

## Origin of Ferroelectricity in Barium Titanate and Other Perovskite-Type Crystals

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The origin of ferroelectricity is attributed to a small change of bond character occurring in a structure whose geometry is compatible with either ionic or homopolar binding. The dipole moments are associated with the electron orbitals of any or all of the atoms concerned, and are not to be identified with the product of effective charge and displacement, which has no physical meaning. The following structures are considered: the three ferroelectric forms of BaTiO<sub>3</sub>, PbZrO<sub>3</sub>, NaNbO<sub>3</sub>, KNbO<sub>3</sub>, NaTaO<sub>3</sub>, KTaO<sub>3</sub>, RbTaO<sub>3</sub>, WO<sub>3</sub>. The type of structure found is discussed in relation to ionic size and available bonding orbitals, and the temperature dependence of the latter. Perovskite-type structures are classified as single and multiple or puckered, and the use of the term 'antiferroelectric' for special cases of the latter class is deprecated. The criterion of ferroelectricity is not the existence of spontaneous polarisation but its reversibility in an applied field.

### 1. Introduction

Ferroelectric materials are so called because of an assumed analogy with ferromagnetism, manifested in their high dielectric constants, the variation of these with temperature near a Curie point, and their 'spontaneous polarization'. It is this last characteristic which is taken as the criterion of ferroelectricity, and as the term has been somewhat loosely used it will be well to discuss what is meant here.

Spontaneous polarization is defined theoretically as the resultant dipole moment per unit volume in the direction in which it is a maximum. Whatever the nature of the individual dipoles, they must have components in that direction which do not cancel out; hence the direction must be a uniterminal axis or polar axis. Observations on the point-group symmetry of the crystal by optical or X-ray methods can give information about the direction in which a uniterminal axis *may* exist; they cannot prove that it *does* exist.

The experimental definition of spontaneous polarization is based on the occurrence of dielectric hysteresis loops in ferroelectric materials. Loops occur for ceramics as well as for single crystals, but only single crystals are relevant for the present discussion. Fig. 1 shows a hysteresis loop for a true single crystal (single-domain crystal; c.f. von Hippel (1950)). The spontaneous polarization is the saturation polarization at zero field, given by  $OA$ . It should be noted that, in contrast to the magnetic case, the position of the axis  $OE$  (line of zero polarization) can only be inserted if the complete loop is determined. If the largest available field is  $E_m$ , and the coercive field  $E_c$ , where  $E_m < E_c$ , and if the crystal is initially polarized as at  $A$ , the observable part of the curve will be  $BC$ , and neither reversal nor hysteresis will be detected, nor can the magnitude of  $OA$  be found. This applies to an ideal crystal. An actual crystal, which includes

imperfections and the local stresses arising from them, may split up into domains in a much smaller external field, because the piezoelectric effect translates the local stresses into local fields, so that the effective

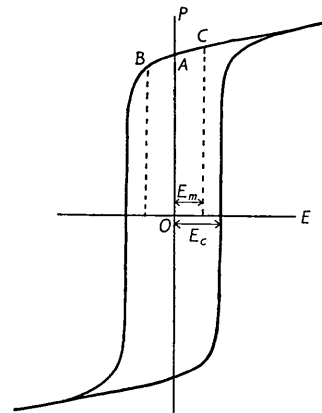


Fig. 1. Hysteresis loop of true single crystal (single-domain crystal).

total field may in places equal the coercive field though the applied field is considerably smaller. Even for actual crystals, however, this is unlikely to happen if the coercive field is sufficiently large.

It is therefore necessary to re-define a ferroelectric as a crystal showing a spontaneous polarization which can be reversed by an *attainable* field, as indicated by a dielectric hysteresis loop. The distinctive character of ferroelectric crystals does not lie in the spontaneous polarization, but in its reversibility. Any crystal with a polar axis can possess a resultant dipole moment, and hence a spontaneous polarization. Such crystals can show pyroelectricity, the change of dipole moment with change of temperature manifesting itself in accumulations of charge at opposite ends of the axis.

This has been discussed by Hulm (1949) who pointed out that Lord Kelvin (Thomson, 1860) had given an explanation of pyroelectricity in terms of a spontaneous polarization: 'When the temperature of the substance is changed, its electropolarization changes simultaneously'. Ferroelectrics are then a special group of pyroelectric crystals in which the spontaneous polarization is reversible.

So far, no assumption has been made about the nature of the individual dipole. Most writers (e.g. Mason, 1950; Slater, 1950) identify it either explicitly or implicitly with the product of effective ionic charge and displacement along the uniterminal axis. The atoms have arbitrary parameters in this direction, and the choice of origin is also arbitrary; it is usually taken at the point occupied by one of the atoms in a related structure with a biterminal axis. Such a choice is not unique, and the displacement of the atoms from special positions is thus not uniquely defined, a point which will be illustrated in § 3 for the case of BaTiO<sub>3</sub>. The point to be stressed here, however, is that this identification of the dipole with the product of charge and displacement is a theoretical step; that spontaneous polarization and atomic displacement, though sharing a common direction, are two physically separate things, detected by different experiments; and that unless this particular theoretical identification is explicitly postulated the two terms should not be used interchangeably, as they have been, in a way which creates confusion in the literature.

Assuming the dipole moment to be thus expressible in terms of atomic displacement, two rather different approaches have been used. Slater (1950), following Devonshire (1949), expresses the free energy in terms of the polarization, taking into account fourth-power terms; this is equivalent to treating the ion as a non-linear oscillator. He considers the combined effect of electronic polarization and an 'ionic polarization' which is the product of ionic charge and displacement considered in the last paragraph. Above the Curie point the ionic displacement and polarization are induced by the field; below it, there is a permanent ionic polarization which is made formally possible by the existence of the fourth-power term. By appropriate thermodynamical treatment, many of the observed properties of the material can thus be explained in terms of the polarization, including in particular the temperature dependence of the dielectric constant above the Curie point (cf. Devonshire, 1951).

A different starting point has been used by Mason & Matthias (1948) in the particular case of BaTiO<sub>3</sub>. Their model emphasises the location of certain shallow potential minima in which the titanium atom may be situated; these are distributed symmetrically round its position in the high-temperature structure and the displacement of the atom into one or other of them constitutes the dipole.

Both theories lead to the conclusion that the polarization is a 'cooperative phenomenon', such that

its appearance in one part of the structure gives rise to an electrostatic field bringing about a similar polarization in neighbouring parts. Though Mason & Matthias attribute the existence of potential minima to homopolar forces, the whole subsequent treatment is in terms of ions and electrostatic forces.

It is a purpose of this paper to question the identification of the dipole moment with the product of ionic charge and displacement, and to show that the partially homopolar character of the bonds must be taken into account. It is not legitimate to identify the concepts of classical electrostatic theory with the detailed features of a structure where quantum theory needs to be invoked, as it does here. While the dipole moment must probably include an ionic contribution, this cannot be treated as physically distinct from the dipole moments of the homopolar bonds and of the unshared electron pairs. The new emphasis on the significance of the homopolar character leaves untouched the successes of the classical electrostatic theory in relating macroscopically observable properties to the polarization, but overcomes the difficulties of that theory in giving a meaning to the spontaneous polarization; and the whole problem of the perovskite-type structures is brought into relation with the crystal chemistry of other complex oxides.

## 2. Structure of cubic and tetragonal BaTiO<sub>3</sub>

The structure of BaTiO<sub>3</sub> is well known (Megaw, 1947). Above the Curie point it is cubic, with a cell side of about 4 Å, and contains one formula-unit per cell. Atoms are at the following positions:

Ti at (0, 0, 0), the corner of the unit cube,  
 Ba at ( $\frac{1}{2}$ ,  $\frac{1}{2}$ ,  $\frac{1}{2}$ ), the body-centring position,  
 O<sub>x</sub>, O<sub>y</sub>, O<sub>z</sub> at ( $\frac{1}{2}$ , 0, 0), (0,  $\frac{1}{2}$ , 0), (0, 0,  $\frac{1}{2}$ ) respectively,  
 the mid points of the cube edges.

All three O's are crystallographically equivalent in the high-temperature form. Below the Curie point the structure becomes tetragonal, by a slight lengthening of *c* and shortening of *a*, the *z* axis being the tetrad axis. Atoms O<sub>x</sub> and O<sub>y</sub> remain equivalent to each other, but are distinct from O<sub>z</sub>. All the atoms may have arbitrary displacements in the *z* direction; the actual magnitudes of these have only recently been determined (Evans, 1951) and will be discussed in § 4 below.

## 3. 'Ionic polarization'

It is necessary to consider in more detail the idea of ionic polarization. A set of parallel dipoles arranged on a cubic lattice give rise to a field, at the same set of points, of magnitude  $P/3\epsilon_0$  m.k.s. units. In BaTiO<sub>3</sub> each of the five atoms in the unit gives rise to one such lattice, with origin at the point specified. The total internal field at any point is the sum of five terms such as  $(1/3\epsilon_0 + S_j)P_j$ , the constant  $S_j$  depending on the

position of the origin of lattice  $j$  with respect to the given point. Luttinger & Tisza (1946) have calculated the  $S_j$ 's, and find that very much the largest contribution to the field by any dipole lattice occurs at points lying on the dipole axis midway between the dipoles. Hence any lattice has its strongest interaction with another displaced relative to it by  $\frac{1}{2}c$  (where  $c$  is the spacing in the line of the dipoles). This condition is fulfilled by the Ti and  $O_z$  lattices, and by them only. A set of Ti dipoles will thus produce strong internal fields at  $O_z$ ; the  $O_z$ 's in turn become dipoles and produce strong fields at Ti. To quote Slater, 'the net 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 does not raise difficulties if the dipoles are attributed to transient displacement of ions from their equilibrium positions above the Curie point. But when permanent displacements have taken place, certain questions must be asked.

First, what physical meaning is to be attached to 'ionic polarization'? Below the Curie point, the equilibrium position of the atom is the displaced position; it is difficult to see how the product of this displacement and the ionic charge can constitute a dipole moment, since the old equilibrium position has no longer any physical significance. There is no centre of symmetry, and the choice of origin along the  $z$  axis is quite arbitrary. It is usually chosen symmetrically with respect to the Ba atoms, but might equally well be taken in a fixed position relative to the oxygen framework. In the first case, the dipole moment of the whole structure, considered as an ionic polarization, is the sum of those due to Ti and O; in the second case, of those due to Ti and Ba. Though the sum is the same in either case, the separate ionic polarizations attributable to each kind of atom are not; hence there can be no unique meaning for the ionic polarizability  $\alpha'$ , which is defined as the ratio of the ionic polarization to the field producing it.

Secondly, the theory fails to show that an arrangement with all the dipoles in parallel orientation would be preferred to one in which they are antiparallel. Compounds with antiparallel arrangement have been termed 'antiferroelectric' (Kittel, 1951). Examples in which some of the displacements are antiparallel are known, and will be discussed in §§ 8-9 below, though the use of a special name for them will be questioned, since they are only part of a wider class of compounds with small displacements of atoms along several directions in space. But in  $BaTiO_3$  the displacements are parallel, yet an application of Slater's theory suggests that an antiparallel arrangement would be favoured (Cohen, 1951).

Thirdly, the theory cannot predict any appreciable displacement of  $O_x$  and  $O_y$ , since the interaction of either of these 'dipole lattices' with any other is small,

very much smaller than that of Ti with  $O_z$ . Experimentally, however, it is now found that the  $O_x$ ,  $O_y$  displacements are of the same order of magnitude as the rest; this must be considered in the next section.

#### 4. Atomic displacements, interatomic distances, and the structure of tetragonal $BaTiO_3$

Estimates of atomic displacements deduced from electrical and optical investigations cannot be taken into account here, since they involve the questions which are at issue. Direct experimental determination by X-ray methods is not easy. Danielson, Matthias & Richardson (1948), from preliminary measurements, gave the Ti displacement as 0.16 Å. Kay, Wellard & Vousden (1949) found the displacements of Ti and  $O_z$  to be less than 0.05 Å and 0.13 Å respectively; they did not consider  $O_x$ . Känzig (1951) found that they were about 0.06 Å and 0.13 Å at room temperature; he too assumed that  $O_x$  was undisplaced. Evans (1951), using Fourier methods without any such presupposition, obtained the following values (taking the origin so that Ba remained at  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ): Ti,  $0.060 \pm 0.005$  Å;  $O_z$ ,  $-0.096 \pm 0.005$  Å;  $O_x$ ,  $O_y$ ,  $-0.080 \pm 0.005$  Å. These will be accepted in what follows. It may be noted that the network of O's moves almost as a whole relative to Ba.

These parameters show up a further difficulty in attempting an explanation entirely in terms of ionic forces. It has often been tacitly assumed that the Ti ion can easily be displaced because the Ti-O distance in the cubic form is greater than the sum of the Goldschmidt radii of  $Ti^{4+}$  and  $O^{2-}$ . Actually this discrepancy merely shows that ionic forces cannot provide the whole explanation of the structure. In the tetragonal form it becomes still clearer that something else is involved. The Ti- $O_z$  distances calculated from the parameters are 1.860 Å and 2.174 Å; the radius sum is 1.96 Å. If the Goldschmidt radii are taken as giving an empirical estimate of the distance at which the repulsive forces become equal to the sum of the electrostatic and van der Waals attractive forces, it is plain that some other large attractive force is necessary to explain the shortening to 1.86 Å. It is too difficult to imagine that an internal field owing its existence to such a shortening of the distance could be responsible for maintaining the shortening against large repulsive forces. It seems more natural to assume that a change has taken place in the Ti atom (or the  $O_z$  atom), resulting either in an extra attractive force or in a reduction of the distance at which the repulsive forces become operative. Such a change must represent an increase in the homopolar character of the atom concerned.

Looked at in this way, a consistent picture can be obtained. In the cubic form, Ti is surrounded by six O's in a regular octahedron. Such an environment is geometrically compatible either with purely ionic packing or purely homopolar binding. There is evidence

that the structure has some homopolar character, and it seems reasonable to suppose that it may best be regarded as intermediate between extremes. As the temperature decreases, there is an abrupt change in homopolar character. This may well correspond to a change in the orbitals contributing to the bonds, but discussion of the point will be deferred to § 6. Whatever it is, it means that the stable homopolar bond system no longer coincides with the stable ionic packing. The configuration taken up will be intermediate between the two, and the interatomic forces can no longer be described as central, but must be given direction. The configuration actually found by experiment is a square pyramid with a very flat base, the distances being as shown in Fig. 2.

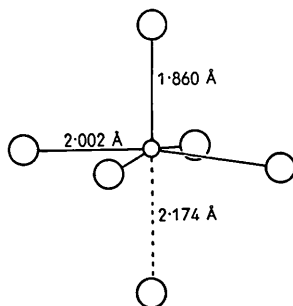


Fig. 2. Environment of Ti in tetragonal BaTiO<sub>3</sub> (perspective drawing).

A change in the bond system of Ti will affect not only the bond Ti-O<sub>z</sub> which is immediately shortened, but also Ti-O<sub>x</sub> and Ti-O<sub>y</sub>, and through them the bond system of the O<sub>x</sub>, O<sub>y</sub> atoms. Consider the environment of O<sub>z</sub>. In the cubic structure, it has two Ti neighbours along [100] and four Ba neighbours in the plane (100). The Pauling electrostatic valencies in Ti-O and Ba-O are  $\frac{4}{6}$  and  $\frac{2}{12}$  respectively, so that in the first instance the Ba-O bonds may be neglected. The Ti-O bonds at O<sub>z</sub> make an angle of 180°, which is characteristic of ionic structures. In homopolar structures, O tends to have bonds at the tetrahedral angle. Hence any increase in homopolar character may be expected to make a bend in the line Ti-O<sub>z</sub>-Ti. If it is assumed that displacements can only take place along the z axis, this implies that both Ti's must have z parameters of the same sign with respect to O<sub>z</sub>, otherwise a straight-line formation would be retained. That is, if the bond-angle at O<sub>z</sub> plays an important part the displacements must be parallel rather than antiparallel.

The homopolar oxygen atom has two negative regions occupying the two remaining tetrahedral directions, representing the unshared electron pairs. These will attract the two Ba ions towards which they jut out, as shown in Fig. 3. Hence Ba will be displaced, relative to the O framework, in the same direction as Ti. Electrostatic repulsion between Ba and Ti will tend to the same result. The actual O<sub>z</sub>-Ba distances (Evans, 1951) are 2.782 Å, 2.896 Å; O<sub>z</sub>-Ba

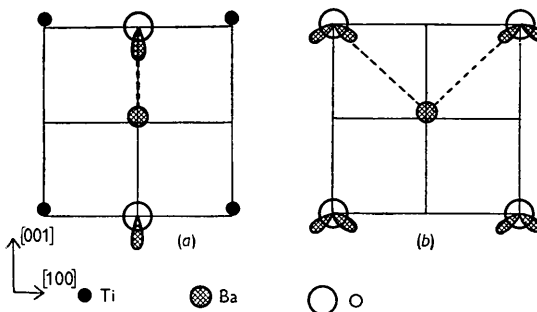


Fig. 3. Environment of O<sub>z</sub> in tetragonal BaTiO<sub>3</sub>. (a) Projection of part of cell on (010), (b) section parallel to (100) at  $x = \frac{1}{2}$ . Directions of unshared electron pairs are shown by shaded regions.

is 2.826 Å. The sum of the Goldschmidt radii, corrected for 12-coordination, is 2.89 Å; uncorrected it is 2.75 Å, and thus the shortening brought about by the extra Ba-O<sub>z</sub> attraction is of the same order as the difference between the radii for 12-coordination and 6-coordination.

The environment of Ba, which consisted originally of 12 equivalent O's at 2.826 Å, is now also somewhat distorted, but because of the long distance and large coordination number the distortions are relatively less important.

Looking at the structure as a whole, it is seen to be a layer structure. The layers, of composition TiO<sub>3</sub>, consist of square pyramids joined by their corners into a continuous sheet, with the apices of the pyramids carrying unshared oxygens. Layers are held together by Ba ions, in slightly irregular 12-coordination. A projection is shown in Fig. 4. A structure like this should have a good cleavage parallel to the layer, and negative birefringence. The former is not easily observable, since mechanical working of a single crystal

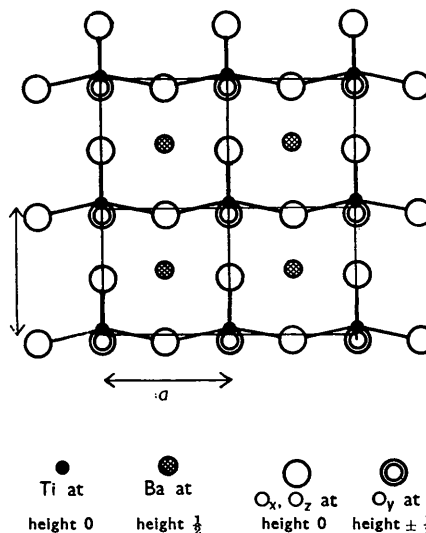


Fig. 4. Tetragonal BaTiO<sub>3</sub>. Projection on (010), showing layers. (Displacements of atoms are exaggerated by a factor of 2.)

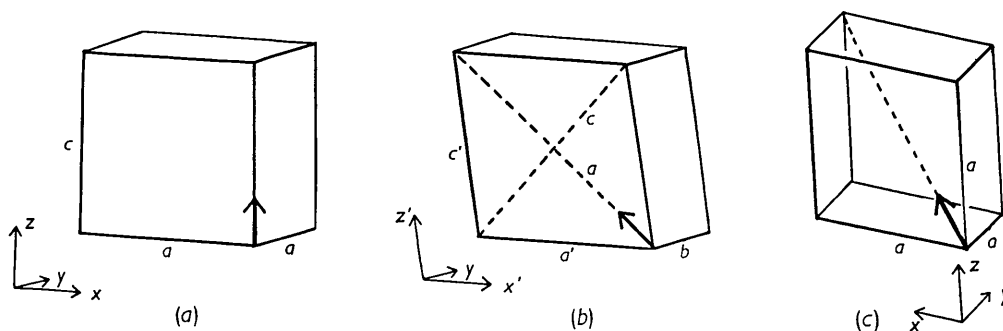


Fig. 5. Unit cells of different forms of  $\text{BaTiO}_3$ : (a) tetragonal, (b) orthorhombic, referred to monoclinic axes, (c) rhombohedral. Angular distortions exaggerated, linear distortions neglected. Arrows show direction of spontaneous polarization. (In (b) the positive directions of  $x'$  and  $z'$  must conventionally include the obtuse angle; this convention has not always been followed in previous papers. The cell edges referred to orthorhombic axes are  $a$  and  $c$ .)

immediately results in twinning (Kay, 1948). The latter has been observed (Forsbergh, 1949); and it is also noteworthy that the larger value of the dielectric constant, like the larger value of the refractive index, lies in the layer (Matthias & von Hippel, 1948), i.e. perpendicular to the atomic displacement.

It becomes unnecessary to invoke 'long-range forces' to explain the transition as a cooperative phenomenon. It is cooperative in the sense in which any change of structure that takes place without destruction of the atomic network is cooperative; but it is achieved by a sequence of nearest-neighbour forces, and cation-cation interactions do not play the determining part.

### 5. Orthorhombic and rhombohedral $\text{BaTiO}_3$

It is desirable to examine the two other forms of  $\text{BaTiO}_3$  with the same ideas in mind. Both unit cells are produced from the cube by simple distortions (Kay & Vousden, 1949; Rhodes, 1949), and contain one formula-unit. (Here and throughout the paper, unless otherwise specified, monoclinic axes corresponding to the original cube edges are used for describing the orthorhombic form.\*) Fig. 5 illustrates them. The direction of atomic displacement is deduced from the nature of the distortion, and confirmed by what is known of the optical properties (Forsbergh, 1949); crystallographically, it must be a uniterminal axis. The magnitudes of the displacements are not known from direct evidence, but it is reasonable to assume that they are much the same in all three forms, since this is true of the spontaneous polarization (Merz, 1949); the two effects must not be identified, but there should be an order-of-magnitude correspondence. For simplicity, we further assume that displacements of Ti and Ba take place relative to an unchanged oxygen framework, as is approximately true for the tetragonal form.

\* Following the notation of Wood (1951), planes and directions of the orthorhombic structure described on monoclinic axes will be distinguished by inverted commas.

Here the explanation put forward by Mason (1950), which is incompatible with these assumptions, could be subjected to experimental test. His model postulates six shallow potential minima arranged octahedrally round the symmetrical Ti site; in the tetragonal form the Ti atom occupies one minimum displaced along the  $z$  axis, in the orthorhombic form it resonates between two minima displaced along  $z$  and  $x$  respectively, and in the rhombohedral form between three minima displaced along  $x$ ,  $y$  and  $z$ . Such structures would give intensities of X-ray reflexions quite different from those of structures with ordinary displacements along  $[10\bar{1}]$  and  $[111]$  respectively; a Fourier synthesis such as that done for tetragonal  $\text{BaTiO}_3$  should distinguish between them. The resonating structures seem unlikely, and will not be further considered.

In the orthorhombic form, a displacement of the expected magnitude along  $[10\bar{1}]$  results in an approach to a tetrahedral environment for Ti (Fig. 6). The two bonds in the '(010)' plane are  $1.9 \text{ \AA}$  in length, those inclined to it and lying in '(110)' are  $2.0 \text{ \AA}$ , while the distances to the remaining two O's in the

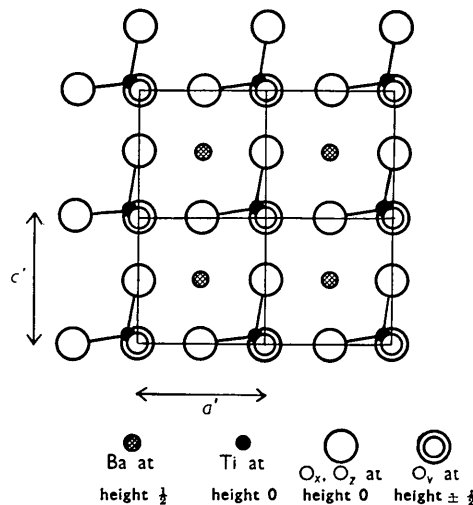


Fig. 6. Orthorhombic  $\text{BaTiO}_3$ . Projection on '(010)'.

Table 1

Modification	Ti atom	O atoms	Linkage of structure
Cubic	Octahedral bonds	180° for all three	Three-dimensional network
Tetragonal	Nearly square bonds with one shorter bond at right angles	Tetrahedral for two; covalent link to single cation for one	Two-dimensional sheets
Orthorhombic	Tetrahedral bonds	Plane 120° for one; covalent link to single cation for two	One-dimensional chains
Rhombohedral	Trigonal-pyramid bonds	Covalent link to single cation for all three	Isolated $\text{TiO}_3$ groups

'(010)' plane are 2.1 Å. The tetrahedra share corners  $\text{O}_y$ , forming continuous chains parallel to  $y$ . The chains are held together by Ba ions—an arrangement which calls to mind chain silicates such as diopside (Bragg, 1937).

The environment of  $\text{O}_y$  is interesting (see Fig. 7). This atom has two Ti neighbours on one side, a single Ba on the other. The distortion of O from ionic is not towards its tetrahedral bond system but towards its plane 120° bond system.

In the rhombohedral form, Ti has three nearest neighbours at 1.9 Å, forming with it a trigonal pyramid. Fig. 6 might serve as a projection of this structure parallel to [010] by deleting one of the two bonds to  $\text{O}_y$ , since the atoms above and below the plane of projection are not now equidistant from Ti, which is above the plane. The distance of Ti from its non-bonded neighbours is again 2.1 Å. Thus we have

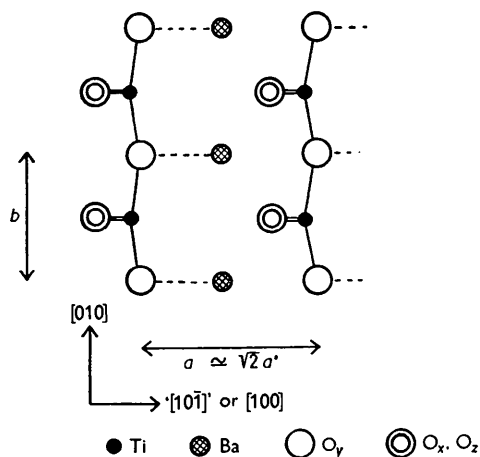


Fig. 7. Orthorhombic  $\text{BaTiO}_3$ . Projection of part of structure on '(010)' or '(001)', showing chains of tetrahedra.

isolated  $\text{TiO}_3$  groups, sharing no corners with others, but forming molecule-ions like the  $\text{CO}_3$  groups in calcite, and held together in the structure by electrostatic bonds to the Ba ions.

## 6. Bond changes with temperature

Comparing the four forms of  $\text{BaTiO}_3$ , we may trace the sequence with decreasing temperature as it is

shown by the Ti bond system, the O bond system, or the linkage of the structure. This is shown in Table 1. It must be emphasised that the descriptions indicate only the *kind* of distortion from the form which may be considered fully ionic; the *degree* of distortion is in fact not so extreme, and suggests that a considerable amount of ionic character is retained throughout the whole series.

The changing linkages in  $\text{BaTiO}_3$  may be compared with those in the silicates. The same variety of structures is shown by the silicate ion (Bragg, 1937): e.g. three-dimensional network in the feldspars, two-dimensional sheets in the micas, one-dimensional chains in diopside, isolated  $\text{SiO}_4$  groups in olivine. Oxygen atoms are there generally of two kinds, those shared between two Si's and those bound to one Si only; the silicate ions, whatever their complexity, are bound together in the structure by other cations, maintaining electrical neutrality. Qualitatively, the description of the titanate structures is strikingly similar. The chief difference is that Si throughout remains tetrahedrally coordinated, and only the numbers of shared corners of the tetrahedra change, whereas in  $\text{BaTiO}_3$  the coordination number and the numbers of shared corners of polyhedra both change together, the decrease in the latter (as compared with the cubic structure) being double the decrease in the former. The Ti-O homopolar bond is weaker than Si-O, and the larger size of Ti allows 6-coordination in ionic packing; hence the contribution of the superimposed ionic structure is qualitatively quite different in  $\text{BaTiO}_3$  from that in the silicates.

The table shows that there is a temperature-dependent sequence in the bond system of the atoms. The question arises whether the change originates in Ti or O, the change in the other following through strain. Perhaps it should rather be asked whether the change originates in the bond  $\text{Ti-O}_1$  or  $\text{Ti-O}_2$  (using  $\text{O}_1$  to denote the atom linked to a single Ti,  $\text{O}_2$  that linked to 2 Ti's). The environment of Ti undergoes more conspicuous changes than that of  $\text{O}_2$ , which suggests that the change either originates in Ti or, originating in Ti-O (which becomes an incipient double bond), affects first the whole Ti bond system and through it the rest of the structure. The effect on  $\text{O}_2$  must be more than a mere elastic distortion,

however. For example, in the tetragonal form  $O_x$  could retain its  $180^\circ$  bond angle in a structure with antiparallel Ti displacements, as in the hypothetical structure of Fig. 8.

Very little evidence is available from structural work about changes of bond character with temperature, but such as there is suggests that homopolar character decreases with increasing temperature. The  $\alpha$ - $\beta$  transition of quartz is of interest here. This is a reversible transition, occurring at  $575^\circ$  C., and involving only very small atomic displacements. From comparison of the parameters in  $\alpha$ (low)-quartz at room temperature (Wei, 1935; Brill, Hermann &

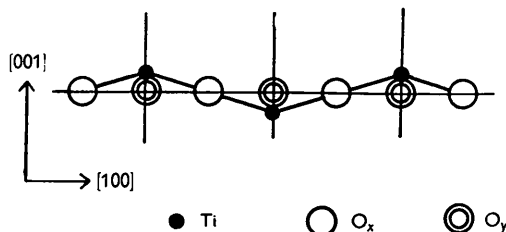


Fig. 8. Hypothetical structure with antiparallel displacement of Ti, projected on (010).

Peters, 1939) and  $\beta$ (high)-quartz (Bragg & Gibbs, 1925; Gibbs, 1926) it appears that the  $SiO_4$  tetrahedron is slightly less regular, the Si-O-Si angle slightly greater, in the high-temperature form. Recent work by Frazer & Pepinsky (1952) shows a similar decrease in regularity for the  $PO_4$  tetrahedron in  $KH_2PO_4$  between  $126^\circ$  K. and room temperature (with no noticeable change over its transition point at  $123^\circ$  K.).

Not much is known about the bond system of Ti. Matthias & von Hippel (1948) have suggested that  $3d$ ,  $4s$ ,  $4p$  orbitals come successively into play. The ground state of Ti is  $3d^24s^2$ , and one might guess that with increasing temperature the sets of bonding orbitals utilized would be  $[d^2]$ ,  $[d^3p]$  or  $[d^2s]$ ,  $[d^2sp^2]$ ,  $[d^2sp^3]$ .

### 7. Bond systems in various perovskite-type structures

In this connection, it is of interest to consider other compounds of perovskite type. Among these, the following have been reported as ferroelectric (though in some cases the classification may need to be reviewed):  $PbTiO_3$  (Shirane, Hoshino & Suzuki, 1950);  $PbZrO_3$  (Roberts, 1950);  $NaNbO_3$ ,  $KNbO_3$ ,  $NaTaO_3$ ,  $KTaO_3$  (Matthias, 1949);  $RbTaO_3$  (Smolenskii & Kozhevnikova, 1951);  $WO_3$  (Matthias & Wood, 1951). Matthias (1950) has suggested that the smaller or 'octahedral' atom must be a rare-gas-type ion, and Matthias & Remeika (1949) have drawn attention to the wider ferroelectric range shown by compounds of Nb and Ta than by those of Ti.

In all these structures, the choice of bonding orbitals

by the octahedral atom will be determined partly by its intrinsic nature, partly by the volume available to it. If its ionic radius is large enough to let it fit exactly into the octahedral hole of the framework made by O's and the large atom, the geometrical conditions of ionic packing are satisfied, and there will be a tendency to use the octahedral bond system. If the radius is rather too small, another bond system will be favoured. The limiting value is not determined purely geometrically, but depends also on how far the atom has an intrinsic preference for using  $d$  orbitals. It is assumed that this tendency is likely to increase towards the right of the Periodic Table, where more  $d$  orbitals are in fact used; here the ground state of the atom may provide a clue.

There is a second effect of ionic radius, concerning the role of the large atom. If it is too small for its site, the oxygen framework will pucker and crumple up round it. This may favour bond systems other than octahedral, but it is likely to result in non-parallel displacement of the atoms, and in large unit cells, multiples of a sub-unit which is a slightly distorted version of the cubic unit.

These ideas may explain the otherwise somewhat puzzling situation in the niobates and tantalates (cf. Vousden, 1951a). The transition temperatures and symmetries of these are given in Table 2, in comparison with those of the titanates. The ground states of Nb and Ta are  $4d^45s$  and  $5d^36s^2$  respectively, so that Nb is likely to have a greater tendency than Ta to form bonds involving  $d^3$ , and both a greater tendency than Ti (which is  $3d^24s^2$ ). When this effect and the size of the octahedral cation work in opposite directions, one cannot predict from present knowledge which will predominate. Apart from this indeterminacy, the transition temperatures of all the compounds in Table 2 fall into place qualitatively. The compounds  $NaNbO_3$ ,  $NaTaO_3$  and  $CaTiO_3$  represent the puckered type with a multiple cell.

In  $WO_3$  there is no large ion, so that the arrangement will depend wholly on the radius and bonding of the W atom. Its ground state is  $5d^46s^2$ , suggesting that it will use  $d$  orbitals readily; hence, though its radius is quite appropriate for 6-coordination, a puckered structure with tetrahedral bonds is likely to persist to a high temperature. This is discussed in more detail in § 8.

### 8. Puckered structures: $NaNbO_3$ and $WO_3$

Puckered structures are recognised as such by their multiple cells, but the exact nature of the atomic displacements from the idealised structure is much more difficult to determine. The only such structure which has been investigated in detail is  $NaNbO_3$  (Vousden, 1951b). This (if one takes the arrangement corresponding to Vousden's Fig. 3(b)) has a tetrahedral environment for the Nb's. There are marked differences in length between the Nb-O distances,

Table 2. Modifications of perovskite-type structures, and their transition temperatures

	CaTiO <sub>3</sub>	SrTiO <sub>3</sub>	BaTiO <sub>3</sub>	NaNbO <sub>3</sub> *	KNbO <sub>3</sub>	NaTaO <sub>3</sub>	KTaO <sub>3</sub>	RbTaO <sub>3</sub>
High temperatures	Orthorhombic, multiple	Cubic, single	Cubic, single	Cubic	Cubic, single	Orthorhombic, multiple?	Cubic	Cubic
			640° C.	640° C.	435° C.			
Room temperature	Orthorhombic, multiple	Cubic, single	Tetragonal, multiple	Tetragonal, multiple	Tetragonal, single	Orthorhombic, single	Cubic	Tetragonal, single?
			370° C.	370° C.	225° C.			
Low temperatures	Orthorhombic, multiple	Cubic, single	120° C.	Orthorhombic, multiple	Orthorhombic, single	Orthorhombic, multiple?	Cubic	Tetragonal, single?
			0° C.	No transition to 100° K.	No transition to 223° K.			
			Orthorhombic, single	No transition to 183° K.	?			
			Rhombohedral, single					

\* Different values are given for the transition temperatures (Wood, 1951; Matthias & Remelka, 1951; Vonsden 1951a).

which fall into three groups; using the notation of § 6, Nb-O<sub>1</sub> is about 1.76 Å, Nb-O<sub>2</sub> about 1.95 Å, and unbonded Nb-O about 2.16 Å as compared with 2.01 Å for the sum of the Goldschmidt radii. The differences are larger than for the corresponding structure in BaTiO<sub>3</sub>, indicating the greater preference for the use of tetrahedral bonds. The tetrahedra form chains parallel to the  $\gamma$  axis, which are puckered, as if in an effort to secure a lower O coordination for the Na atom. In the idealized cubic structure, the Na-O distance would be 2.78 Å; the sum of the Goldschmidt radii (corrected for 12-coordination) is only 2.40 Å. The corresponding distance in cubic KNbO<sub>3</sub> is 2.86 Å, the sum of the radii 2.78 Å. By distortions of the magnitude found experimentally in NaNbO<sub>3</sub>, some of the Na-O distances are reduced to about 2.5 Å. (Doubts about Vonsden's structure expressed by Pepinsky (1952) have been answered by Vonsden (1952); but even if the space-group were incorrect, the parameters would probably not be greatly affected.)

A puckered or multiple perovskite-type structure is also found in WO<sub>3</sub> at room temperature (Braekken, 1931). The oxygen parameters are not known, but unless the displacements from ideal positions are unexpectedly large the environment of the W's is tetrahedral, the tetrahedra forming chains. The three sets of W-O distances are about 1.65, 1.8, 2.05 Å respectively, as compared with the radius sum of 1.94 Å.

It is important to notice that neither example of a puckered structure, NaNbO<sub>3</sub> or WO<sub>3</sub>, has its atomic displacements confined to one direction in space. In NaNbO<sub>3</sub>, the Na and O atoms are displaced in two directions at right angles, and the same is true of the W atoms in WO<sub>3</sub>. There seems no structural reason to suppose that displacements in puckered structures in general should be more restricted. In fact, a better fit is likely to be achieved if puckering can occur in two dimensions. In PbZrO<sub>3</sub>, antiparallel displacements of Pb atoms in the (010) plane have been recorded (Sawaguchi, Maniwa & Hoshino, 1951) but the displacements of Zr and O have not been determined, and may well be at right angles. This is relevant to the argument against the term 'antiferroelectric' which is advanced at the end of the next section.

### 9. Effect of applied electric field

In tetragonal BaTiO<sub>3</sub>, probably the largest dipoles are those associated with the unshared electron pairs at the O atoms. These dipoles are of two kinds, O<sub>1</sub> and O<sub>2</sub> being different. It should be possible to estimate their magnitude, but this will not be attempted here. Qualitatively, it seems obvious that either should be fairly easily reversible in direction by an applied field; that is, both atoms lie in a potential minimum separated, along the  $z$  axis, by a low barrier from a second symmetrical minimum. Such a state of affairs



has been postulated before for  $O_1$  (Devonshire, 1949; Mason & Matthias, 1948) but not for  $O_2$ . The geometry of the structure shows that it must be so for  $O_2$ ; the angle  $Ti-O_2-Ti$  is about  $170^\circ$ , and the  $O_2-Ba$  bonds are not strong, so that reversal of direction in an applied field should be easy. There seems no need to postulate a large internal field.

The same explanation applies to the structures of other symmetry. In each case there is a reversal of direction of the bond angle at  $O_2$ , and a transfer of  $O_1$  from one cation to another.

It is of interest to notice that at low temperatures very much larger coercive fields are needed to produce reversal (Hulm, 1949). If the necessary fields were in the end unattainably large, the crystal at those temperatures could no longer be classed as ferroelectric, yet the transition to an inactive pyroelectric state would have been fully continuous. Thus the condition of a ferroelectric with 'frozen-in' dipoles is exactly that of an ordinary pyroelectric crystal.

Comparison may be made with the 'electrical twinning' of quartz. Fig. 9 shows a diagram of such

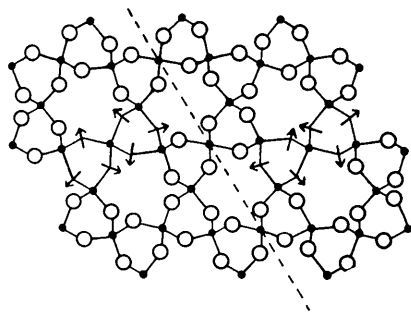


Fig. 9. 'Electrical' twin of quartz; projection on 0001). Arrows indicate comparable dipoles in the two halves. Broken line shows trace of composition plane, which is parallel to diad axis in either half.

a twin, in which arrows have been used to indicate the direction of the dipoles at the oxygen atoms of one repeat unit in each individual. It is clear that the components of the separate dipole moments along the symmetry axis (which is not in this case a unique axis) are reversed in the two halves. This kind of twinning can be induced or eliminated (Wooster, 1947; Thomas & Wooster, 1951) by applying appropriate mechanical stresses near the  $\alpha$ - $\beta$  transition temperature, at which the two halves of the twin become identical. The bond angle  $Si-O-Si$  is not reversed—this was hardly to be expected since its value is about  $144^\circ$  (Wei, 1935)—but the bond system at the Si atom changes orientation as a whole, probably by distortion through the angular distribution appropriate to  $\beta$ (high)-quartz.

From the assumption of permanent dipoles, another deduction follows. If the alignment is not dependent on the internal field produced by the dipoles themselves, a structure with non-parallel dipoles can ex-

perience as great a polarizing force as one with parallel dipoles. The dipoles can only set themselves parallel to the field, however, if there is available a polar structure with energy not very much greater than the original; this may be adopted under the influence of an applied field, and the crystal is then ferroelectric.

Here  $PbZrO_3$  is of interest. Shirane, Sawaguchi & Takagi (1951) found that very pure  $PbZrO_3$  shows no dielectric hysteresis loop below the Curie point, unless very high fields are used, when the loop is anomalous. They conclude that the material becomes ferroelectric at high field strengths, explaining it on the assumption that there exist structures with parallel and antiparallel displacements, not differing much in energy, and that the former can be adopted under the influence of an applied field. Their argument would be unaltered by the more general assumption that the non-ferroelectric structure may contain displacements unrestricted in direction. There is evidence for the existence of several different but related structures in solid solutions of Ba and Sr in  $PbZrO_3$  (Shirane, 1951).

It is possible that this effect may explain the reported anomalies in  $NaNbO_3$ . The structure described by Vousden (1951*b*) cannot have spontaneous polarization, yet Matthias & Remeika (1951) obtain dielectric hysteresis loops. It is by no means obvious that the difficulty could be explained away by assuming an error in Vousden's space-group determination, as Pepinsky (1952) suggests, since the cation displacements are not deduced from the space-group. It is possible that there exists a less stable related structure, which is the true ferroelectric structure. This might account for some of the discrepancies between X-ray and optical measurements of the transition temperature, reported by Wood (1951). It would be interesting to know what changes are observed in X-ray photographs of single crystals in a strong applied field.

There is no definite evidence that  $WO_3$  is ferroelectric at or above room temperature, though the existence of spontaneous polarization could be masked by the high electrical conductivity. The room-temperature structure is not polar, and the bond angle at  $O_2$  (on the assumptions of § 8) differs from  $180^\circ$  by about  $19^\circ$ , as compared with about  $7^\circ$  in  $NaNbO_3$ ; hence any polar structure which could be derived from it by reversal of dipole directions is likely to involve more strain. Recently, however, Matthias & Wood (1951) have reported a form of higher symmetry below  $-50^\circ C.$ , which shows hysteresis loops. Possibly this may be rhombohedral, and if so the homopolar structure to be superimposed on the ionic consists of  $WO_3$  molecules.

It has been suggested that  $PbZrO_3$  (Sawaguchi, Maniwa & Hoshino, 1951) and  $WO_3$  at room temperature (Matthias & Wood, 1951) are 'antiferroelectric'. The present discussion questions the use of the word. There does not seem to be any distinct class of structures with antiparallel displacements, and it is not

easy at an early stage of a structure determination to be sure what all the displacements are; it seems likely that only polar structures, i.e. those with parallel displacements, are ferroelectric, and that non-polar structures with displacements in two dimensions can be transformed into polar structures as readily as those in which displacements are antiparallel. The word 'antiferroelectric' is therefore a misnomer; it was suggested by an analogy with ferromagnetism which does not hold. Experimentally it is possible to distinguish puckered or multiple structures from single-unit structures by X-ray methods; and structures with spontaneous polarisation can be detected by dielectric hysteresis loops, or by movement of domain boundaries in an electric field. These are clear-cut distinctions while other classifications are largely hypothetical. Perhaps a new word is needed for the large class of substances with abnormal electrical properties but no detectable spontaneous polarization, to include ferroelectrics above their Curie point.

### 10. Summary and conclusion

The treatment given above is qualitative rather than quantitative. In contrast to most of the theoretical work which has been done on the subject, it puts the emphasis on the directed bonds in the structure; admitting that structures such as  $\text{BaTiO}_3$  are to be regarded as partly ionic and partly homopolar, it looks for the dipoles required by any formal theory to the localization of electron orbitals accompanying homopolar bonding. Earlier work which recognised the importance of homopolar forces (e.g. Matthias & von Hippel, 1948; Mason & Matthias, 1948; Kay & Vousden, 1949) nevertheless considered their effects only when they were restricted to the original Ti-O directions; here it is assumed that such effects cannot be treated in isolation, but are related to changes in bond angle at all the atoms. This treatment brings the structures of the perovskite family into relation with those of other oxides, and offers a possibility of explaining the very great variety of ways in which the ideal cubic structure is modified in actual compounds. Only the perovskite group of ferroelectrics has been considered in this paper, but the recently-discovered ferroelectrics of ilmenite type,  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  (Matthias & Remeika, 1949), must eventually be included in any comprehensive treatment. The attribution of the peculiar properties of  $\text{BaTiO}_3$  to linear chains of Ti-O-Ti-O dipoles cannot easily be adapted to explain the effect in  $\text{LiNbO}_3$ ; but an approach which considers the preferred bonding orbitals of the atoms looks capable of a wider generalization.

The origin of ferroelectricity must thus be sought in a small change of bond character occurring in a structure whose geometry is compatible with either homopolar or ionic binding; this results in a small displacement of certain atoms which, held by homo-

polar forces, constitute permanent dipoles. An explanation like this would include the  $\text{KH}_2\text{PO}_4$  group of ferroelectrics as well as the  $\text{BaTiO}_3$  group; if, as Frazer & Pepinsky (1952) suggest, a change in the bond system of the K atom is responsible for the transition, the analogy is very close. In general, if the bond angles allow a structure in which the dipoles have parallel orientation, and if the displacements are so small that the potential maximum at the undisplaced position forms only a low barrier, reversal of the dipoles can easily be effected by an external field, and ferroelectricity results. The existence of a spontaneous polarization attributable to atomic arrangement in the low-symmetry structure is the postulate required by the thermodynamic theories; the present paper is an attempt to explain how that polarization arises.

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## Existenzbeweis für eine eindeutige Röntgenstrukturanalyse durch Entfaltung. I. Entfaltung zentrosymmetrischer endlicher Massenverteilungen

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With the help of the folding (*Faltung*) theorem of Fourier transformation a proof is given that the electron-density distribution in matter of *finite size* and *having a centre of symmetry* (or *anti-symmetry*) can be calculated from the X-ray diffraction data alone. For this the fine structure of reflexions, i.e. the general distribution of the scattered intensity in Fourier space and not the integral intensities of reflexions only, must be known.

After elimination of Thomson and polarization factors as well as collimation and other relevant experimental errors, the corrected intensity is transformed through inverse Fourier transformation to the so called *Q*-function of physical space. This continuous *Q*-function is then transformed into a lattice-peak-function having sufficiently small cell dimensions (*Rasterung der Q-Funktion*). From this 'latticed' *Q*-function the required electron-density distribution can be obtained through a folding (*Faltung*) polynomial of finite degree. The electron-density distribution is obtained automatically as a lattice-peak-function having the same cell as that of the *Q*-function. This process gives the solution of an integral equation of the second degree from any one of its boundary values. For the limiting case of infinitely small cells of the lattice, the folding polynomial of infinite degree in Fourier space reduces to a special polynomial of degree  $\frac{1}{2}$ , which is identical with the Fourier transform of the required continuous electron-density distribution. This proves the inherent consistency of this method.

It is to be noted that for matter of infinite size, such a method of evaluation of necessity fails since the *Q*-function is then infinitely extended and consequently has no boundary values.

### I. Einleitung und Problemstellung

Wenn man aus dem an einem Stoff gewonnenen Röntgenbeugungsbild eindeutige Rückschlüsse auf die atomare Struktur des untersuchten Stoffes machen will, stösst man bekanntlich auf einige grundsätzliche Schwierigkeiten. Ist nämlich  $2\theta$  der Streuwinkel,  $\lambda$  die benutzte Röntgenwellenlänge,  $s_0$  ein Einheitsvektor in Richtung der einfallenden,  $s$  in Richtung der gestreuten Röntgenstrahlung, also

$$b = \frac{s-s_0}{\lambda}; \quad |b| = \frac{2 \sin \theta}{\lambda} \quad (1)$$

der reziproke Ortsvektor im Fourerraum,  $x$  der Ortsvektor im physikalischen Raum und  $\rho(x)$  die gesuchte Elektronendichteverteilung im Stoff, so ergibt sich die gestreute Intensität bekanntlich zu

$$J(b) = \beta(b)|R(b)|^2, \quad (2)$$