has been given by Devonshire (1954).

6 Pirene's theory of potassium dihydrogen phosphate

6.1. Pirene (1949) criticizes Slater's theory for its neglect of the long-range forces. He points out that the electrostatic energy of dipole interaction is $\frac{1}{2}\beta P^2$, and if β is of the order of magnitude of the Lorentz factor, $4\pi/3$, this is several times greater than the short-range energy.

Pirene postulates that the polarization may be divided into two parts. The first is a proton part P_p , wholly due to displacements of the proton with a certain amount of tightly-bound electron cloud which moves with it, the effective charge being ρe , with $\rho < 1$. The second part is a 'ground polarization' P_g , including all other effects such as electronic polarization and displacement of other ions.

The proton polarization gives rise to an internal field with field factor β_p . It is assumed that the ground polarization is proportional to the proton polarization, so that we may write

$$P_p = y(P_g + P_p) = yP \quad (10.14)$$

The constancy of ρ is also assumed.

The potential well in which the protons move must be anharmonic, in order to allow a polarized state to be in equilibrium. (This point is discussed in connection with Devonshire's and Slater's theories of BaTiO_3 , § 8.1 and 9.1.) Pirene found it satisfactory to assume a well with a square profile in the direction of spontaneous polarization—that is, one in which the polarization is saturated, so that increase in potential energy does not result in increased displacement. This is in fact the assumption of a fixed-magnitude dipole. The vibrations of the proton are then treated by quantum mechanics. If the energy of the first level is E_0 , all relevant properties of the material can be expressed in terms of the four parameters β , y , ρ and E_0 .

Pirene is concerned to explain the isotope effect—the difference in the properties of KH_2PO_4 and KD_2PO_4 . In his model, this is due to the fact that all levels are lower by a factor of 2 for D than for H, and hence the polarizability, the polarization, and the Curie temperature are all higher for the D compound.

6.2. To obtain numerical values, Pirene chooses his four parameters to satisfy three experimental quantities: the transition temperatures of KH_2PO_4 and KD_2PO_4 , and the saturation polarization of the former. He then calculates the saturation polarization of KD_2PO_4 and the Curie constants of both compounds (the constant C in the Curie-Weiss law) and obtains good agreement. He also deduces the change of energy at the transition, and finds it to be 25 cal. mol.⁻¹

for KH_2PO_4 , 90 cal. mol. $^{-1}$ for KD_2PO_4 . These are of the same order of magnitude as the values observed (cf. Table 3.5) and the difference between the two is in the same direction.

The numerical values of the parameters are informative. The field constant β is 5.97, as compared with $4\pi/3 = 4.19$. The effective charge ρ is 0.27, as compared with 0.40 for water; Pirenne is satisfied with this order-of-magnitude agreement, but one may note that a higher effective charge would be expected in KH_2PO_4 , which has a short O—O distance, 2.49 Å, and a relatively long O—H distance, 1.07 Å, than in H_2O , where the situation is reversed, with O—O = 2.76 Å, O—H = 0.99 Å. The ratio of proton polarization to total polarization, y , is 0.206. This is thought by Pirenne to be rather low, but perhaps it should not be surprising in view of the rather large displacements of the atoms other than hydrogen; the point is considered from the structural point of view in § 12.4.

The value of E_0 is 0.683×10^{-2} eV. This predicts an infra-red absorption band in the region of 166 cm. $^{-1}$ for KH_2PO_4 , and 83 cm. $^{-1}$ for KD_2PO_4 . Pirenne considers that these may correspond to observed bands at 195 cm. $^{-1}$ and 148 cm. $^{-1}$ respectively (La Lau, 1947).

6.3. Pirenne's theory is satisfactory so far as it goes, but it leaves a good deal of the mechanism unexplained. The difficulty that the proton shifts are nearly perpendicular to the direction of spontaneous polarization has not been cleared up, but may perhaps not be a serious one in this treatment. A good deal of the interesting and important detail is obscured by the assumption of an undifferentiated 'ground polarization'. The low value of y found empirically suggests that this 'ground polarization' has an important rôle, and seems to some extent to justify Slater's postulate that long-range forces could to a first approximation be neglected.

The quantum-theory treatment of energy levels is undoubtedly valuable. Its predictions will need to be correlated with the newer experimental data, derived from neutron-diffraction experiments, concerning the mean positions and thermal amplitudes of the protons.

This theory, like all the others, throws no light on the choice of arrangement actually adopted by the ordered structure.

7 Mason and Matthias's theory of barium titanate

7.1. The theory put forward by Mason and Matthias (1948) and amplified and modified by Mason (1949) is essentially one of permanent dipoles, capable of taking up any of 6 different positions. At high temperatures all positions are equally probable, at low temperatures there is an ordered arrangement.

10. MODEL THEORIES: PARTICULAR APPLICATIONS

The dipole arises as follows. It is supposed that, because of the large volume available to Ti within its octahedron, its equilibrium position will be an off-centre one, displaced towards one of the six oxygens. This state of affairs would also be favoured by the existence of homopolar forces. The potential wells are separated by an energy barrier of height Δu . The dipole moment is proportional to δ , 'the displacement of the titanium from the mid position of the unit cell', but there may be some added contribution 'if the oxygen moves in towards the titanium'. (It is not clear how 'the mid position of the unit cell' is defined.) If the Ti atom carries a charge $4e$,

$$\mu = 4e\delta \quad (10.15)$$

The polarization consists of two parts, a part P_d due to dipole polarization, and a part P_a due to all other effects. Both contribute to the internal field, and in the first form of the theory the field factor $4\pi/3$ was used for both; but in the later modification a lower factor β was assigned to the dipole part, because of the 'shielding of adjacent molecules'. (This is the same as Mason's assumption in Rochelle salt, § 3.1, equation 10.02.) As before, the dielectric constant ϵ_0 at low temperatures, where the dipoles are completely ordered and cannot change position, is used to define a polarizability γv . Comparison with equation (9.16) shows that, if we subtract the atomic polarization

$$\frac{\gamma E}{1 - 4\pi\gamma/3}$$

we obtain a 'measured dipole polarization' which is the product of the permanent dipole moment and a factor

$$1 + \frac{\beta\gamma}{1 - 4\pi\gamma/3}$$

Thus the effect of the shift of electronic charge is to enhance the measured dipole moment.

When an external field E is applied, say along the z axis, the potential energy of the dipoles associated with two of the wells, those at $\pm(0, 0, \delta)$, changes by $\pm F\mu$, while that of the other four is unaltered. Since $F\mu$ is known, a partition function can be constructed. It is in the actual form of the partition function that this 6-position theory differs from the 2-position theory of KH_2PO_4 . If we write $P' = P_z/(\eta\mu)$, where P_z is the polarization along the z axis, it gives

$$P' = \frac{\sinh \left[a \left(P' + \frac{E_z}{\beta\eta\mu} \right) \right]}{2 + \cosh \left[a \left(P' + \frac{E_z}{\beta\eta\mu} \right) \right]} \quad (10.16)$$

FERROELECTRICITY IN CRYSTALS

The condition for spontaneous polarization is that P' shall have non-zero values for $E_z = 0$; this turns out to be

$$a \geq 3 \quad (10.17)$$

At the Curie point, therefore,

$$\frac{\beta n \mu^2}{k T_0 (1 - 4\pi\gamma/3)} = 3 \quad (10.18)$$

$$\text{or} \quad T_0 = \frac{\beta n \mu^2}{3k(1 - 4\pi\gamma/3)} = \frac{aT}{3} \quad (10.19)$$

The dielectric constant above the Curie point is found from (10.16), which gives

$$\frac{P_z}{E_z} = \frac{a}{\beta(3 - a)} = \frac{T_0}{\beta(T - T_0)} \quad (10.20)$$

Substituting this in equation (9.18), we obtain the equation for the dielectric constant above the Curie point,

$$\varepsilon = \varepsilon_0 + \frac{C}{T - T_0} \quad (10.21)$$

$$\text{where} \quad C = \frac{4\pi a T}{3\beta} \left(1 + \frac{\beta\gamma}{1 - 4\pi\gamma/3} \right) \quad (10.22)$$

7.2. Equations 10.19, 10.21, and 10.22 allow the evaluation of β and μ from the experimental observations. Mason finds that β is 0.142 and μ is 1.56×10^{-18} c.g.s. units. The very small value of β must indicate strong shielding of the dipoles. From these numerical values Mason calculates the spontaneous polarization and the dielectric constant for the tetragonal crystal, and finds they agree with those observed.

The theory has been extended to the two low-temperature forms by assuming that at the transition to orthorhombic the crystal becomes 'ferroelectric along two directions simultaneously' and at the transition to rhombohedral along three. To achieve this, the Ti atom spends equal times between two wells such as those at $(\delta, 0, 0)$ and $(0, 0, \delta)$ in the orthorhombic case, and between three wells such as those at $(\delta, 0, 0)$, $(0, \delta, 0)$, and $(0, 0, \delta)$ in the rhombohedral case.

7.3. The theory has been criticized in considerable detail by Jaynes (1953). He points out that because of the six possible positions of the dipole it would predict an entropy change of $k \ln 6$ per unit cell, that is, of 3.6 cal. mol.⁻¹ deg.⁻¹, whereas the observed value (though not very exactly known, see Table 4.5) is about 0.1 cal. mol.⁻¹ deg.⁻¹. Such a low entropy change is quite incompatible with an order-

10. MODEL THEORIES: PARTICULAR APPLICATIONS

disorder transition (see, by way of contrast, the value for KH_2PO_4 , Table 3.5).

The first form of the theory, where β was given the value $4\pi/3$, could not account satisfactorily for the constants in the Curie-Weiss law. The modified form, which makes it an adjustable parameter, cures some of the discrepancies but not all. Experimental observations of ϵ and T show that the constant ϵ_0 in equation 10.21 cannot be greater than 10; yet from the theory it should be identified with the low-temperature dielectric constant, which is of the order of 90.

Another difficulty, of the kind common to many of these theories, is the meaning to be given to the dipole μ . A displaced atom does not in itself constitute a dipole, and cannot give rise to a Lorentz field acting on other similarly displaced atoms.

The extension of the theory to the low-temperature forms is rather unsatisfactory. It implies that while the tetragonal form is fully ordered, a new disorder appears at the transition to orthorhombic, where Ti has a choice of two sites. This kind of disorder at low temperatures is very improbable, and there is no experimental evidence in its favour.

8 Devonshire's model theory of barium titanate

8.1. Devonshire (1949) considered the dipole moment of an atom vibrating in the field of its neighbours. In contrast to most of the other theories, the dipole moment is not fixed-magnitude. It depends on the displacement r from the equilibrium position. The potential energy of the atom is of the form $ar^2 + br^4$. This increases more rapidly with displacement than it would for a harmonic oscillator; or, to put it the other way round, the displacement changes less for a given change in potential energy. It is not, however, the extreme case of a square well, or a fixed-magnitude dipole (cf. § 6.1), where the displacement does not change *at all* with the potential energy.

The values of a and b are different for the different ions. They can be evaluated from the force constants of the structure, which in turn are derived by the application of the Born postulate, namely that each pair of ions with charges e_1 , e_2 , separation r , has a potential energy of the form

$$\frac{e_1 e_2}{r} - \frac{\mu}{r^6} + \frac{\nu}{r^9} \quad (10.23)$$

The dipole moment is proportional to the displacement r and to a quantity z which represents the effective charge.

The partition function and hence the Helmholtz free energy is constructed in terms of the a 's, b 's, z 's, and the field factor β , which

is given its Lorentz value of $4\pi/3$. By comparison with equation (8.12), the constants χ^x , ξ^x and λ are found in terms of a , b , z and β .

8.2. Devonshire made numerical estimates of various quantities derived from these, and compared them with those derived by other methods. Reasonable agreement was obtained.

The treatment shows that the temperature coefficient of polarizability is the sum of two terms: a small positive term resulting from lattice expansion, and a larger negative term involving the first power of the b 's, giving the direct effect of the thermal vibrations. Since ferroelectricity requires a net negative temperature coefficient of the polarizability, it is now seen to require an anharmonic term in the potential energy of the atomic vibrations.

The theory has been criticized for its use of $4\pi/3$ as the field factor for all atoms.

9 Slater's theory of barium titanate

9.1. Slater's theory (1950) has a good deal in common with Devonshire's model theory, but introduces two new features, dealt with below. On the other hand he does not evaluate the constants a and b ; and though he stresses the importance of the fourth-power term in the potential energy (the term in b) in making ferroelectricity possible, he does not try to find an explanation for it in terms of structural forces.

The first new feature of the theory is its emphasis on the physical meaning of the polarizabilities. Each atom is assumed to have an electronic polarization, and the Ti (but none of the others) has also an ionic polarization. The corresponding polarizabilities are α_j and α_i . We saw from equation 9.06 that the condition for an infinite dielectric constant is

$$\frac{\beta\alpha_M}{v} = 1 \quad (10.24)$$

which becomes, when we replace the macroscopic polarizability by the sum of the separate polarizabilities, and β by the Lorentz factor $4\pi/3$,

$$\frac{4\pi}{3} \left(\sum \frac{\alpha_j}{v} + \frac{\alpha_i}{v} \right) = 1 \quad (10.25)$$

The values of α_i/v are known experimentally (see Table 9.1); for Ti and Ba, Slater used the results of Shockley (1948), while for O, since it differed in different compounds, he chose a value to give the electronic polarizability of the crystal as a whole correctly. He found

$$\frac{4\pi}{3} \sum \frac{\alpha_j}{v} = 0.61 \quad (10.26)$$

10. MODEL THEORIES: PARTICULAR APPLICATIONS

which would give, if all the assumptions were correct,

$$\frac{4\pi}{3} \frac{(\alpha_i)_{Ti}}{v} = 0.39 \quad (10.27)$$

9.2. The second new feature of Slater's theory was his recalculation of the field constants β . Consider a simple cubic lattice (Fig. 10.3), of side a , carrying point dipoles at the origin of coordinates A , the

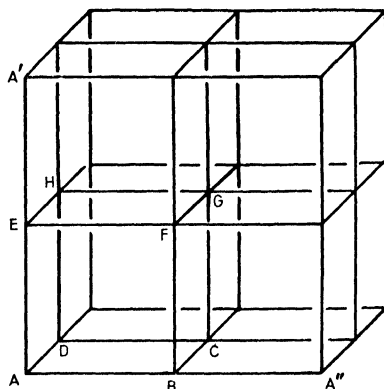


Fig. 10.3. Key diagram for discussion of Lorentz field at various points on a simple cubic lattice.

Cell side $AA'' = a$.

dipole direction being AA' . Then according to the Lorentz treatment the field factor is $4\pi/3$ at other lattice points of the set A , such as A' , A'' , etc., but not at B , C , D , etc. It is however possible to evaluate the field at all these points, and this has been done by Luttinger and Tisza (1946, 1947). Their results are given in Table 10.1. The striking feature is the very large value of the factor at points midway between dipoles in the direction of their dipole moment.

If we change the origin, so that $(0, 0, 0)$ is no longer the position of the dipole but the point where the field is to be examined, the column in Table 10.1 headed 'coordinates' becomes 'components of vector displacement of dipole from point where field is to be examined'. We can then apply the results to BaTiO_3 . Using Fig. 10.3, and subscripts referring to Table 10.1, we have

$$\left. \begin{aligned} F_{Ti} &= E + [\beta_A P_{Ti} + \beta_G P_{Ba} + \beta_E P_{O1} + (\beta_B + \beta_D) P_{O2}] \\ F_{Ba} &= E + [\beta_G P_{Ti} + \beta_A P_{Ba} + \beta_C P_{O1} + (\beta_F + \beta_H) P_{O2}] \\ F_{O1} &= E + [\beta_E P_{Ti} + \beta_C P_{Ba} + \beta_A P_{O1} + (\beta_F + \beta_H) P_{O2}] \\ F_{O2} &= E + [\beta_B P_{Ti} + \beta_H P_{Ba} + \beta_F P_{O1} + (\beta_A + \beta_C) P_{O2}] \end{aligned} \right\} \quad (10.28)$$

FERROELECTRICITY IN CRYSTALS

TABLE 10.1

Values of field factor at points on a simple cubic lattice with dipole placed at origin

Position of point on Fig. 10.3	Coordinates	Field factor β
<i>A</i>	0, 0, 0	$\frac{4\pi}{3}$
<i>G</i>	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	
<i>B</i>	$\frac{1}{2}, 0, 0$	$\frac{4\pi}{3} - 15.040 = \frac{4\pi}{3}(1 - 3.58)$
<i>D</i>	$0, \frac{1}{2}, 0$	
<i>C</i>	$\frac{1}{2}, \frac{1}{2}, 0$	$\frac{4\pi}{3} + 4.334 = \frac{4\pi}{3}(1 + 1.31)$
<i>E</i>	$0, 0, \frac{1}{2}$	$\frac{4\pi}{3} + 30.080 = \frac{4\pi}{3}(1 + 7.16)$
<i>F</i>	$\frac{1}{2}, 0, \frac{1}{2}$	$\frac{4\pi}{3} - 8.668 = \frac{4\pi}{3}(1 - 2.62)$
<i>H</i>	$0, \frac{1}{2}, \frac{1}{2}$	

Since we know the polarization of each atom in terms of its polarizability and the field acting on it, given by a set of equations such as

$$P_{Ti} = \left(\frac{\alpha_j}{v} + \frac{\alpha_i}{v} \right) F_{Ti} \quad (10.29)$$

the equations can be solved to give the separate polarization of each kind of atom and the dielectric constant of the crystal as a whole.

9.3. Slater considers three cases.

(i) If the electronic polarizabilities are all zero, the dielectric constant is given by

$$\epsilon = 1 + \frac{\frac{4\pi\alpha_i}{v}}{1 - \frac{4\pi}{3} \cdot \frac{\alpha_i}{v}} \quad (10.30)$$

Then at the Curie point we must have

$$\frac{4\pi}{3} \cdot \frac{\alpha_i}{v} = 1 \quad (10.31)$$

10. MODEL THEORIES: PARTICULAR APPLICATIONS

ii) If the ionic polarizabilities are all zero, we obtain an expression for the optical or high-frequency dielectric constant:

$$\epsilon = 1 + \frac{4\pi \sum \beta_j \alpha_j}{1 - \sum \beta_j \alpha_j} \quad (10.32)$$

Using the actual values of β_j , the result is not very different from that when all the β 's are taken as $4\pi/3$.

iii) When an ionic polarizability is assigned to Ti, and the calculation is carried out, it gives the result

$$\frac{4\pi}{3} \cdot \frac{\alpha_i}{v} = 0.06 \quad (10.33)$$

That is, the ionic polarizability of Ti is only 1/16 of what it would need be if there were no electronic polarizability (cf. (10.31)), or 1/6 of what it would need to be if the field factor $4\pi/3$ applied throughout (10.27)). In other words, the effect of a fairly small ionic polarizability is enormously enhanced by the existence of a large electronic polarizability. The size of the enhancement is due to the particular values of the β factors, which in turn are due to the arrangement of atoms in rows of alternating Ti and O parallel to the dipole direction. To quote Slater: 'The Ti ions, by their polarization, polarize the nearest O ions, and these in turn act back on the Ti ions; and the result is to build up the polarization of both types of ions, resulting in linear chains of dipoles all pointing in the same direction, the positive end of one to the negative end of the other, and producing spontaneous polarization below the Curie point.'

This theory of Slater's has proved very stimulating, but there are a good many difficulties attached to it.

Two important criticisms are due to Cohen (1951). He pointed out that, since the internal field acts on the displaced atoms, the correct values of β are those referring to the displaced positions, and not (as Slater assumed) those for special positions with all coordinates 0 or $\frac{1}{2}$. Further, he found nothing in the theory to show why *parallel* displacements are favoured in adjacent Ti-O chains; it would rather suggest that they should be *antiparallel*. A partial answer to this has been given by Takagi (1953).

One can also criticize the treatment of the polarizabilities. As we have seen (Chap. 9, § 4.7) it is not legitimate to equate the ionic polarizability with the difference between the experimental values at optical and low frequencies. Further, there is no real justification for assigning the whole ionic polarization to Ti; it was done because the normal volume available to Ti suggested a looseness of binding.

Takagi's analysis has shown, however, that ionic polarizations can only have meaning with reference to *pairs* of mutually-displaced atoms.

This difficulty has been avoided by Roberts (1951), who uses the total polarizability. He solves a set of equations like (10.28) to find empirical values for the field factors, using polarizabilities determined from simpler compounds (Chap. 9, § 4.6). The results are different for different compounds, and markedly different from the special-position values in Table 10.1. The work has been carried further by Gränicher and Jakits (1954), who find that, in the series of solid solutions $(\text{Ba,Sr})\text{TiO}_3$, the field factors all vary continuously with Ti-O distance, but the curves have a rapid change of slope just inside the boundary of the tetragonal phase.

If the theory has to be re-stated in terms of dipoles which will give this particular variation of the internal field with Ti-O distance, it has lost the simplicity of the original model. Possible reasons for the departure from theoretical values of the internal field are discussed by Jaynes (1953).

9.5. One apparent advantage of Slater's theory is the very natural way in which it predicts that the direction of spontaneous polarization will be along the z axis, the direction of the Ti-O chains of dipoles. This however becomes a disadvantage when we try to apply the theory to other structures, or to the two low-temperature forms of BaTiO_3 , where there are no such chains along the polar axis.

9.6. An application of the theory to a different structure, that of ilmenite, was made by Schweinler (1952). Though the particular mechanism of interaction between the ions was quite different, he found that the order of magnitude of the polarizabilities to fit his treatment was the same as for BaTiO_3 . It seems possible that this type of theory is not as sensitive to the particular magnitudes of the field factors β as might at first have been supposed. There is in fact no experimental evidence for the existence of ferroelectricity in the ilmenite structure, since LiNbO_3 and LiTaO_3 , originally thought to have this structure, are now known to be different (see Chap. 5, § 5.3). Schweinler's treatment is not concerned with the detailed atomic displacements, and might perhaps be equally applicable to the actual LiNbO_3 structure; but if so it suggests that this line of approach cannot be of much use in predicting the occurrence of ferroelectricity.

A re-examination of Slater's theory for BaTiO_3 , using Slater's postulates but a quantum-theory treatment, was made by Barrett (1952). He found no significant differences from the original theory.

10. Jaynes's mechanical-deformation treatment of barium titanate

10.1. An interesting approach of quite a different kind has been suggested by Jaynes (1950). If the atoms can be treated as rigid spheres, the type of deformation actually observed in BaTiO_3 can be explained as an attempt at better packing conditions. Since the Ba-O contacts are too tight, the O atoms are squeezed out, so that the Ba-O sheet is no longer plane but puckered. This gives an expansion perpendicular to the layer and a lateral contraction in it. The two lower-symmetry forms can be explained by further stages of the same process.

In this case, the polarization is wholly a dipole effect due to the displacement of O with respect to Ba. This displacement can be calculated geometrically in terms of the lattice strain. If we assume that the O atom has a charge $2e$, and use the experimental value of the lattice parameter a , the strain is given in terms of the oxygen pole polarization P_a ,

$$-\frac{\Delta a}{a} = 3.8 \times 10^{-12} P_a^2 \quad (10.34)$$

The experimental value of the ratio of the strain to the square of the polarization is 1.2×10^{-12} , suggesting that P_a is just over half the total polarization. It is interesting to see that this crude argument predicts the order of magnitude of the lattice strain correctly.

10.2. Though the approach is interesting and unusual, it cannot be taken very seriously as it stands. A displacement of the order of magnitude actually observed would increase the Ba-O distance by about 0.1%—an amount which is less by a factor of at least 10 than the limits of tolerance of the Goldschmidt radii.

11. Jaynes's electronic theory of barium titanate

11.1. Jaynes (1953) has put forward another theory which he has developed more seriously. He considers that the oxygen octahedra in BaTiO_3 are the significant feature—that the crystal's 'electronic structure is such that the oxygen octahedron must be thought of as a single unit rather than as a structure of several independent parts'. He assumes that its internal electronic quantum state is a linear combination of two states of opposite parity which lie close together in energy, so that the combination has a non-zero dipole moment. Its polarization depends on the internal field at the centre, which in turn depends on the polarization and the field factor β . There are also contributions to the total polarization from the electronic polarization of other atoms, and possibly from dipole polarization due to displaced atoms, each with its own field factor.

FERROELECTRICITY IN CRYSTALS

For simplicity, he begins by considering the case where there is a single field factor β , and the polarization consists of a part due to the octahedron, P_o , and a part due to everything else, P_a . Then

$$F = E + \beta(P_a + P_o) \quad (10.35)$$

A background polarizability γv is defined by the relation

$$P_a = \gamma F \quad (10.36)$$

The polarization P_o is due to the mixing of states in the octahedron. To find it, Jaynes constructs the appropriate partition function, and thence derives a relation between P_o , E and T in terms of μ , the maximum dipole moment due to the mixing of states; Δ , half the energy difference between the states; β ; and γ . The Curie temperature T_0 is given by

$$\tanh \frac{\Delta}{kT_0} = \frac{2K}{1+K} \quad (10.37)$$

$$\text{where} \quad \frac{1}{K} = \frac{\beta \mu^2 / v}{\Delta(1 - \beta \gamma)} \quad (10.38)$$

The maximum polarization is

$$P_m = \frac{1}{1 - \beta \gamma} \cdot \frac{\mu}{v} \sqrt{1 - K^2} \quad (10.39)$$

At temperatures close above the Curie point,

$$\eta = c_1 + \frac{c_2}{T - T_0} \quad (10.40)$$

where c_1 and c_2 are known functions of T_0 , Δ , β and γ . From the experimental values of T_0 , P_m and c_2 it is possible to evaluate Δ , μ , and the function $\beta(1 - \beta \gamma)$.

11.2. There is not very much evidence with which to test the theory. Jaynes finds that the theoretical entropy change agrees with that observed. The energy difference between the two states of the octahedron, 2Δ , is found to be $4kT_0$; it is insensitive to possible errors in the experimental data. It predicts an infra-red absorption line at about 10×10^{-4} cm.

The values of β and γ (which are not separately determinable) offer some difficulty. Reasonable values of γ are only compatible with low values of β , about 0.5. This difficulty persists even in an improved form of the theory where separate values of β are determined for the different atoms.

11.3. Jaynes suggests that one of the advantages of the electronic theory is that it does not require the existence of atomic displace-

10. MODEL THEORIES: PARTICULAR APPLICATIONS

ments. One might rather say that it does not require the introduction of dipole moments attributed to atomic displacements. It is noticeable, however, that the difficulties with the internal field characteristic of so many of these theories have not been overcome; and, like most of the others, it does nothing to explain the adoption of the particular ow -symmetry form observed.

2 The structural approach

2.1. We have seen from the foregoing that the essential feature of a model is that it should provide a unit in the structure capable of existing in two states, one symmetrical and one polar, with an energy difference between them which is fairly small and is temperature-dependent. (In Devonshire's and Slater's theories of $BaTiO_3$, the polar state is replaced by a continuous range of polar states.) If the symmetrical state is achieved by a random distribution between two polar states (as in Slater's theory of KH_2PO_4) the transition is an order-disorder one; but this is not an essential feature.

When the units are built together to form the crystal, the state of each unit, and of the crystal as a whole, will depend on the interaction between them. If we abandon the idea that the difference in energy is self-caused by the interaction, we have to explain it in terms of short-range forces, affecting the relation of the atom to its near neighbours—in other words, in terms of the atomic environment. It is not easy to treat this quantitatively, but qualitatively we can make a useful beginning.

2.2. It was shown in Chap. 6 that ferroelectricity and antiferroelectricity in oxides is associated with the off-centre position of a high-valency 'cation' in an oxygen polyhedron; further illustrations were available from Chap. 7. We take this as the first postulate of the structural theory, and qualify it by noting that the central atom must have appreciable covalent character—that its bonds to its neighbours must be 'semi-polar' in the sense used by Eucken and Büchner (1934); thus, Ti, Nb, or W may show the effect, but probably not Na or Ba. Whether Pb acts in the same way, or whether it merely serves to polarize the octahedron surrounding another atom, is still an open question.) The unit in these structures is then to be taken as the polyhedron with its enclosed atom. In this respect the present treatment agrees with that of Jaynes (§ 10).

The second postulate is that the particular off-centre formation adopted depends on the bond requirements of the enclosed atom, influenced perhaps by the volume available to it and the degree of polarization of the oxygens by any other cations.

The third postulate is that there is interaction between the polyhedra through the oxygen atoms at the shared corners; that this brings in the bond-angle requirements of the oxygens; and that these will be strongly influenced by their packing with respect to their other neighbours. It is in fact the environment of the other atoms which decides whether a structure with individual polar units will be ferroelectric or antiferroelectric.

These ideas have been developed for the oxide structures and their qualitative application has been discussed in Chap. 6 (see also Megaw, 1952, 1954). We cannot take them much further quantitatively. We can however see whether the same approach can be used for the hydrogen-containing ferroelectrics.

12.3. Here we have to consider two possibilities: the off-centre cation, and the behaviour of the hydrogen bond. Though each needs to be considered separately, we must remember that they are not independent—that they will interact with each other through the short-range forces. As with the oxides, the question whether a ferroelectric or an antiferroelectric state is preferred will depend on the bond systems and environments of the other atoms which link together the polar units.

In KH_2PO_4 , for example, it seems clear that the energy states of the hydrogen in its bond are largely responsible for the transition, as suggested by Pirenne; but the different energy-levels of P in its central and off-centre states must also be taken into account, and will probably make the larger contribution to the dipole moment. Whether the off-centre movement of K has any covalent effect is not certain. It is however the particular environment needed by this atom which determines the orientation of the ordered tetrahedra, and thus causes the ferroelectricity; in $\text{NH}_4\text{H}_2\text{PO}_4$ the different requirements of NH_4 lead to an antiferroelectric ordering.

In Rochelle salt, on the other hand, there is no order-disorder effect in the hydrogen bonds, and the off-centre movement of K is the cause of the transition, as we saw in Chap. 2, § 11. It is somewhat unexpected to find a significant amount of covalent character in a K-O bond, as this explanation implies. It is worth noticing, however, that the K-O and Na-O bonds are the strongest intermolecular forces in Rochelle salt, and that therefore the amount of covalent character need not be absolutely large to be important. The H bonds are of secondary importance only; their rearrangement comes about through the action of short-range forces when the K atom triggers the transition.

12.4. Though the structural approach is, at the present stage of knowledge, essentially qualitative, one might attempt to see how it

could be given a rather crude quantitative formulation in electrostatic terms. A permanent dipole moment must be attributed to the oxygen polyhedron with its off-centre cation, and also to the OH group. The former could be expressed as the product of an effective charge on the cation and its displacement from the geometrical centre of the octahedron, but this would only serve as a definition of the effective charge. In neither case is the dipole an induced one; it may produce electronic polarization in other ions in the structure, but it will not itself be greatly influenced by any feed-back from them—in other words, we expect a rather small field factor. It will however be strongly influenced by interaction with its neighbours through sharing of oxygen atoms in common. Thus the long-range forces, though they may not be negligible in their contribution to the total energy, will be of relatively small importance in deciding between the stabilities of different possible structures. (The situation is closely analogous to that which arises in considering the stability of polymorphic forms of ordinary ‘ionic’ structures, where attempts to predict the occurrence of NaCl or CsCl structures, for example, from their electrostatic energy have not been very successful.)

12.5. These ideas are only tentative, but they suggest how a new theory, based on covalent bond systems, could take over many of the concepts of the existing theories and give them meaning in terms of crystal structure. They have the advantage of explaining how antiferroelectric as well as ferroelectric states can arise in structures of the same family. They have also served to explain qualitatively the existence of ferroelectricity or antiferroelectricity in the miscellaneous substances of Chap. 7, so far as their structures are yet known. It remains to be seen whether they will do so for other materials as new knowledge is obtained.

Until theoretical knowledge of covalent bond systems in semi-polar compounds is further advanced, we expect to obtain our information from studies of the bond-formations actually observed in a wide range of such compounds at different temperatures. In tackling the problem, whether quantitatively or qualitatively, we are likely to gain more insight into the ways in which complicated structures are put together. An inquiry that began with the electrical properties of a few rather peculiar and abnormal materials has spread out and deepened until now we see it as needing help from, and therefore contributing to, our whole knowledge of the architecture of solids.

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FERROELECTRICITY IN CRYSTALS

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GLOSSARY OF CRYSTALLOGRAPHIC TERMS

(Words printed in italics indicate cross-references)

ANGSTRÖM UNIT. By definition, this is 10^{-10} metre. Older determinations of crystal spacing (up to about 1942) were in terms of Siegbahn's table of X-ray wave-lengths, whose absolute values were based on Millikan's determination of the electronic charge. When the error in this was realized, the unit in which spacings had hitherto been expressed was re-named '*kilo-X unit*' or kX. In 1947 a new table of X-ray wave-lengths was adopted, with the conversion factor $1 \text{ kX} = 1.00202 \text{ \AA}$. The difference is only important when spacings have been measured with an accuracy approaching 0.2%, or better. When early accurate results are quoted by later authors, it is not always clear whether they have known to make the appropriate correction to the units, and confusion may arise. (See for example footnote on p. 35.)

ATOM. Throughout this book, the word is taken to include charged atoms or ions.

ATOMIC PARAMETERS. Parameters fixing the position of atoms within the *unit cell*, relative to a chosen origin. They are now generally stated as decimal fractions of the cell edges; formerly they were often stated in degrees, i.e. three-hundred-and-sixtieths of the cell edges.

AXES OF REFERENCE (also called axes of coordinates, or crystallographic axes). Any set of three non-parallel lines, not all coplanar, which are translation directions in the *lattice* may be chosen as axes of reference. The usual conventions are as follows: (i) *Symmetry directions* are chosen when they exist. (ii) Directions not fixed by symmetry are chosen so as to define the *unit cell* of smallest volume and, subject to this, the translation directions are those along which the shortest repeats occur and between which the angles are $\leq 120^\circ$ and $\geq 90^\circ$. (iii) If there is a single *triad*, *tetrad* or *hexad* axis it is called *z*, if only one symmetry direction of not more than 2-fold symmetry it is called *y*. (iv) The naming of the other axes of reference is decided according to the *axial ratio*, the conventions used by chemists and mineralogists being different.

There are however two principles which ought to over-ride these: that if axes have already been allocated in earlier work to

GLOSSARY

the substance being investigated or to a closely-related structure they should not be changed unless the new axes are obviously very much more convenient; and that when a structure of low symmetry has a conspicuous relationship to a higher symmetry the axes that display this naturally should be chosen. Changes of axes should not be made merely to satisfy conventions of type (iv); where this has been done in the literature it is liable to cause confusion. The other conventions are based more strongly on convenience, and cause more difficulties if they are disregarded; but even so they are not to be regarded as sacrosanct. It is sometimes useful (as in the case of an *orthorhombic* shear of a cube or square prism) to define two alternative sets of axes for use in different circumstances, and to state explicitly which is being used on any given occasion. (The relation between *hexagonal and rhombohedral axes of reference* is of this kind.)

Attempts have been made in the text to apply the principle of uniformity between related structures, even when it means changing the axes chosen by authors who have done original work on isolated members of a larger family. It is not easy to be completely consistent, but the attempt is necessary in order to avoid even greater confusion in the future.

AXIAL RATIO. The ratio of the lengths of any pair of edges of the *unit cell*. If two of the three non-parallel sides are equal by symmetry, it is usual to quote c/a , where c is the unique edge; if the three are unequal, the ratios are conventionally written as $a/b : 1 : c/b$.

AXIS OF SYMMETRY. An n -fold *rotation axis* repeats every point in the structure to give an equivalent point at the same distance from the axis in a direction making an angle $2\pi/n$ with that of the first point. An n -fold *screw axis* gives a displacement of $(m/n) R$ for each rotation of $2\pi/n$, where R is the repeat distance along the axis and m an integer less than n .

The only values of n compatible with infinite three-dimensional periodic repetition are 1, 2, 3, 4, and 6 (of which 1 is an identity operation and should perhaps not be regarded as an axis).

See also *inversion axis*.

BODY-CENTRED LATTICE. See *lattice*.

CELL DIMENSIONS. Alternatively known as *lattice parameters*.

CENTRE OF SYMMETRY. A symmetry element at a fixed point in a finite or infinite system, such that, for every point whose distance from it has components u, v, w , there is another equivalent point whose distance has components $\bar{u}, \bar{v}, \bar{w}$. It is usual if possible to

GLOSSARY

choose the origin of coordinates at a centre of symmetry; then for every point x, y, z , there is an equivalent point $\bar{x}, \bar{y}, \bar{z}$.

CLASS, CRYSTAL (or symmetry class). The class of three-dimensional structures possessing the same *point group* of symmetry elements. The symbol denoting the class states, in terms of an agreed convention, the essential symmetry elements and their direction relative to the *axes of reference* (compare *space group*).

COORDINATION NUMBER. The number of atoms which are immediate neighbours of a given atom; in an ionic structure, the number of anions surrounding a cation (see p. 84).

CRYSTAL SYSTEM. See *system*.

DIAZ AXIS. A two-fold *axis of symmetry* (see also p. 7).

DOMAIN (in a ferroelectric or antiferroelectric material). A part of a twinned crystal which is itself a true single crystal. A 'single-domain' crystal is a true single crystal throughout.

FACE-CENTRED LATTICE. See *lattice*.

FORMULA-UNIT. The set of atoms named in the chemical formula. In a *homodesmic* structure it is incorrect to speak of 'molecule' or 'molecular weight', since the molecule is coextensive with the crystal. It is still often convenient to refer to a representative set of atoms as a whole instead of naming each kind individually, and the term 'formula-unit' makes this possible.

GENERAL POSITION. A point in a structure not lying on a *centre of symmetry*, *rotation axis*, *mirror plane*, or *inversion centre*. (Compare *special position*.)

GLIDE PLANE. See *plane of symmetry*.

HEXAD AXIS. A six-fold *axis of symmetry*.

HEXAGONAL AND RHOMBOHEDRAL AXES OF REFERENCE. Any crystal with a triad or hexad *axis of symmetry* may be described on either hexagonal or rhombohedral axes of reference; but for purposes of calculation, or for drawing diagrams of the structure, as well as for describing the physical properties, the former are nearly always much simpler. If the crystal actually has a *rhombic lattice*, the relations between the most convenient unit cells are:

$$\mathbf{a}_H = \mathbf{a}_R - \mathbf{b}_R, \quad \mathbf{b}_H = \mathbf{b}_R - \mathbf{c}_R, \quad \mathbf{c}_H = \mathbf{a}_R + \mathbf{b}_R + \mathbf{c}_R.$$

The rhombohedral unit cell then contains one lattice point, and the hexagonal unit cell three, at $(0, 0, 0)$ and $\pm(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$.

HEXAGONAL LATTICE. A *lattice* which can be described using a primitive *unit cell* with two equal sides inclined at 120° to each

GLOSSARY

other and at 90° to the third side. This name is given to the lattice whatever *axes of reference* are in fact used. (Compare *rhomboidal lattice*.)

HOMODESMIC STRUCTURE. A structure joined throughout by interatomic forces of the same order of magnitude (as contrasted with a molecular structure).

HOMOPOLAR BONDS. Strong interatomic bonds which do not depend on electrostatic central forces between charges of opposite sign. (See footnote on p. 9.)

IDEAL STRUCTURE. A simple high-symmetry structure to which some actual structure under discussion approximates. It may or may not itself be the actual structure of some other material or of the same material at a different temperature.

INDICATRIX. See footnote on p. 70.

INVERSION AXIS. An inversion *axis of symmetry* combines rotation through an angle $2\pi/n$ with inversion about a point on the axis. With one exception, inversion axes can be more simply (though sometimes less elegantly) described as a combination of other symmetry elements. The exception is the tetrad inversion axis, $\bar{4}$. If this axis is parallel to z and the inversion centre at 0, 0, 0, it gives a set of equivalent points at x, y, z ; $\bar{x}, \bar{y}, z$; $y, \bar{x}, \bar{z}$; $\bar{y}, x, \bar{z}$.

KX UNIT. $1 \text{ kX} = 1.00202 \text{ \AA}$; see *Ångström unit*.

LATTICE. A lattice is a set of points which are identical in themselves and in their surroundings (including in this both the content and the orientation of their environment). All points of the lattice are *translation-equivalent*: they may be derived from each other by the repeated operation of three vectors, the primitive lattice translations, chosen so that they mark out a parallelepiped with lattice points at its corners only.

A lattice is characterized by the set of *symmetry directions* it possesses, and their relation to the primitive lattice translations. There are fourteen independent combinations, known as the Bravais lattices.

For naming the lattice type it is more convenient to ignore the symmetry (which is expressed elsewhere in the *space group* symbol) and consider only the direction of the *axes of reference* relative to the primitive translations. This is most conveniently done in terms of the set of lattice points contained in the *unit cell*. The same lattice may then have several different names according to the choice of unit cell. (Exceptions are *hexagonal lattice*, *rhomboidal lattice*, see below.)

GLOSSARY

The following are the only names which can occur with conventional choice of unit cells; other less conventional choices may be made, but are harder to work with and have not been given names. The conditions stated below must be satisfied whatever point in the structure is taken as origin of the unit cell.

A *primitive lattice* (symbol *P*) has lattice points at the corners of the unit cell only; there is one lattice point per cell.

A *body-centred lattice* (symbol *I*, for 'innenzentrierte') has lattice points at the centre of the unit cell, the points with coordinates $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, which are translation-equivalent to those at the corner; there are thus two lattice points per cell.

A *face-centred lattice* has points at the centre of one pair of faces (single-face-centred, symbol *A*, *B*, or *C*) or all three pairs of faces (all-face-centred, symbol *F*) which are translation-equivalent to those at the corners; there are two or four lattice points per cell respectively.

A rhombohedrally-centred lattice (symbol *R*) has a hexagonal unit cell with points at $\pm(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$ which are translation-equivalent to those at the corners; there are thus three lattice points per cell. It is a way of naming a *rhombohedral lattice* which specifies particular axes of reference.

The name *hexagonal lattice* is restricted to the Bravais lattice which can be described using a primitive hexagonal cell, whatever axis of reference are currently being used; and the name *rhombohedral lattice* to the Bravais lattice which can be described using a rhombohedrally-centred hexagonal cell, whatever axes of reference are currently being used.

The term 'lattice' is loosely used by some writers to mean an assemblage of atoms, either all the atoms of the structure or a selected set of them (sometimes called a '*sub-lattice*'). This is unfortunate, as it can lead to a good deal of confusion. Any account of crystal structures ought to keep strictly within the correct geometrical definition. Alternative words for describing sets of atoms are structure, framework, network, assemblage, array.

UNIT CELL PARAMETERS. The lengths of edges of the *unit cell* and the interaxial angles.

SYMMETRY PLANE. See *plane of symmetry*.

MONOCLINIC. See *system*.

MULTIPLE CELL. A *unit cell* which can be divided into a number of *sub-cells*, identical with each other in shape and volume, and nearly but not quite identical in content. Two extreme types may be distinguished. In the first the numbers and kinds of atoms in

GLOSSARY

each sub-cell are identical but their coordinates differ slightly; in the second the coordinates are identical but the atoms in at least some of the corresponding sites are different. The second type occurs chiefly in solid solutions (e.g. alloys with '*superlattices*') and too little is known about possible examples among ferroelectrics and antiferroelectrics to include any discussion of it in the text.

(The term 'multiple cell' has also been used, though not in this book, as synonymous with 'non-primitive unit cell'. The two usages are quite different.)

'OFF-CENTRE' CATION. A cation enclosed in a nearly regular polyhedron of oxygen atoms, situated at a significant distance from its geometrical centre.

ORTHORHOMBIC. See *system*.

PACKING REQUIREMENTS. The geometrical conditions which follow from Goldschmidt's rules for the arrangement of atoms in crystal structures (see p. 83).

PLANE OF SYMMETRY. A *mirror plane* operates so that any point in the structure is repeated on the normal to the plane at an equal distance on the opposite side of the plane. A *glide plane* (applicable to infinite periodically-repeating structures only) operates so that reflection across the plane, followed by a displacement of half (more rarely, one-quarter) the repeat distance in some direction parallel to the plane, brings the whole system to self-coincidence.

POINT GROUP. A combination of symmetry elements which, when applied, leaves one point unaltered (it thus cannot include glide planes or screw axes). There are 32 such combinations, and they characterize the 32 crystal *classes*. (Compare *space group*.)

POLAR CRYSTALS. Crystals possessing *polar symmetry*. There is an unfortunate ambiguity between this use of the phrase, which refers to the geometrical and macroscopic physical properties, and the use (not adopted in this book) which refers to the atomic structure, meaning crystals possessing polar bonds, i.e. crystals whose atoms carry opposite electrical charges. The latter are more conveniently called 'ionic crystals'.

POLAR SYMMETRY. Symmetry which allows a non-zero resultant vector in the structure (see p. 7).

POLARITY OF BONDS. Relative magnitude of contributions of electrostatic and homopolar forces to bond energy; for example, in '*semi-polar bonds*' both contributions are significant.

GLOSSARY

POLARITY OF CRYSTAL. Sense of the vector describing the unidirectional property under discussion, e.g. spontaneous polarization or relative displacement of atoms.

POLYMORPHISM. Occurrence of a solid of given chemical composition with different crystal structures, i.e. in different phases. These may be found in different temperature ranges, or may exist together indefinitely at the same temperature (not necessarily in equilibrium).

PRIMITIVE LATTICE. See *lattice*.

PSEUDOSYMMETRIC STRUCTURE. A structure derived geometrically from a higher-symmetry *ideal structure* by small displacements of the atoms from the *special positions* occupied in that structure; it has thus lost some of the symmetry elements of the ideal structure, without acquiring any others. (The atoms may still lie in special positions of lower point symmetry: for example, in ideal perovskite the cations lie at the intersection of three tetrad axes, while in tetragonal BaTiO_3 they are still on the one tetrad which is retained.)

PYROELECTRIC. See p. 7.

RHOMBOHEDRAL LATTICE. A *lattice* in which the three primitive translations are equal and equally inclined to one another at an angle other than 90° , thus defining a primitive *unit cell* which is a rhombohedron. It is the only lattice possessing a *symmetry direction* not coinciding with a primitive lattice translation which is nevertheless named for the primitive unit cell, and the name is generally retained whatever *axes of reference* are used to describe it. The rhombohedral axes of reference are defined by the primitive unit cell. The lattice may alternatively (and often more conveniently) be described on *hexagonal axes of reference*, in which case there is a rhombohedrally-centred unit cell, with lattice points at $(0, 0, 0)$, $\pm(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$. In either case the lattice symbol is *R*.

Note (i) that a *hexagonal lattice* and a rhombohedral lattice are essentially different, whatever axes are used to describe them; (ii) that a crystal of the trigonal system (i.e. with a single triad axis) may have either a hexagonal lattice or a rhombohedral lattice, while one belonging to the hexagonal system (i.e. with a hexad axis) can only have a hexagonal lattice; (iii) that the cubic lattice may be treated as a special case of the rhombohedral but not of the hexagonal lattice.

The word 'rhombohedral' is restricted in this book to crystals with rhombohedral lattices.

ROTATION AXIS. See *axis of symmetry*.

GLOSSARY

SCREW AXIS. See *axis of symmetry*.

SEMI-POLAR BONDS. See *polarity of bonds*.

SPACE GROUP. A combination of symmetry elements which can occur in a three-dimensional periodically-repeating structure. The symbol denoting the space group states, in terms of an agreed convention, the *lattice* type, the essential symmetry elements present, and their direction relative to the chosen *axes of reference*. Since the symbol for the same space group may look very different according to the choice of axes, and the rules for conversion from one set of axes to another require practice before they can be used with ease, the identity of the space group is also made clear by quoting its serial number in a list in the International Tables for X-ray Crystallography (1952); this number is independent of the choice of axes.

To find the *point group* from the space group, the lattice symbol *P*, *A*, *B*, *C*, *F*, *I*, or *R* must be dropped, all glide planes *a*, *b*, *c*, *d*, or *n* must be replaced by mirror planes *m*, and the subscript dropped from all screw axes.

SPECIAL POSITIONS. Positions in the *unit cell* lying on *centres of symmetry*, *rotation axes*, *mirror planes* or *inversion centres*. An atom on any one of these elements will not be repeated by that element, and therefore fewer such atoms are needed for a symmetry-equivalent set than if they were in *general positions*.

SUB-CELL. See *multiple cell*.

SUB-LATTICE. See *lattice*.

SUPERLATTICE. This term results from an unfortunate mistranslation of the German 'Ueberstruktur' or 'overstructure', and has added to the misunderstanding of the term '*lattice*'. It was originally applied to alloy systems, but has been used in the literature with such a range of meanings that it cannot now be redefined, and it is better to avoid it. In its commonest usage 'superlattice' is synonymous with '*multiple-cell structure*' and 'superlattice reflections' an abbreviation for 'reflections peculiar to a multiple-cell structure'.

SYMMETRY DIRECTION. A direction occupied by an *axis of symmetry* (other than a 1-fold axis) or by the normal to a *plane of symmetry* or by both simultaneously.

SYMMETRY ELEMENTS. See *axis of symmetry*, *centre of symmetry*, *inversion axis*, *plane of symmetry*.

SYSTEM, CRYSTAL. A group of crystal *classes* conventionally taken together because their *point-group* symmetry has certain elements

GLOSSARY

in common. Their description is most convenient in terms of *symmetry directions*. The *triclinic* system has none (though it may have a *centre*); the *monoclinic* system has one only, not higher than 2-fold; the *orthorhombic* system has three mutually at right-angles, none higher than 2-fold. The trigonal, hexagonal and tetragonal systems have respectively a single *triad*, *hexad* or *tetrad* axis (*rotation* or *inversion*). (In American usage, the trigonal system is not separated from the hexagonal.) The cubic system has four triad axes, equally inclined to each other, along the body diagonals of the cube.

The symmetry directions are generally the most convenient choice as *axes of reference* with which to describe the geometrical as well as the physical properties of the crystal. An exception occurs for those crystals of the trigonal system (in American usage, included in the hexagonal system) which possess a *rhombohedral lattice*, where the choice between *hexagonal* and *rhombohedral axes of reference* has to be made in different ways for different purposes.

When symmetry directions exist but are not chosen as axes of reference, the geometrical description of the crystal will be that appropriate to a system with lower symmetry than the true one (e.g. a crystal of the orthorhombic system may be described in terms of the monoclinic system).

TETRAD AXIS. A four-fold *axis of symmetry*.

TETRAGONAL. See *system*.

TRANSLATION-EQUIVALENT POINTS. See *lattice*.

TRIAD AXIS. A three-fold *axis of symmetry*.

TRICLINIC. See *system*.

UNIT CELL. A parallelopiped such that each edge lies in a row of *lattice* points and is equal to the shortest repeat distance in that row. The unit cell may be located anywhere in the structure, but is most conveniently chosen so that its corner (which usually serves as the origin of coordinates) is at a *centre of symmetry* (if one exists). The directions of the edges form the *axes of reference*.

INDEX

(Authors' names are not given except in connection with theoretical treatments; they will be found in lists of references at the ends of chapters.)

- Abnormal volume conditions, see *volume*
- Absorption band, 70
- Alkali halides, 168, 173
- Ammonium dihydrogen phosphate, 17, 45-7, 48, 53-4, 137, 177, 186, 200
deuterium-replaced, 17, 46-7
- Ammonium hydrogen periodate, 18, 137-40, 141, 142
deuterium-replaced, 139
- Ammonium-substituted Rochelle salt, 13, 17
- Ångström unit, 203
- Angular changes, 24, 48, 51, 64, 65, 67, 91, 98
- Anharmonicity, see *vibrations*
- Anomaly in dielectric constant, see *dielectric constant*
- Anomaly in specific heat, see *specific heat*
- Antiferroelectric, definition, 15
examples, 17-18
- Antiferroelectricity, nature of, 15-16, 133, 136
evidence for, 87, 92, 99-100, 108, 111-12, 119, 120, 140, 142
theories of, 131, 162-3, 177, 199-200
- Antiparallel displacements, see *displacements*
- Arsenates, ferroelectric, 13, 44, 49, 53
- Atomic parameters, 203
- 'Average atom', 130
- Axes of reference, definition, 203-4
choice of, 24, 41, 46, 62, 86, 96, 133, 203-4
change of, 35, 62-3, 89-90, 96, 204
hexagonal and rhombohedral, 103, 205, 207, 209
- Axial ratio, definition, 204
temperature changes in, 65-6, 70, 94, 96, 98, 109, 120
dependence on firing temperature, 66
in relation to physical properties, 98-9
(see also *lattice parameters*)
- Axis of symmetry, definition, 204
- Axis, diad, 6-7, 26, 41, 205
hexad, 205
inversion, 41, 206
tetrad, 41, 67, 69, 145, 211
triad, 69, 103, 211
- Barium titanate, structure, 17, 58-65, 132
properties, 6, 65-80
theoretical treatment, 151-60, 166, 188-99
comparison with other materials, 13, 49, 86, 90, 94, 98, 100, 101, 105, 106, 107, 108, 109, 111, 112, 113, 115, 119, 124, 126, 127, 128, 146, 168, 169
- Barium titanate, hexagonal, 65
- Barium titanium oxide, 58
- Barium zirconate, 88, 92, 112, 117, 120
- Barkhausen jumps, 4, 32, 43, 50
- Biassing field, see *field* and *Curie point*
- Birefringence, see *double refraction*
- Bond, covalent, 9, 33, 127, 128, 129, 130, 133, 137, 147, 176, 200
directed, 126
electrostatic, 9
homopolar, 9, 125, 183, 206
hydrogen, see *hydrogen bond*
ionic, 131
metallic, 131, 132
semi-polar, 9, 199, 208
energy of, 127
temperature dependence of, 129, 146
dipoles associated with, 8, 9, 176, 180
- Bond angles at oxygen atom, 62, 124-5, 129, 132, 133, 200
- Bond lengths, 39, 54-5, 61, 107, 126-7, 183, 188
- Bond strength, 9, 185, 200
- Bond system, homopolar or covalent, 127, 129, 131, 199-201
of particular atoms, 55, 130, 131, 146
- 'Bootstrap theory', 166
- Born theory of structure, 191

INDEX

- oron compounds, 125
- utterfly loops', 78, 100, 112, 117
- admium niobate, 13, 127, 128, 142-7, 148, 159
- admium tantalate, 148
- aesium chloride, 201
- aesium dihydrogen phosphate, 13, 45
- aesium iodate, 140
- alcium titanate, 87, 89-92, 96, 124, 126, 127
- atastrophe, Lorentz, 169
- ation size, effect on structure, 33, 85-7, 90, 93, 124-6, 127-8, 130, 131
- ation, off-centre, 124, 126-30, 131, 133, 189, 199-201, 208
- ell dimensions, see *lattice parameters*
- entre of symmetry, 204
- lack of, 1, 7, 25, 43, 61, 115
- eramic material, difference from single crystal, 73, 146
- 'arge distribution in atom, 9 (see also *electron cloud*)
- 'arge on atom, effective, 131, 174, 187-8, 189, 197, 201
- 'arge, surface, 3, 14, 29, 44, 116
- 'hemical effect at Curie point, 27
- 'hemical nature of Rochellesalt, 182-3
- 'lamped dielectric constant, see *dielectric constant*
- 'lamping, effect on crystal, 12, 67, 158, 159, 160, 161, 177
- internal, 54
- 'lass, crystal, 7, 205, 208 (see also *polar class*)
- of Rochelle salt, 1, 7, 24
- 'lausius-Mosotti relation, 170, 173
- 'lose packing, 59, 87, 103, 141
- 'oercive field, see *field*
- 'olloidal potassium dihydrogen phosphate, 43
- 'one ferroelectrics, see *ferroelectrics*
- 'ooperative transition, see *transition*
- 'oordination number, 84-5, 93, 105, 124, 126, 140, 205
- 'ovalent bond, see *bond*
- 'ovalent forces, see *forces*
- 'ristobalite, 11, 125
- 'rumped structure, 124-5, 132
- 'rystallographic terms, ix, 1, 203-11
- 'urie constant, 77, 111, 113, 159, 187, 191
- Curie point, definition and occurrence, 4, 14
- particular cases, 27, 44, 58, 94, 95, 103
- theoretical treatment, 157, 169, 187, 198
- effect of biasing field, 5, 13, 14, 16, 78, 111-12, 113, 116, 146
- effect of composition, 27, 78, 95, 119, 120, 148
- effect of pressure, 13, 28, 77-8
- effect of deuterium substitution, 27, 34, 44, 54, 140, 182, 185, 187-8
- unattainable, 14, 137
- of water, 169
- Curie point, lower, 5, 52, 182-3
- Curie-Weiss law, statement and occurrence, 5, 14
- experimental results, 31, 53, 77, 89, 91-2, 111, 113, 136, 137, 146, 147
- theoretical treatment, 154, 160, 161, 167-8, 171, 172, 177, 185, 186, 187, 190-1
- Deuterium substitution, see *Curie point*
- Devonshire's model theory of BaTiO_3 , 191-2
- Devonshire's phenomenological theory of BaTiO_3 , 151-60
- Devonshire's theory of antiferroelectricity, 162-3
- Diad axis, see *axis*
- Dielectric constant, definition and discussion, 5-6
- theoretical treatment, 152, 154, 160, 167, 170-2, 177, 181, 182, 189-91, 192, 194-5
- of particular materials, 30-1, 53-4, 75-7, 89, 91-2, 95, 101-2, 108, 109, 111, 113, 116, 119, 120, 136, 137, 140, 142, 146, 147
- near transition point, 5, 14, 55, 167-8
- clamped, 6, 186
- optical, 173, 195
- Dielectric constant anomaly as criterion of antiferroelectricity, 15-16, 17, 54, 99-100, 108, 112, 136, 142
- Dielectric hysteresis, see *hysteresis*
- Dielectric stiffness, see *stiffness*
- Dielectric susceptibility, see *susceptibility*

INDEX

- Dipoles, fixed-direction, 165-6, 168, 172, 191, 193
 - induced, 165
 - permanent or fixed-magnitude, 8, 165-6, 168-9, 171, 172, 180, 187, 188, 191
 - point, 172, 175, 193
 - rotating, 171, 179, 181
 - nature and identification of, 8, 9, 15, 16, 17, 131, 133, 174, 177, 191, 199-201
 - in particular materials, 101, 136, 180, 183, 184-5, 189, 195-6, 197
 - in relation to bonds, 8, 9, 176, 180
 - distortion by field, 171-2
 - water molecules as, 8, 169, 179
- Dipole array, 162, 166, 168, 193
- Dipole moment, definition, 8, 166
 - direction of, 16, 17, 101, 163, 184-6
 - temperature dependence of, 182-3, 186
- Dipole moments, and atomic displacements, 15, 131, 174-5, 180, 182-3, 184-5, 189-90, 191, 199-201
 - and spontaneous polarization, 8, 16, 163
 - of part of structure, 8, 9, 15, 16, 131, 133, 136, 163, 198, 199-201
 - in particular models, 180, 184, 186, 189, 191
- Dipole polarization, see *polarization*
- Directed bond, see *bond*
- Discontinuity at transition, experimental, 10, 29, 49, 55, 65, 70, 73, 74, 75, 80, 94
 - theoretical, 152-4, 159-60, 185
- Disorder, see *order-disorder*
- Disorder in hydrogen positions, see *hydrogen*
- Displacement of atoms, antiparallel or parallel, 62, 99, 106, 111, 129, 130, 131-2, 133, 136, 195
 - in multiple structure, 18
 - in pseudosymmetric structure, 10, 62-3, 65, 90, 98, 100-2, 103-5, 106-7, 109, 115, 119, 124-32, 136, 139-40, 144
 - in relation to dipole moment, 15, 131, 174-5, 185, 188, 191, 195, 196, 197-201
 - in relation to lattice distortion, 63, 65, 99, 197
- Displacement of central cation in octahedron, 62, 98, 101-2, 103, 105, 106, 107, 139, 191 (see also *cation*, *off-centre*)
 - of hydrogen atom in bond, 38-9, 42, 182-5, 186, 187
 - of Nb atom, 98, 100-2, 103, 126-9, 144-5
 - of P atom, 42, 139, 185
 - of Pb atom, 109, 111, 115, 130
 - of Ti atom, 62, 126-9, 188-91
 - of W atom, 106-7, 126-9
 - of Zr atom, 130
- Displacive transition, see *transition*
- Distortion of electron cloud, see *electron cloud*
- Domain, definition, 205
- Domain size, 24, 43, 79
- Domain texture (see also *twinning*), 32, 33, 67, 107, 108, 141, 143
 - effect of pressure, 13, 33
 - visible in polarized light, 33, 69, 79
- Domain walls, thickness of, 33, 44, 79
 - energy of, 43-4, 79
 - movement in field, 33, 79-80, 99-100
 - optically observed, 69, 79
- Domains as twin components, 12, 43, 67, 205
- Double refraction, 70, 71, 98-9, 111
- Effective charge on atom, see *charge*
- Effective field, see *field*
- Elastic coefficients, 49, 78, 158, 160
- Elasto-optical coefficients, 98
- Electron cloud of atom, distortion of, 127, 131, 172, 175-6, 183
- Electronic theory of BaTiO₃, 197-9
- Electrostatic valence (see also *bond strength*), 9, 124, 127
- Energy, potential, 181, 187, 189, 191-2
 - zero-point, 182
 - of structural unit, 176, 199
 - of structure, 129, 201
 - of transition (see also *heat*), 109, 111, 116, 119, 120, 140, 141, 146, 177, 182, 187
- Energy difference, between polymorphic forms, see *stability*
 - between states, 184, 189, 198
- Energy levels, 187-8, 200

INDEX

- Entropy, experimental results, 48-9,
72, 94, 116, 129, 140, 141, 146
theoretical relations, 159, 177, 182,
185, 190, 198
- Environment, atomic, 9, 85, 127, 199-
200 (see also *bond system*)
of particular atoms, 42, 54-5, 90,
138, 140, 141, 143, 145-6, 180
of NH_4 group, 45-6, 47
of potassium atom, 21, 33, 38, 42
- Etching to show domains, 69
- Eucken and Büchner's treatment of
polarizability, 175
- Expansion, thermal (see also *lattice
parameters*), 28, 48, 108, 109, 111,
113, 116, 119, 126, 165, 167, 182-3,
186, 192
- Extinction, optical, 69, 71
X-ray, 25, 80
- Ferrimagnetism, 16
- Ferroelectric, definition, 14
characteristic properties, 14, 108,
131, 133-4, 199
distinction from antiferroelectric, 17,
99-100, 111-12, 116, 119, 132, 136,
200
- Ferroelectricity, discovery of, 1
origin of name, 1
in multiple structures, 87, 133, 136
induced, 78, 100, 102, 112, 117, 119
- Ferroelectrics, cone and line, 16, 17,
87, 101, 133, 145-6, 163
hydrogen-containing, 133, 147, 200
- Ferromagnetism, analogy with, 1, 3, 4,
5, 12, 15, 16, 79, 80
Langevin-Weiss theory, 171, 179
- Field, biasing, 17 (see also *Curie
point*)
coercive, 3, 8, 14, 31, 52, 75, 105, 137,
186
effective, 167
internal, 160, 166, 168-9, 170, 176,
180-1, 187, 189, 197, 199 (see also
field factor)
local, 166-7
Lorentz, 168-9, 173, 192
threshold, 100, 112, 117, 119
orienting effect of, 13, 52, 71
- Field factor, theoretical discussion,
169, 176, 193-5, 201
particular theories, 170, 181, 187,
189, 191, 192, 195, 196, 197-8
- Field factor, numerical values, 182,
186, 187, 188, 190, 194, 198
- Field gradient, 176
- First-order transition, see *transition*
- Force constants of BaTiO_3 , 193
- Forces, attractive and repulsive, 127,
176
central, 83-4, 126
covalent, 176
directed, 9, 84, 126
electrostatic or ionic, 9, 83, 124, 126,
166
homopolar, 84, 133, 178, 189
long-range and short-range, 165-6,
167, 175-8, 183, 185, 186-7, 188,
199-200
- Formula-unit, 205
- Fourth-power term in expression for
potential energy, 191, 192
- Fowler's theory of Rochelle salt, 179
- Free energy (see also *Helmholtz free
energy* and *Gibbs function*), 112,
129, 151, 157, 159-60, 162, 169,
184-5
- Frequency, of applied field, 172, 175
of atomic vibrations, natural, 172,
175
- General positions, see *positions*
- Gibbs function, 151-3
- Goldschmidt polyhedra, 133
- Goldschmidt's rules, 83-5, 208
- Guanidine aluminium sulphate hexa-
hydrate, 14, 137
- Hafnates, 92, 112-13
- Heat of transition (see also *energy of
transition*), 49, 72, 94, 99
- Helmholtz free energy, 158, 177, 184,
191
- Hexagonal axes, see *axes of reference*
- Hexagonal barium titanate, see *barium
titanate*
- Hexagonal lattice, 205-6, 207, 209
- 'Hinge effect', 134
- Homodesmic structures, 84, 205, 206
- Homopolar, see *bond* and *forces*
- Hydrogen atoms, location of, 23, 26, 39
positions of, 38-9, 42, 47, 139, 141,
182, 186
ordering of, 42, 55, 139, 181, 183-4,
200
effective charge on, 188

INDEX

- Hydrogen bond, 23, 26, 27, 34, 38-9,
42, 46, 47, 54-5, 136, 138, 139, 140,
180, 183, 184, 185, 186, 200
- Hydroxyl group, 183, 184, 201
- Hysteresis, dielectric, as criterion of
ferroelectricity, 14, 15, 16, 100,
108, 116, 119, 136, 137, 146
theoretical treatment, 154-5, 157
- Hysteresis loop, double, 100, 112
forced, 78, 112, 117, 154-5
experimental methods for observing,
2
shape of, 3, 4, 50, 73
- Hysteresis, thermal, 24, 29, 30, 66, 73,
77, 78, 95, 114
- Ideal perovskite, see *perovskite*
- Ideal structure, 206
- Ilmenite, 85, 87, 103-5, 196
- Indicatrix, 70, 71, 98-9, 111
- Infra-red absorption, x, 172, 182, 188,
198
- Intensities of X-ray reflections, 25,
52-3, 61, 69, 115, 119, 144
- Interaction theory, Mueller's, 160
- Internal field, see *field*
- Ionic bonds, see *bonds*
- Ionic character of oxygen, see *oxygen*
- Ionic radius, see *radius*
- Isomorphous compounds, 27, 44-5,
137, 147
- Isotope effect, see *Curie point, effect of
deuterium substitution*
- Jaynes's electronic theory of BaTiO_3 ,
197-9
- Jaynes's mechanical-deformation
theory of BaTiO_3 , 197
- Kittel's theory of antiferroelectricity,
162
- Kurchatov's theory of Rochelle salt,
179
- kX unit, 206
- Lambda-peak, see *specific heat*
- Langevin-Weiss theory, see *ferro-
magnetism*
- Latent heat (see also *heat of transition,
energy of transition*), 73, 111
- Lattice, 18, 206-7
- Lattice parameters, 207
change with composition, 78, 115
change with temperature, 28-9, 47-8,
55, 65, 91, 94, 96, 100, 109, 113
dependence on crystal size, 66
- Lead compounds, structural features
in, 120, 130-2
solid solutions of, 114-20
- Lead hafnate, 112-13, 115, 120
- Lead niobate, 18, 127, 147-8
- Lead oxide, 130, 131
- Lead tantalate, 148
- Lead titanate, 13, 86, 108-11, 114, 115,
126, 127, 128, 130-1, 132
- Lead zirconate, structure, 111, 130
properties, 79, 111-12
antiferroelectric behaviour, 15, 17,
111-12
comparison with other materials, 87,
98, 100, 102, 113, 114, 115, 117,
118, 119, 120, 130-1
- Line ferroelectrics, see *ferroelectrics*
- Lithium ammonium tartrate mono-
hydrate, 18, 135-6
- Lithium niobate, 13, 87, 93, 103-5, 125,
126, 128, 132, 137, 141, 196
- Lithium tantalate, 93, 105, 137, 196
- Lithium thallium tartrate monohydrate,
14, 27, 136-7
- Long-range forces, see *forces*
- Lorentz catastrophe, see *catastrophe*
- Lorentz theory of internal field, 168-9,
170, 193
- Lorentz factor (see also *field factor*),
169, 192
- Lower Curie point, see *Curie point*
- Magnesium oxide, 127
- Mason's theory of Rochelle salt, 179-
183
- Mason's treatment of KH_2PO_4 , 186-7
- Mason and Matthias' theory of
 BaTiO_3 , 166, 188-91
- Mechanical properties, x
'Mixed state', 163
- Mobility of domain wall, see *domain
walls, movement*
- Model theories, general remarks, 151,
161, 162, 163, 165
particular examples, 179-201
construction of, 176-7
- Mueller's theory of Rochelle salt,
160-1, 166

INDEX

- Multiple cell, 207, 210
- Multiple structure, 18, 86-7, 133
 - examples, 92, 95-6, 106, 109, 111, 113, 115, 116, 140, 141
- Neumann's rule, 7
- Neutron diffraction, contrast with X-ray, 26
 - results of, 26, 35, 39, 42, 52, 61, 108-9, 136
- Niobates, general features of, 127
- Non-polar symmetry, 7, 15, 99, 174, 175
- Nuclear resonance method, results of, 94, 176
- Observable properties, required for definition, 9, 15, 170, 175
 - used for checking theories, ix, 162, 177, 181-2, 186, 187, 190, 192, 198
- Octahedra, as dipoles, 131
 - as structural units, 107, 131-2, 133-134, 143, 197, 199
 - displacement of cation in, see *displacement* and *cation, off-centre*
 - distortion of, 90, 107, 131
 - polarization of, 131, 199
 - regularity of, 61-2, 111, 124, 130, 143, 147
- Octahedra, centrosymmetric, 90, 102, 138, 140
- Octahedral bond system, 127
- Octahedral environment, 127, 141
- Octahedral framework, 59, 85, 102, 105, 109, 124-5, 127, 132, 133, 142-3, 145-6, 147
- Octahedral sites for cations, 87, 103-5
- 'Off-centre cation', see *cation*
- Onsager's theory of internal field, 168-9
- Optical evidence, for structure, 102, 111
 - for transition, 96, 143
 - for twinning, 69
- Optical properties, 70-1, 98-9, 111
- Order of transition, see *transition*
- Order-disorder effects, 179, 186, 189-191, 199, 200
- Ordering of hydrogen atoms, see *hydrogen*
- Origin, choice of, 42, 59, 60, 143
- Overlap between wave-functions, 175-176
- Oxygen atom, bond angle at, see *bond angle*
 - environment of, 180, 183
 - ionic character of, 125, 132
 - polarizability of, see *polarizability*
 - polarization of, see *polarization*
- Oxygen packing, 59, 87, 103, 105, 141, 197
- Packing effects, 124, 126, 127, 132, 133-4, 197, 208
- Paraelectric, 18, 86, 92
- Partition function, 176-7, 181, 184, 189, 191, 198
- Permanent dipoles, see *dipoles*
- Permittivity, see *dielectric constant*
- Perovskite (mineral), 89, 90
- Perovskite family, 13, 17, 83-121
- Perovskite structure, 124-34, 137, 140, 141, 143, 147
 - ideal, 58, 85, 86, 89
 - small-cell, 86, 133
- Phenomenological arguments, 166, 185
- Phenomenological theories, general features, 150-1, 161-2
 - particular cases, 151-63
- Phosphates, ferroelectric, 13, 44, 45, 53
- Phosphorus atom, displacement of, see *displacement*
 - environment of, see *environment*
- Piezoelectric coefficients, x, 51, 158, 160, 177
- Piezoelectric effect, 4, 179
- Piezoelectricity, definition of, 1
 - occurrence of, 7, 61, 63, 105
 - absence of, 139
- Pirenne's theory of KH_2PO_4 , 187-8
- Plane of symmetry, 208
- Point atoms, 9, 172, 175-6
- Point dipoles, see *dipoles*
- Point group, 208
- Polar axes, direction of, 7, 63, 65, 100-1, 145
- Polar classes, 7, 14, 115, 144
- Polar crystals, 166, 174, 208
- Polar symmetry, 166, 208
 - and ferroelectricity, 14-15
 - and multiple cell, 89
- Polar units in structure, 9, 199-200
- Polarity, of bonds, 208

INDEX

- Polarity—*contd.***
 of crystal, 32, 209
 reversal of, 50, 79
- Polarizability**, 160, 170-6, 181, 185,
 187, 189, 192, 194-5
 background, 198
 electronic, 172-5, 192, 194-5, 201
 experimental, 173, 192
 ionic, 174-5, 192, 195
 macroscopic, 167, 169, 170, 173-4, 192
 orientation, 160, 171
 total, 173, 196
 temperature coefficient of, 192
- Polarizability of oxygen atom**, 173
- Polarizabilities**, additivity of, 173
- Polarization**, dipole, 180-1, 199, 197
 electronic, 172, 175, 181, 187, 192,
 197
 ground, 187-8
 induced, 166, 174
 ionic, 174-5, 181, 192, 195-6
 proton, 187-8
 remanent, 50
 saturation, 50, 187
 spontaneous, see *spontaneous polarization*
 theoretical treatment, 151, 156, 160,
 162, 166-7, 170-2, 177, 184, 186,
 189-90, 194, 196, 198
 of oxygen atoms, 131, 180, 183, 195,
 197, 199
 interaction between ionic and elec-
 tronic, 175, 195
- Polarizing power of 'cation'**, 128, 131,
 133, 199
- 'Poling'**, 13
- Polymorphism**, 18, 45, 95, 201, 209
- Positions**, general, 20, 38, 42, 205
 special, 11, 20, 38, 42, 136, 210
- Postulates**, of model theories, 151
 of phenomenological theories, 150,
 160
 of structural theory, 199-200
 concerning low-temperature struc-
 tures, 177
- Potassium atom**, environment of, see
environment
 rôle of in transition, 33, 200
- Potassium dideuterium phosphate**, 45,
 49, 52, 54, 187-8
 monoclinic form, 45
- Potassium dihydrogen phosphate**,
 structure, 35-43
- Potassium dihydrogen phosphate**,
 properties, 47-54
 theoretical treatment, 54-5, 159,
 183-8, 199
 comparison with other materials, 13,
 16, 61, 79, 133, 137, 138, 139, 140,
 163, 200
- Potassium iodate**, 140
- Potassium niobate**, 13, 86, 93-5, 99,
 101, 102, 126, 128, 146, 159, 176
- Potassium tantalate**, 13, 95
- Potential energy**, see *energy* and *fourth-
 power term*
- Potential wells**, 180-1, 182, 183, 186-
 187, 189-90, 191
- Powder photographs**, 60, 86, 91, 95-6,
 111, 115, 119
- Pressure**, effect on Curie point, see
Curie point
 effect on domain texture, see *domains*
- Principal vibration direction**, see *vibra-
 tion direction (optical)*
- Pseudosymmetric structure**, 11, 12, 14,
 18, 209
- Pseudosymmetric transition**, see *transi-
 tion*
- Pyrochlore structure**, 14, 128, 142-3,
 147-8
- Pyroelectric effects**, 29, 32, 75
- Pyroelectric test for ferroelectricity**,
 112, 116, 120
- Pyroelectricity**, definition, 7
 and spontaneous polarization, 7, 8
- Quadrupole term**, 175
- Quantum-theory treatment**, 176, 187-
 188, 196, 197-8
- Quartz**, 10, 18, 125
- Radius**, atomic or ionic, 83-5, 126, 147,
 173, 197
- Radii**, additivity of, 83
- Raman spectra**, x
- Reconstructive transition**, see *transition*
- Refractive index**, 69, 70, 71, 111, 173
- Repulsive forces**, see *forces*
- Reversibility of spontaneous polariza-
 tion**, 3, 8, 14
 of structure, 52
 of transition, 10
- Rhombohedral axes**, see *axes of refer-
 ence*
- Rhombohedral lattice**, 209

INDEX

- Rhombohedral phase in system (Ba,Pb)(TiZr)O₃, 64-5, 93, 105, 112, 114, 115, 116, 117, 119, 130-1
- Roberts's treatment of ionic polarizability, 174, 196
- Rochelle salt, structure, 11, 20-6, 33, 183
 - symmetry, 1, 6, 7, 10, 20, 24-6
 - properties, 1, 3, 4, 5, 6, 10, 11, 13, 14, 17, 27-33
 - theoretical treatment, 8, 160-1, 166, 168, 179-83, 200
 - comparison with other materials, 50, 79, 133, 135, 136, 186, 189
- Rochelle salt, deuterium-substituted, 13, 25, 27, 30-2, 161, 182
- Rubidium dihydrogen phosphate, 13, 45, 53
- Rubidium iodate, 140
- Rubidium tantalate, 103
- Second-order transition, see *transition*
- Seignette electricity, 2
- Semi-polar bond, see *bond*
- Sesquioxides, A and C, 87
- Short-range forces, see *forces*
- Silver hydrogen periodate, 18, 135, 138, 139-42
- Single crystal, dielectric hysteresis, 4, 50, 73
- Size of crystal, effects due to, 43-4, 66
- Slater's theory of BaTiO₃, 166, 169, 192-6
- Slater's theory of KH₂PO₄, 166, 177, 183-6, 187, 199
- Sodium chloride, 9, 201
- Sodium iodate, 139
- Sodium niobate, structure, 95-8, 102, 132
 - properties, 98-102
 - forced change of phase, 100
 - theoretical treatment, 163
 - comparison with other materials, 13, 17, 87, 107, 111, 124, 126, 128
- Sodium potassium tartrate tetrahydrate, see *Rochelle salt*
- Sodium tantalate, 103
- Solid solution, nature of, 130
 - examples of, 27, 78, 88, 92, 93, 102, 112, 114-20, 143, 146, 148
- Solution of Rochelle salt, rate of, 27
- Space group, definition, 210
 - discussion, 24, 41, 60-1, 63, 144
- Special positions, see *positions*
- Specific heat, 29, 48-9, 71-3, 91, 108, 109, 140, 141
- Splitting of X-ray reflections, 24, 43, 69, 86, 96, 143
- Spontaneous polarization, definition, 3
 - experimental values, 31-2, 50-2, 73-75, 94, 136, 137, 146
 - as criterion of ferroelectricity, 14, 15, 16
 - as observable quantity, 3, 9, 116
 - direction, 137, 196
 - reversibility, 3, 8, 14
 - absence, 47
 - temperature dependence, 4, 116, 161
 - relation to strain, 51, 197
 - relation to symmetry, 6, 7, 99
 - relation to pyroelectricity, 7, 8
 - comparison with theory, 157, 161, 167, 177, 181, 186, 190
- Stability of polymorphic structures, 83, 95, 100, 112, 125, 129, 201
- Stiffness, dielectric, 152-4, 161-2
- Stress, effect on Curie point, see *Curie point*
- Stresses, local, effect of, 4, 10, 33, 49, 55, 67, 73, 80
- Strontium titanate, 89, 91, 127
- Structural theory of ferroelectricity, x, 133-4, 199-201
- Structural units, octahedra as, see *octahedra*
 - energy of, see *energy*
- Structure-building principles, 83-5, 124-7, 178, 201
- Sub-cell, 18, 86, 89-90, 96, 105, 106, 111, 113, 120, 125, 133, 207
- Superlattice, 18, 210
- Surface charges, see *charges*
- Susceptibility, dielectric, definitions, 5
 - initial, 5, 6, 160
 - reciprocal, 30, 152
 - adiabatic and isothermal, 177
- Symmetry axis, see *axis*
- Symmetry change at transition, 33, 42, 47, 144, 177, 185-6
- Symmetry direction, 210
- Symmetry, polar, see *polar*
 - in relation to physical properties, 6, 7, 69
 - in relation to ferroelectricity and antiferroelectricity, 14, 15, 16, 17, 47, 99

INDEX

- Symmetry, in relation to polymorphism, 18
 - of Rochelle salt, see *Rochelle salt*
- System, crystal, 210–11
- Szigeti's treatment of polarizability, 175
- Takagi's treatment, of antiferroelectricity, 177
- Takagi's treatment of ionic polarization, 175, 195–6
- Tantalates, 93, 95, 103, 105, 127
- Tartrates (see also *Rochelle salt*), 13, 14, 27, 135–7
- Temperature factors (see also *vibrations, thermal*), 61, 126
- Temperature of transition, variations in, 49, 80
 - theoretical treatment, 181, 187
- Thermal expansion, see *expansion*
- Thermal hysteresis, see *hysteresis*
- Thermal vibrations, see *vibrations*
- Thermodynamic arguments, 10, 55, 150, 160, 162
- Tilleyite, 125
- Titanium atom, displacement of, see *displacement*
 - volume available for, 127, 189, 195
- Tolerance factor, 85–7, 147–8
- Topological character of transition, 11, 105, 137, 141
- Transition, cooperative, 179
 - first and second order, 10, 55, 80, 152–4, 158–60, 161, 168, 169, 185
 - displacive and reconstructive, 10, 65, 126
 - pseudosymmetric, 11, 15, 16, 17, 42, 159–60
 - forced, 78, 100, 112, 117
 - mechanism of, 33, 54, 129, 139, 183, 200
 - volume changes at, 66, 108, 109, 111, 113, 116, 119, 120
- Tridymite, 11
- Tungsten trioxide, 13, 17, 106–8, 126, 128, 129, 132
- Twin laws, 67, 70
- Twin texture, see *domain texture*
- Twinning, 12, 24, 43, 67–70, 89, 90, 107
- Twins, 90° and 180°, 67–9, 79
- Unit cell, 211
- Uniterminal axis, 69
- Vibrations, atomic, 72, 175, 187
 - thermal, 39, 43, 61, 115, 126, 129, 165, 168, 188
 - anharmonicity of, 192
- Vibration direction (optical), 99
- Volume changes, see *transition*
- Volume conditions for cation, abnormal, 127, 189, 195, 199
- Walls, see *domain*
- Water, Curie point of, 169
 - effective charge on hydrogen atoms in, 188
- Water content of Rochelle salt, 3, 29
- Water molecules as dipoles, 8, 179
- Wave function of atom, 129
- Wells, potential, see *potential*
- X-ray evidence for atomic positions, 9, 26, 38, 42, 61, 63, 132, 182
- X-ray method, compared with optical, 96
 - compared with neutron diffraction, 26
- X-ray reflections, intensities, see *intensities*
 - splitting, see *splitting*
- Yttrium tantalate, 148
- Zero-point energy, see *energy*
- Zirconates, 92, 111–12

