FERRO-ELECTRICITY IN CRYSTALS

HELEN D. MEGAW

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

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

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.

<div align="right">HELEN D. MEGAW</div>

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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*

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1 Dielectric hysteresis

1.1. The discovery of the phenomenon later to be known as ferro-electricity 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

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* 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.

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.
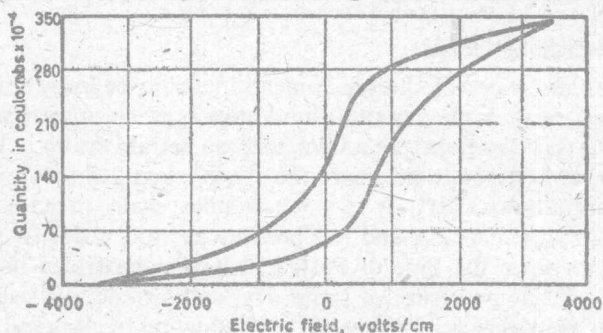
Fig. 1.1. Dielectric hysteresis loop for Rochelle salt (Valasek, 1921).
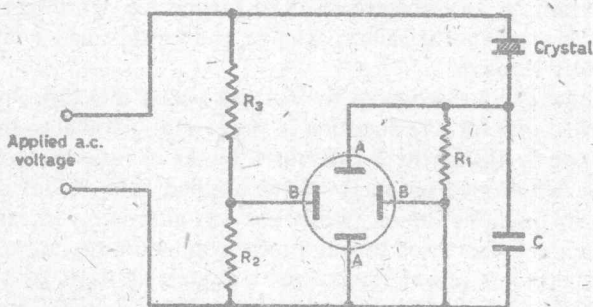
Fig. 1.2. Circuit for investigating hysteresis loop (Sawyer and Tower, 1930).

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.

1.3. 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 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.

Fig. 1.3. Dielectric hysteresis loop: illustrative diagram.

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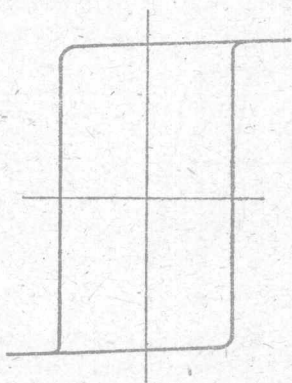
Fig. 1.4. Dielectric hysteresis loop for a true single-domain crystal.

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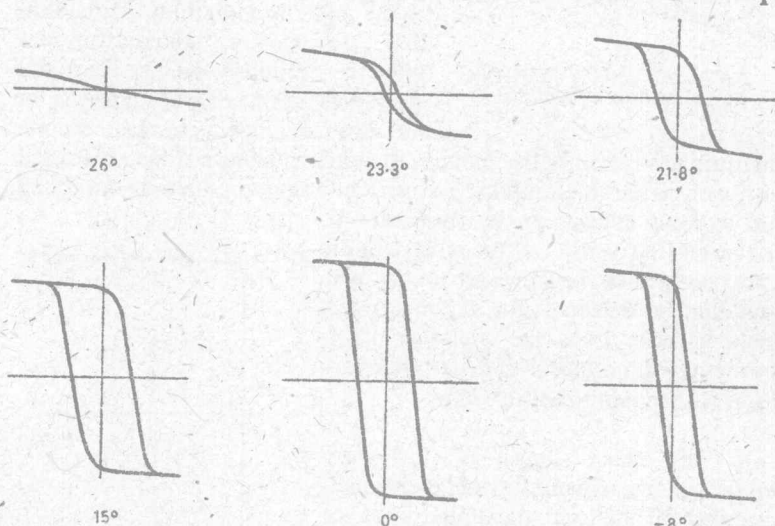
Fig. 1.5. Dielectric hysteresis loops for Rochelle salt at different temperatures (Sawyer and Tower, 1930).

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

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 biassing 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

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

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.

B

5

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

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.

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 ortho-rhombic, 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 experi-mental 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 dis-continuity 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 displace-ments 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 distor-tions 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

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.

Buerger'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 parallelopiped 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.