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Ferroelectricity and Crystal Structure. II

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Ferroelectrics are crystals with pseudosymmetric structures of polar symmetry in which the direction of polarity can be reversed by an applied field. They are found when the directed bond system of certain atoms changes with temperature while the ionic character of the structure is still important. If only one kind of atom suffers such a change, the resulting displacements are likely to have non-polar symmetry; if two change together, there is a good chance that the displacements of each kind of atom will all be parallel, and the substance therefore ferroelectric. These ideas are applied to the perovskite family, where the importance of the homopolar character of the O atom is emphasized; to KH_2PO_4, where the significance of the K atom is deduced from the geometry of the structure, and the contrast with $ND_4D_2PO_4$ is discussed; to Rochelle salt, where attention is again directed to the K atom, and the chemical implications of theories of ordering in the hydrogen bond are noted; and to $LiNbO_3$, where the room-temperature structure found by Bailey is shown to be that of a 'frozen ferroelectric' derived from the ideal perovskite structure.

1. Introduction

In a recent paper (Megaw, 1952) on perovskite-type structures, the view was put forward that ferroelectricity occurred in structures which were partly ionic, partly homopolar in character. When ionic packing and the directed bond systems of the atoms concerned independently require the same geometric arrangement, a relatively simple symmetrical structure results. Change of temperature may, however, bring about a change in the directed bond system. If the structure is still mainly ionic, the superposition on the ionic packing of an approximation to the new bond system may lead to a small distortion of the original structure and not to its complete breakdown. The pseudosymmetric structure so formed has a free energy not very different from the original or ideal structure. If it belongs to a polar class it will possess a spontaneous polarization; an externally applied field can then force it through the ideal structure to a polar structure with reversed direction. It is this reversible spontaneous polarization which constitutes ferroelectricity*.

Recent experimental work, in particular that of Frazer & Pepinsky (1953) on KH_2PO_4 and of Wood, Merz & Matthias (1952) on $ND_4D_2PO_4$, suggests an extension of these ideas. It is of interest to consider why some of these pseudosymmetric transitions lead to structures of polar symmetry and some do not. The present paper is an attempt to examine this problem.

In the discussion of $BaTiO_3$ in the previous paper, it was emphasized that the transition from the cubic to the tetragonal structure involved bond-angle changes both for the titanium and the oxygen atoms. It was not possible to draw a conclusion as to which atom was responsible for initiating the transition; it was pointed out, however, that a change in the titanium angle alone could have been accommodated in a structure with doubled cell dimensions and antiparallel displacements of titanium atoms.

The view now put forward is that a transition to a structure with polar symmetry requires the simultaneous operation of changes in the homopolar bond systems of two different kinds of atom in the structure. Where only one kind of atom undergoes such a change (assuming that the structure does not break down altogether) it satisfies its bond-angle requirements by bringing about displacements of neighbouring atoms in such a way that they are equal and opposite in different parts of the structure, so that geometrically the structure as a whole suffers as little distortion as possible. If in the original structure there is only one such atom per unit cell, a new unit cell of at least double the volume results. On the other hand, where two atoms are simultaneously able to change their bond system, there is a good chance that the specific distortion of environment required by one kind of atom may fit in with that required by the other in such a way that the original repeat distance of the cell is preserved, adjacent atoms of the same kind are displaced in the same direction, and the symmetry is polar.

This hypothesis is put forward only as a general guiding rule for the interpretation of pseudosymmetric structures. It is probably not capable of very rigid formulation. It seems to be of value in explaining the structures in the three groups of ferroelectrics on which most work has been done so far, namely those typified by Rochelle salt, KH_2PO_4 and $BaTiO_3$, and it is interesting to find that it can be used to explain $LiNbO_3$.

It is postulated that the bond system of any atom

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* This was recognized and explicitly stated by Jaffé (1937) in an important paper, but has since been largely overlooked.

depends on the temperature, and that it becomes more homopolar as the temperature decreases. Decrease in the number of bonds corresponds to an increase in homopolar character. There is also an effect of volume: if an abnormally large volume is available to an atom, it favours an increase in homopolar character. These points were developed in the previous paper. It seems probable that there is another effect of temperature when the ionic character of the structure is important: the radius of a cation increases relatively to that of oxygen as the temperature rises, so that the coordination number of ionic packing may also increase. ('Radius of a cation' here implies the packing radius when the ion is undergoing its thermal vibrations.) In this way the volume available to the oxygen atoms changes.

The application of these general principles to the different groups of ferroelectrics follows.

2. $BaTiO_3$ group

(Structures considered: $BaTiO_3$, $CaTiO_3$, $SrTiO_3$; $KNbO_3$, $NaNbO_3$; $PbTiO_3$, $PbZrO_3$.)

While $BaTiO_3$ is the best-known and most fully investigated example of this group, the present point of view suggests that the isomorphous $KNbO_3$ is more typical. The Nb atoms tend to form homopolar bond systems at room temperature under normal conditions; Ti does so only if given an abnormally large volume (as in $BaTiO_3$). It is known that O has a tendency to form homopolar bonds, making an obtuse angle between the bonds meeting at O. This may be the most stable state for O at room temperature, as seems probable from the common occurrence of such obtuse angles at O in inorganic structures, the 180° angle being found only when it is imposed by the requirements of other ions in the structure. If this assumption is correct, then a transition from the ideal structure must be triggered by the change in Nb or Ti. In any case the change in bond angle at O is a vital factor. The alternation of O and cation, each with bond angles differing from 180° by equal amounts, enables a structure to be adopted in which all the cation displacements are parallel.

That the tendency of the cation to form unsymmetrical bond systems is the essential factor can be seen by comparing $SrTiO_3$ and $KNbO_3$. If the effect were one of volume alone—if the Goldschmidt criterion for the ideal cubic perovskite structure were a sufficient condition—both should be cubic, since both have a tolerance factor very close to unity. Yet $KNbO_3$ is orthorhombic at room temperature. In $SrTiO_3$ there is no abnormal volume available for Ti to induce a change from its octahedral bond system; and without that there is no room for a movement of the O's and hence no opportunity for a change in the O bond angle. Hence $SrTiO_3$ remains cubic.

By contrast, $CaTiO_3$ provides an example showing changes in the bond angle at O but not at Ti. This is possible because the relatively small size of Ca allows displacements of O. Some work on the structure of $CaTiO_3$ has been done by Bailey (1952). He finds that this is orthorhombic, with sides approximately $\sqrt{2}a$, $2a$, $\sqrt{2}a$ (where a is the side of the ideal cube) and space group probably *Pcmn*. The Ti's lie on symmetry centres; the O positions are such that each TiO_6 octahedron is tilted approximately as a whole about the centre, remaining regular, adjacent octahedra being tilted in opposite directions. In this way the change of bond angle at O is achieved without any change in the octahedral environment of Ti, but at the expense of a multiplication of the sides of the unit cell. The approach to cubic symmetry as the temperature rises (demonstrated by Bailey) can be attributed to an increase in the obtuse angle at O, caused either by an increase in the ionic character of O or by an increase in the relative size of the Ca ion, or by both factors acting together.

In $NaNbO_3$ a structure similar to that of $CaTiO_3$ would have been expected if the bond system had remained octahedral. The obtuse angle at O is possible because Na, like Ca, is small enough to allow tilting of the NbO_6 octahedra. The structure actually found is more complicated; the cell dimensions are $\sqrt{2}a$, $4a$, $\sqrt{2}a$, and the Nb atoms (unlike the Ti) are no longer on special positions without arbitrary parameters. It seems clear that the changes of bond angle at Nb, added to the crumpling up of the O framework round Na, are responsible for this complexity. The resulting structure has not polar symmetry (Vousden, 1952); the evidence concerning its electrical properties and possible transitions is conflicting (Matthias & Remeika, 1951; Wood, 1951; Cross, 1953) but suggests the possibility that other pseudosymmetric structures may exist. An increase in the relative size of Na, a consequence of increased temperature, might lead to a structure isomorphous with $KNbO_3$.

In $PbTiO_3$, another factor must be taken into account: Pb, unlike the alkaline earth atoms, cannot be treated as essentially ionic. The structure of PbO (Moore & Pauling, 1941; see also Wells, 1950) shows that the homopolar bond system plays an important part; in this the Pb–O bonds form a flat tetragonal pyramid with Pb at the apex. In $PbTiO_3$ at room temperature the axial ratio is 1·06 compared with 1·01 for $BaTiO_3$; if the displacement of Pb relative to the O framework is correspondingly large, it will make the environment of Pb approximate to what it is in PbO. Hence the large axial ratio and high Curie point of $PbTiO_3$ compared with $BaTiO_3$ can be explained as a consequence of bond formation by Pb.

In pure $PbZrO_3$ (Sawaguchi, Maniwa & Hoshino, 1951), though neither the O nor the Zr positions are known, it seems likely that the observed antiparallel displacements of Pb perpendicular to the c axis, combined with a pseudo-tetragonal axial ratio of less than unity, achieve the same pyramidal environment for Pb by tilting the ZrO_6 octahedra without distortion about the Zr position.

This interpretation of the series $PbTiO_3$, $BaTiO_3$, $SrTiO_3$, $CaTiO_3$ differs essentially from that of von Hippel (1952), who correlates high Curie point with low strength of the bond from divalent cation to oxygen, and estimates bond strength from the melting point of the corresponding oxides. He does not consider the packing requirements of the small Ca ion in $CaTiO_3$, the anisotropy of the PbO structure, or the tendency to homopolar character of Pb.

3. KH_2PO_4 group

(Structures considered: KH_2PO_4, tetragonal KD_2PO_4, $NH_4H_2PO_4$, $ND_4D_2PO_4$, monoclinic KD_2PO_4.)

The idea that a simultaneous change in two different bond systems is characteristic of a ferroelectric transition is also applicable to the KH_2PO_4 group. In KH_2PO_4 and one form of KD_2PO_4 the transition from the high-temperature structure (space group $I\bar{4}2d$) to the ferroelectric structure (space group $Fdd2$, with x and y axes rotated through 45° relative to $I\bar{4}2d$) is generally believed to be due to a change in the hydrogen bond, which brings about an ordering of the H or D atoms. Slater's theory (1941), which gives a quantitative treatment along these lines, provides no explanation of the particular type of ordering which is actually adopted (Fig. 1(*a*)). Wood *et al.* (1952) have recently shown experimentally that a different type of ordering occurs in $ND_4D_2PO_4$ (to which $NH_4H_2PO_4$ is probably similar) (Fig. 1(*b*)). This, isomorphous with KH_2PO_4 in its high-temperature form, undergoes a transition to an orthorhombic structure with space group $P2_12_12_1$, the axes being coincident with those of $I\bar{4}2d$. Yet the authors show that here too the transition is caused by a change in the hydrogen bond; and the same conclusion is reached theoretically by Nagamiya (1952). These facts can be reconciled by the hypothesis that something other than the change in the hydrogen bond is also an essential factor in bringing about the transition in KH_2PO_4. It will be shown below that it must be a change in the bond system of the K atom.

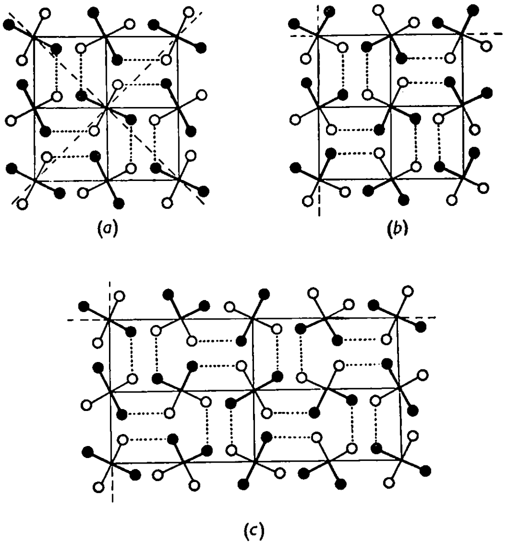

Fig. 1. Ordered arrangement of hydrogen atoms in different possible structures of KH_2PO_4 family. (*a*) Orthorhombic KH_2PO_4; (*b*) orthorhombic $ND_4D_2PO_4$; (*c*) monoclinic KD_2PO_4 (suggested). Axes of reference (with interaxial angles idealized to 90°) are shown by dashed lines, OH^- by solid circles, O^{2-} by open circles.

The importance of the K atom can be seen if the restrictions on the positions of the atoms in KH_2PO_4 are considered. In the tetragonal form, K and P are in special positions, with no arbitrary parameters. The O atoms are in general positions, and are all crystallographically equivalent. Each P is surrounded by O's at the corner of a tetrahedron, which is fully specified by the length p of the P–O bond and the angle ϱ it makes with the tetrad axis; if this angle were 54°44′, the tetrahedron would be regular. Its orientation in the structure is specified by the angle φ which the projection of P–O makes with the x axis. Each K is surrounded by 8 O's, in two sets of 4. One set, forming a steep-sided tetrahedron, consists of O's contributed by the PO_4 tetrahedra immediately above and below the K atom; the distances $K–O_1$ depend only on p, ϱ and the cell parameter c. The other set consists of O's contributed by PO_4 tetrahedra centred in the same (001) plane as the K, and forms a flat tetrahedron; the distances $K–O_2$ depend on p, ϱ, the cell parameter a and the angle φ. Below the transition point, each set of four equal K–O distances is replaced by two equal pairs.

Frazer & Pepinsky (1953) give the following values for the K–O distances and the length of the hydrogen bond at different temperatures:

	$K–O_1$	$K–O_2$	O–H–O
Room temperature	2·79 Å	2·82 Å	2·53 Å
126° K.	2·85	2·79	2·44
116° K.	2·81, 2·89	2·78, 2·79	2·51

They call attention to the importance of the K ion, and to the fact that at room temperature the $K–O_1$ and $K–O_2$ distances are nearly equal. They suggest that as the temperature falls, contraction of the hydrogen bond causes an inequality in length of the two kinds of K–O bond. Thus the K atom can build up a large thermal vibration parallel to the z axis, which ultimately 'locks in' to a permanent displacement, and so brings about the ordering of the H atoms.

The weak point in this argument is seen when the interatomic distances are examined in detail. If the lattice parameters were fixed, a shortening of the hydrogen bonds as the temperature decreased would result in a turning of the PO_4 tetrahedra about the z axis and a consequent small *increase* in the $K–O_2$ distance, while the $K–O_1$ distance remained unaltered. This is in contradiction to experiment. More rigorous examination indicates no reason for a relative change in the K–O distances. There are five arbitrary parameters needed to describe the structure; two of these are the a and c lattice parameters, while the other three may be taken as the Cartesian coordinates of any O ion, or more conveniently as its cylindrical coordinates, p, ϱ, φ, defined above. If the K atom is wholly ionic, the only requirements to be satisfied are five in number: the lengths of the P–O, O–H–O, and two independent K–O bonds, and the angle of the PO_4 tetrahedron. Since the number of adjustable parameters is equal to the number of requirements, the structure can exist with a regular environment of the K atom whatever the length of the hydrogen bond, and there is no reason why a transition should occur.

This argument suggests that the KH_2PO_4 structure should not be sensitive to the size of the cation, providing it is large enough to allow eight O neighbours. Further, since on this assumption the PO_4 tetrahedron is unconstrained, one would expect it to be regular at all temperatures, whereas Frazer & Pepinsky found that it was elongated at room temperature and only became regular approaching 126°K.

It does not seem possible to get out of this difficulty except by assuming that the K atom has also bond-angle requirements which must be satisfied. Then the transition can be explained by a change in the homopolar bond system of K from an 8-fold to a 6-fold set. It is very noticeable that below the transition point six of the K–O distances are nearly equal to each other and markedly shorter than the other two.

Though $NH_4H_2PO_4$ is isomorphous with KH_2PO_4, its cell dimensions are significantly different, and this affects the environment of NH_4 (Ubbelohde & Woodward, 1942). The four O's of the flat tetrahedron are much nearer to NH_4 than the four of the steep tetrahedron (2·87 and 3·09 Å respectively) (Ueda, 1948); the tetrahedron is not so flat as in KH_2PO_4, but is still far from regular. In the ordering process, half of the O's become OH^-, the other half O^{2-}; but of either kind, two are derived from the steep tetrahedron and two from the flat one. According to Pauling's rules, one would expect NH_4 to have as neighbours O^{2-} rather than OH^-. The distances could be equalized by a shift of two O's towards NH_4^- and two away from it, effecting a change of orientation of the NH_4 bond system as a whole. Perhaps the rather large discontinuous atomic shifts required (about 0·2 Å) may be responsible for the observed shattering of the crystal at the transition (Busch, 1938).

Thus in KH_2PO_4 the change in the bond system of the K atom and the change in the hydrogen bond together result in the type of order which has symmetry *Fdd*2, and is therefore polar. In $ND_4D_2PO_4$, on the other hand, the environment of the ND_4 group retains its symmetry requirements, which can best be satisfied if the displacements associated with the ordering of the hydrogens are antiparallel in different parts of the structure.

In passing it may be noted that the monoclinic form of KD_2PO_4 (Ubbelohde & Woodward, 1942), which is probably isomorphous with TlH_2PO_4 (Matthias, Merz & Scherrer, 1947) and the second form of RbH_2PO_4 (Bärtschi, Matthias, Merz & Scherrer, 1945), appears from its cell dimensions to belong to the same structure family as KH_2PO_4: $a \simeq a_{\text{tetrag.}}$, $b \simeq 2a_{\text{tetrag.}}$, $c \simeq c_{\text{tetrag.}}$, $\beta = 92°$. Assuming that it differs only in the ordering of the H's and the consequent small displacement of other atoms, it is possible to predict an arrangement compatible with the cell dimensions, the observed symmetry ($P2_1$) and the pseudosymmetry. This is shown in Fig. 1(*c*). It seems possible that it may contain long hydrogen bonds ($\sim$2·70 Å) because these would be favoured by the presence of large cations such as Rb and Tl with lower polarizing power (Bernal & Megaw, 1935), as well as by the substitution of D for H.

4. Rochelle salt

The structure of this in the ferroelectric state is unfortunately not known.* Nevertheless it is possible to draw certain conclusions from the symmetry.

As with KH_2PO_4, the transition in Rochelle salt has been attributed to changes in one or more of the hydrogen bonds that are known to exist in the high-temperature form, and this point will be discussed in more detail below. It seems, however, that a change in the bond system of the K atom is an essential factor here too. The argument is based on symmetry considerations. The high temperature form (Beevers & Hughes, 1941) has the space group $P2_12_12$, which has a fourfold general position; the unit cell contains 4 formula units $NaKC_4H_4O_6 . 4H_2O$. All the atoms are in general positions except K, which are on two sets of special positions of twofold symmetry. Now if an atom in a general position changes its bond system slightly, so that the other atoms adjust themselves without a complete breakdown of the structure, the lattice parameters may perhaps change discontinuously, but there is no change of symmetry. If, however, an atom in a special position changes its bond angles—whether spontaneously or in response to a change in its enclosing volume—its symmetry may be lowered, and with it the symmetry of the whole structure. In Rochelle salt, small displacements of any atom but K are compatible with the existing orthorhombic symmetry; it is only displacement of one of the K atoms which will result in lowered symmetry and hence in a polar class.

The environments of the two K atoms are very different, and one of them, K_1, is distinctly abnormal. The nearest neighbours are two O's from –COO groups at 2·79 Å, and two H_2O's at 3·01 Å; all other distances are greater than 3·20 Å. This too-large environment

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* *Note added in proof, 8 January* 1954.—Preliminary results have recently been reported (Rao, Frazer & Pepinsky, 1953). The very general arguments advanced in this section about the symmetry of the crystal and the incorrectness of the accepted hydrogen-bond system are confirmed by the experimental work of these authors, which shows further that a more radical amendment of the bond system is needed. The full structure will be awaited with interest.

tends to induce a homopolar bond system in K, if the analogy with $BaTiO_3$ can be accepted; and at a certain temperature the change takes place and a lowered symmetry results. The hydrogen bond then controls the transition only through its effect on the oxygen parameters, and one cannot say *a priori* which of the numerous hydrogen bonds in the structure will be most important. It is possible, with a structure of this complexity, that orthorhombic symmetry below the lower Curie point may be regained not by a reversal of the transition at the upper Curie point but by a further change in the environment of another atom and consequent readjustment of the whole. This would make Rochelle salt comparable with solid solutions of $PbZrO_3$ such as $Pb(Ti_{0.05}Zr_{0.95})O_3$ (Shirane, Suzuki & Takeda, 1952), where, however, the atomic displacements are very much bigger.

This explanation attaches less importance to the role of the hydrogen bond than do most of the existing theories, which are difficult to reconcile with chemical considerations. If Beevers & Hughes's structure contains ordinary tartrate ions and water molecules there is only one way in which the H's can be placed on their O–O bonds. All the bonds are unsymmetrical. Only one is short enough (2·56 Å) to allow resonance of H between two positions in the bond to be considered; this would correspond to the transition:

$$-COO^- + H_2O \rightleftarrows -COOH + OH^- .$$

This statement is the chemical corollary of the postulate of two potential wells of unequal depth which forms the starting point of Mason's theory (1947*a*, *b*). Resonance of this kind is not now believed to occur (see, for example, Coulson, 1952), and, even if such a tautomeric equilibrium could be supposed present, any change in it resulting from a change of temperature would have equal and opposite effects in the two bonds, and hence could not affect the orthorhombic symmetry.

5. $LiNbO_3$

(Structures compared with $LiNbO_3$: $FeTiO_3$, $LiTaO_3$, $KNbO_3$, rhombohedral $BaTiO_3$, $CdTiO_3$.)

It is interesting to see how ideas of the kind put forward above can account for the ferroelectric properties of $LiNbO_3$.

The structure has been determined by Bailey (1952). It is related to that of ilmenite, but with certain very significant differences which will be mentioned below. The X-ray evidence admits of two possible structures, differing in the arrangement of Li atoms relative to Nb. Of these, one is very much more plausible than the other, on grounds of symmetry and of the linkages of LiO_6 and NbO_6 octahedra, and its correctness will be assumed.

The space group is $R3c$; the unit cell is rhombohedral, with $\alpha = 55°53'$, containing 2 formula units. The dimensions of the corresponding hexagonal cell (containing 6 formula units) are $a_H = 5{\cdot}147$, $c_H = 13{\cdot}856$ Å. The cations occur in pairs of sites u, u, u; $\frac{1}{2}+u$, $\frac{1}{2}+u$, $\frac{1}{2}+u$. For Li, $u \simeq 0{\cdot}18$; for Nb, $|u| = 0{\cdot}02$, but its sign relative to Li is not known. The O's lie approximately in special positions of $R\bar{3}c$, with parameters represented by x, $\frac{1}{2}-x$, $\frac{1}{4}$, where $x = 0{\cdot}628$. The origin has been taken midway between layers of O's. Probably the O positions are more accurately given by parameters of the general position of $R3c$, which can be written x, $\frac{1}{2}-x-\varepsilon$, $\frac{1}{4}+\varepsilon$. It is likely that ε is small; it has not been detected experimentally, but this would be difficult, since it would lead only to second-order differences in the X-ray intensities. Its effect on the positions of the O's would be such as to increase the volume available to the Li atoms near the positions $u = 1/6, 4/6$, and distinguish this pair of sites from the unoccupied pair at $2/6, 5/6$, whose volume would be decreased.

Ilmenite itself ($FeTiO_3$) (Barth & Posnjak, 1934) has a unit cell of very similar dimensions, but the space group is $R\bar{3}$, and the cation sites are in pairs $\pm(u, u, u)$, where $u \simeq 1/3$ for Fe, $1/6$ for Ti. Successive short Fe–Ti vectors thus point in opposite directions, whereas all short Nb–Li vectors point in the same direction. The O's are again approximately at the special positions of $R\bar{3}c$, but the parameter x is $0{\cdot}550$. The ideal parameter for hexagonal close-packing is $0{\cdot}583$ $(= 7/12)$; thus $FeTiO_3$ and $LiNbO_3$ deviate in opposite directions from the ideal. This is shown in Fig. 2 (*a*)–(*c*).

Explanation of ferroelectricity

Though the structure of $LiNbO_3$ established by Bailey is polar, it is not immediately obvious how there can be a reversal of the direction of the polar axis such as is found in other ferroelectrics. The sense of the polar axis is fixed by the Nb → Li direction, and a displacement of Nb from $+0{\cdot}02$ to $-0{\cdot}02$ cannot affect this.

It is important to notice, however, that the structure has been determined at room temperature, whereas Matthias & Remeika (1949) state that the abnormal electrical properties begin to be noticeable only at high temperatures. No details are published, but the effects are said to happen at higher temperatures than for the isomorphous $LiTaO_3$, where they set in above 200° C.

The suggestion put forward here is that $LiNbO_3$ at room temperature is an example of a 'frozen ferroelectric', which is simply a pyroelectric crystal whose direction of polarity is maintained by structural forces too big to be overcome by the available applied fields. At higher temperatures reversal can be made to occur, but it involves atomic displacements bigger than those hitherto observed.

The ideal structure whose distortion gives rise to pyroelectric $LiNbO_3$ is the cubic perovskite structure. This is somewhat unexpected, but the relation can be seen by comparing Figs. 2(*c*) and 2(*d*). As the oxygen

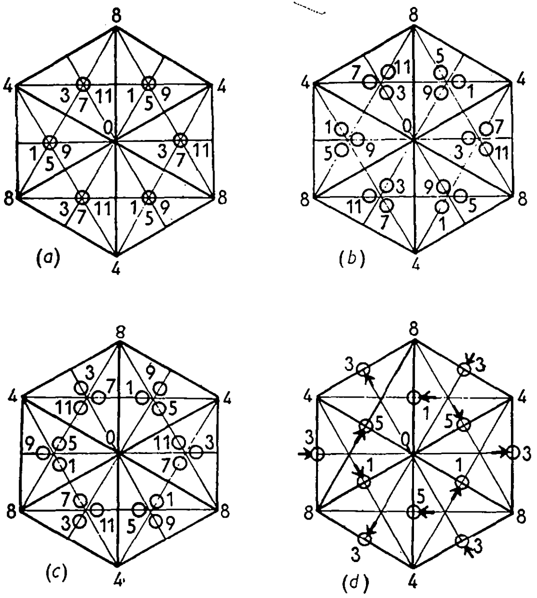

Fig. 2. Structures related to $LiNbO_3$: projection of rhombohedral unit cell, showing oxygen packing. Figures indicate heights (expressed as twelfths of repeat distance along triad axis) above plane through origin perpendicular to axis. (*a*) Ideal hexagonal packing; (*b*) ilmenite; (*c*) $LiNbO_3$; (*d*) ideal cubic packing, with one-quarter of the sites vacant. In (*d*), the three upper layers are omitted for clarity; arrows show how the positions are derived from (*c*). Oxygen parameters are not drawn to scale.

parameter changes from 0·628 to 0·75, the O's move to the positions shown in Fig. 2(*d*). This is the oxygen packing of the perovskite structure. The octahedron at height zero retains its existence; the environments of points at heights 1/6 and 2/6 become completely altered, while the point at height 1/4 acquires regular twelve-coordination*.

It is therefore suggested that ferroelectricity in $LiNbO_3$ represents a transition from one polar rhombohedral structure, through ideal perovskite, to the rhombohedral structure of reversed direction. Fig. 3(*a*)–(*c*) shows this sequence of changes for the cations. Only the cations move parallel to the triad axis (if the origin is kept fixed midway between oxygen planes). Oxygen atoms move only in planes perpendicular to the axis.

One obvious difficulty in this explanation is the magnitude of the displacements involved. Using the parameters given above, the displacement of Li is $(0\cdot50-2\times0\cdot18)\times13\cdot86 = 2\cdot0$ Å, that of O is

$$2\times\frac{0\cdot75-0\cdot628}{0\cdot75-0\cdot583}\times\frac{1}{6\sqrt{3}}\times5\cdot15 = 0\cdot7\ \text{Å}.$$

Two facts must however be remembered. First, the parameters of Li and O may change very much with the temperature; an increase in each would tend to reduce the corresponding ferroelectric shift. Secondly, the amplitude of thermal vibration increases rapidly with temperature, and this would encourage shifts of larger magnitude at high temperatures.

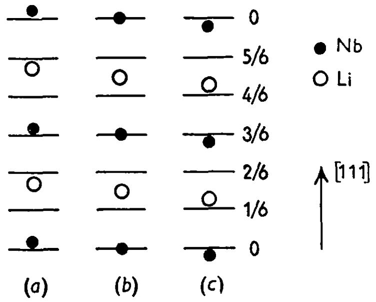

Fig. 3. Reversal of polarity in $LiNbO_3$, illustrating displacement of cations (parameters not to scale). (*a*) Rhombohedral polar structure; (*b*) ideal perovskite structure; (*c*) rhombohedral polar structure with axis reversed. (*N.B.* The relative signs of Nb and Li displacements are not known.)

There is no direct evidence on the first of these two effects, and it might be difficult to prove it experimentally, since the contributions of Li and O to the X-ray intensities are in any case small. Bailey has however shown that in $LiTaO_3$, which is isomorphous with $LiNbO_3$, the rhombohedral angle α increases with temperature; this indicates a spreading-out of the O layers such as would be expected from an increase in the Li and O parameters.

If this interpretation of the ferroelectricity is correct, it implies that at high temperatures $LiNbO_3$ (and the isomorphous $LiTaO_3$) will have a structure of perovskite type. It might be possible, by making suitable mixed crystals, to show the transitional stages, and for this purpose a study of the system (Li, Na)NbO_3 should be of interest.

Explanation of structure

The structure of $LiNbO_3$, considered as a distortion of perovskite, is to be explained by assuming that Nb retains its preference for a non-octahedral bond system up to fairly high temperatures. The cooperation of this and the obtuse-angle requirement of the O atom leads to a distorted structure with a small repeat distance; since Li is small, there is room for the O displacement. The decrease in relative size of Li as the temperature falls has the effect that at room temperature the O displacement is too large to allow easy reversal, and the crystal gradually ceases to be ferroelectric while remaining pyroelectric.

It should be noted that the unit cell of ferroelectric $LiNbO_3$ has double the volume of the ideal cubic cell. This is due only to the displacement of the oxygens from the ideal positions; all the cation displacements are identical. It is an example of a doubled cell which becomes polar. While illustrating the general principles put forward in the introduction, it shows the

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* The relationship here suggested between the ideal perovskite and room-temperature $LiNbO_3$ structures is the same as that between the ReO_3 and VF_3 structures (Jack & Gutmann, 1951).

danger of making rigidly formulated hypotheses about the possible geometries of ferroelectrics.

The structure of $LiNbO_3$ may be compared with the rhombohedral variant of $BaTiO_3$. The latter is believed to have a cell containing 1 formula-unit; the displacements of its cations from the ideal are the same in kind as, though much less in magnitude than, those of $LiNbO_3$, while its O's are assumed to be undisplaced perpendicular to the triad axis. A small displacement of the O's might not be observable, however, because of its very small effect on the intensities. It therefore seems possible that rhombohedral $BaTiO_3$ may in fact have a doubled cell, and that it represents the early stages of a distortion which $LiNbO_3$ shows fully developed.

It is interesting to consider the dimorphism of $CdTiO_3$ (Posnjak & Barth, 1934). This possesses the true ilmenite structure when prepared below 1000°C. but inverts irreversibly to a perovskite-type structure when heated above this temperature. Whether it is truly cubic at high temperatures is not known; when cooled to room temperature it is isomorphous with $CaTiO_3$. The true ilmenite structure cannot be attained by any distortion of a perovskite structure, even though both contain regular octahedral environments for the divalent cation, because the sequence of cations along the original triad axis is essentially different. Thus the transition from true ilmenite to ideal or distorted perovskite involves serious rearrangement of the structure and is irreversible, while that from $LiNbO_3$ to appropriately distorted perovskite can be completely continuous. For this reason it is misleading to classify the $LiNbO_3$ structure as a member of the ilmenite family.

6. Conclusion

There is one general principle underlying the treatment of all these substances given above: that the structure of a ferroelectric is not something essentially different from the structures of substances without anomalous electrical properties. Any explanation of the ferroelectricity of a given substance must start by assuming a knowledge of its structure; but to find the reason why a particular structure occurs is a problem of far wider application, not confined to the limited field of ferroelectrics. Explanations in terms of interactions of dipole lattices are finally unsatisfactory, however useful as a basis of quantitative work on the physical properties of the substances for which they are devised, because they can only be formulated for very simple structures, and cannot easily be extended to structures which are not electrically abnormal. On the other hand, the qualitative concepts of ionic size and environment and directed bond systems are of use throughout the whole field of crystal chemistry. Hence an explanation in these terms is likely to give a more general insight into the origin of ferroelectricity, though it falls far short of providing a quantitative formulation. If it is recognized that dipoles can be formally picked out as integral parts of *any* partly homopolar structure (as von Hippel (1952) has noted), the connection with the quantitative theories can be seen and the formal limitations of these and their restriction to particular cases becomes obvious.

One other point needs emphasis. For a proper understanding of a structure the positions of *all* its atoms must be known. The accident that certain cations are more easily located experimentally than the anions has tended to overemphasize the importance of their positions. It is clear from the above discussion that information about their environments is the important thing. This needs a knowledge of the oxygen positions, which is often lacking; failing experimental data, simplifying assumptions are sometimes made which obscure the very point at issue. When the space-group symmetry of a structure is known, it is possible in favourable cases to describe the environments qualitatively even though the actual distances are not determined, and this is better than nothing. Where only cation sites are known, it is difficult to see what is really happening; for the explanation of ferroelectricity, as for the understanding of the structure as a whole, the relationship of all the atoms must be taken into account.

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The Crystal Structure of Ammonium Oxide

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At low temperatures ammonia forms two stable hydrates $NH_3.H_2O$ and $2NH_3.H_2O$, ammonium hydroxide and ammonium oxide respectively. The hydroxide is hexagonal with $a = 11{\cdot}21 \pm 0{\cdot}05$ Å and $c = 4{\cdot}53 \pm 0{\cdot}02$ Å at $-95 \pm 10°$ C. The oxide is orthorhombic (space group *Pbnm*) with $a = b = 8{\cdot}41 \pm 0{\cdot}03$ Å and $c = 5{\cdot}33 \pm 0{\cdot}02$ Å at $-95 \pm 10°$ C. The structure of ammonium oxide contains planar chains of alternating ammonia and water molecules bonded by hydrogen bonds of the O–H···N and N–H···O type. The chains are cross linked into a three-dimensional lattice by hydrogen bonds of the latter type. The open spaces in the lattice contain the remaining ammonia molecules, each having a single hydrogen bond to the molecular lattice.

Introduction

The system ammonia–water has been investigated by many workers (Rupert, 1909, 1910; Smits & Postma, 1911; Postma, 1920; Elliott, 1924; Hildenbrand & Giauque, 1953). All results indicate that the system has two stable hydrates $NH_3.H_2O$ and $2NH_3.H_2O$, which will be referred to as ammonium hydroxide and ammonium oxide respectively. The crystal structure of neither of the two hydrates has been reported. The values mentioned for the melting points vary for the different investigators. Hildenbrand & Giauque (1953) report 194·15° K. for the hydroxide and 194·32° K. for the oxide.

The crystal structure of the oxide and the lattice constants of the hydroxide have been determined by X-ray diffraction and the results are described below. Hildenbrand & Giauque (1953) have found that the oxide has a transition region at about 50–55° K. As our determination was made at about −100° C. our results pertain to the high-temperature form only.

Preparation of the samples

The required amounts of ammonia and water vapor were measured out in a gas burette and condensed in a thin-walled Pyrex glass capillary with liquid nitrogen. Each capillary had a small bulb blown at the end to permit the use of a sizable sample. In order to have the liquid of the desired composition, an allowance was made for the fact that the vapor has a higher ammonia content than the liquid. After being filled, the capillary was sealed off and used as the X-ray diffraction sample.

The ammonia was prepared from ammonium chloride C.P. according to the method of Overstreet & Giauque (1937). The water was distilled twice.

Apparatus

The following Roentgenphotographs were taken: Debye–Scherrer, oscillation, and equi-inclination Weissenberg. The sample was mounted vertically in the Debye–Scherrer and oscillation cameras and horizontally in the Weissenberg camera. It was cooled with a stream of cold nitrogen gas produced by electrical heating of liquid nitrogen in a small Dewar. An automatic refilling mechanism governed by a float made possible a series of exposures on one crystal extending over several days. The quantity of cooling gas and the size of the duct were so chosen that frosting-over was not troublesome.

The preliminary investigations and the measurement of the lattice constants were made with the Debye–Scherrer camera of diameter 180 mm.

The structure factors were determined from the