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The Structure of Ferroelectric Sodium Niobate at Room Temperature

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Single crystals of ferroelectric sodium niobate have been studied by X-ray diffraction. The unit cell is orthorhombic with dimensions $5{\cdot}5682 \times 15{\cdot}5180 \times 5{\cdot}5052$ A., and contains 40 atoms. The space group is $P22_12$. A very unexpected feature of the structure is that the niobium ions are displaced from the special positions in the ideal perovskite structure by 0·11 A. in opposite directions along the a axis. This axis is equivalent to the polar axis in orthorhombic $BaTiO_3$, and the result that the structure is non-polar is in contradiction to the generally accepted theory of the spontaneous polarization of this group of ferroelectric substances.

A general consideration of the factors determining the space group of any pseudosymmetrical compound leads to an explanation of the space group and unit-cell size. A similar orthorhombic distortion, accompanied by atom displacements, occurs in certain other non-ferroelectric perovskite-type compounds in which there is a misfit of packing of the atoms. This suggests that, as a similar misfit occurs in $NaNbO_3$, the displacements can be described in terms of this misfit of the atomic radii in the structure, and that the orthorhombic distortion which results from the ferroelectricity would therefore lower the energy associated with these displacements. The shifts cannot, however, be completely explained in terms of these packing considerations alone, but can be accounted for if there is in addition an appreciable proportion of homopolar bonding between the niobium and oxygen atoms.

1. Introduction

In another paper (Vousden, 1951*b*) a description is given of the determination of the unit-cell dimensions at room temperature of certain pseudocubic compounds of niobium and tantalum, the ferroelectric properties of which were recently reported by Matthias (1949). It is shown that the symmetry of sodium niobate at room temperature is orthorhombic, and that the pseudocubic distortion, which is of the order 1 %, is similar to that which barium titanate shows between −5 and −90° C. (see Forsbergh, 1949; Kay & Vousden, 1949). Both compounds have also a tetragonal, pseudocubic phase (Fig. 1 (*a*)) at higher temperatures. Fig. 1 (*b*) shows the orthorhombic type of distortion referred to pseudocubic axes. The symmetry is monoclinic if referred to these axes, but is orthorhombic if referred to new axes a, c bisecting the angle (β) between the monoclinic axes a', c' (Fig. 1 (*c*)).

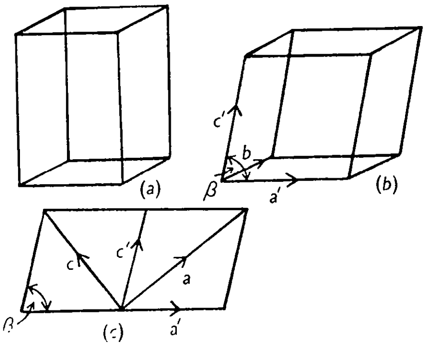

Fig. 1. (*a*) Tetragonal distortion. (*b*) Monoclinic distortion. (*c*) Relation between the orthorhombic and monoclinic axes.

The slight distortion of the structure from cubic, and also the general dependence upon the index of the intensities of reflexions in the powder photograph clearly showed that any displacements of the atoms from the ideal perovskite positions must be very small. All reflexions observed could be indexed on the assumption of a primitive monoclinic cell of approximate dimensions $4 \times 4 \times 4$ A., and with these cell dimensions only polar or random displacements of the atoms could take place along one of the orthorhombic axes. As the material is ferroelectric the former would be expected, and by analogy with $BaTiO_3$ the polar axis should be a and the space group $B2mm$. Now, at high Bragg angles intensity anomalies were observed, and in particular the 505 and 701 reflexions were absent. Taking into account the background intensity, this implied that these intensities must be not greater than about one-quarter of those of the 050 and 107 reflexions, whereas if the atoms occupied the special positions in the unit cell the intensities of the corresponding pairs of reflexions would be equal. At the value of $\sin\theta/\lambda$ for these reflexions the niobium atom contributes 99·7 % to the total intensity, and it therefore follows that the intensity differences can be explained only if the niobium atom is displaced along the a axis; simple calculation shows that the order of

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displacement must be 0·1 A. There are then two possibilities: either the displacements are random, and *b* is actually about 4 A.; or else the true axial length is a multiple of this, and the different niobium atoms in the larger unit cell are displaced in opposite directions along the *a* axis. In the latter case the resultant weak reflexions must be undetectable because of the background intensity. An X-ray investigation of single crystals of the substance was therefore undertaken in order to investigate this problem, a brief account of the results having already been reported (Vousden, 1951*a*).

2. The production and optical properties of suitable crystals

Crystals of sodium niobate ideally suited for X-ray investigation were prepared by dissolving the polycrystalline material in sodium chloride at high temperatures. No detailed investigation of the factors influencing the production of large crystals was undertaken, but the following conditions proved satisfactory for this investigation. The solvent/solute ratio was about 3, the melt was heated to 1100° C. in a platinum crucible for several hours, and was then cooled to 750° C. in a few hours. During this time the solvent mostly evaporated and needle-shaped crystals resulted. These were of cubic habit, of length up to 1 mm. with cross-section varying from 10^{-6} to 10^{-4} cm.^{2}. The average degree of twinning was much less than that of $BaTiO_3$ in the orthorhombic phase (see Kay & Vousden, 1949), and a few untwinned crystals were found in which the *b* axis was normal to the axis of the needle. Under polarized light these showed either symmetrical or straight extinction, depending on whether *b* was parallel or perpendicular to the direction of the incident light respectively.

Crystals in which *b* was parallel to the needle axis always showed straight extinction, and any twinning across (101) was undetectable. Eight different crystals of this type, which appeared untwinned, were shown by X-ray Laue photographs to be twinned across (101). Twinning across (111) was rather rare, and no lamellae corresponding to those in $BaTiO_3$ were observed (see Forsbergh, 1949; Kay & Vousden, 1949), although areas of crystal closely twinned about (101) were quite common.

3. Choice of crystal and measurement of unit-cell dimensions

The desirable experimental conditions for the structure analysis of a pseudosymmetrical compound are discussed elsewhere (Vousden, 1952). In order to obtain accurate comparative intensities the crystal must be untwinned and of square cross-section. Moreover, in order to reduce the absorption corrections, which have not been calculated for a square crystal, the crystal thickness d must be appreciably less than $2/\mu$, where μ is the linear absorption coefficient. The crystal chosen for rotation about *a*′ (or *c*′) satisfied all these requirements, except that about 5 % of its volume was a small twin component; this, however, caused little difficulty because its position was accurately known. The crystal dimensions were 0·020 × 0·020 × 0·2 mm., which corresponds to $d/\mu = 0{\cdot}74$. The exposure required for a complete rotation photograph of this crystal, using a camera of radius 3 cm., was 10 days.

For rotation about *b* it was necessary to choose a similar crystal with the needle axis perpendicular to the rotation axis, as no untwinned crystal with *b* parallel to the needle axis was found (§ 2). Even though a crystal was chosen in which the length/width ratio was as small as possible the absorption factor was still large and variable, so that, except in special cases, no accurate intensity measurements could be made from these photographs.

Complete rotation photographs about the *a*′ (or *c*′) and *b* axes with filtered Cu $K\alpha$ radiation showed the dimensions of the monoclinic unit cell to be nearly 8 × 16 × 8 A. instead of about 4 × 4 × 4 A. as obtained from the powder photographs. Subsequent indexing showed that this cell was *B*-face centred, and consequently the true orthorhombic cell is primitive and contains forty atoms. Its dimensions are therefore

$$5{\cdot}5682 \times 15{\cdot}5180 \times 5{\cdot}5052 \text{ A.},$$

using the accurate values of the cell dimensions which were obtained from the powder photographs (Vousden, 1951*b*), where no extra weak reflexions, corresponding to the doubling or quadrupling of cell dimensions, were visible.

4. Space-group determination

Only the observation of reflexions which may be extinguished can give conclusive information regarding the space group of a pseudosymmetrical compound. This is because of the extreme weakness of certain groups of reflexions from this type of structure (see Vousden, 1952). Such reflexions may not be distinguishable from the background intensity even with small oscillation photographs and heavily filtered radiation.

In $NaNbO_3$ there were no absences attributable to glide planes, and the 001 reflexion showed that there cannot be a screw axis parallel to *c*. The reflexions $h00$ and $0k0$ were absent for h and k odd. From this information the possible space groups are $P22_12$, $P2mm$, $Pm2m$, $Pmm2$, $Pmmm$, $P222$, $P2_12_12$ and $P2_122$. Now since the atoms are known to be only slightly displaced from the special positions of the perovskite structure, it follows that if the atoms are assigned these positions the symmetry operations of the space group must bring similar atoms into coincidence. This condition rules out the seventh and eighth possibilities.

Suppose now the space group were $P222$. The rotation axis parallel to *b* must pass through the niobium atoms, and these atoms could then be displaced only along this axis. However, the powder photographs conclusively establish a displacement parallel to a, so that this possibility may be rejected. For similar reasons $Pmmm$, $Pmm2$ and $Pm2m$ may be ruled out. Conclusive evidence for the rejection of $P2mm$ is given in § 8, and, anticipating this result, one may therefore definitely say that the space group is $P22_12$ if the symmetry is orthorhombic.

Any polarization of the structure would remove two of the symmetry axes, and would result in a shear of the face perpendicular to the polarization. This would change the space group to $P2$ or $P2_1$. A careful determination by X-rays of the equivalence of the appropriate spacings showed, however, that any shear of the faces was less than 0·3′. Also, the optical extinction directions were shown to be parallel to the orthorhombic axes within 0·2°. A shear of one of the faces ($\delta\theta$) would cause a change of extinction direction of the order $\delta\theta/\delta s$, where δs is the orthorhombic strain, because the photoelastic constants in a cubic crystal will be all of the same order of magnitude. Since $\delta s \sim 10^{-2}$ it may be concluded that $\delta\theta < 0{\cdot}1'$, so if there is any deviation of the symmetry from orthorhombic, then this deviation is less than $\frac{1}{300}$ of the observed orthorhombic deviation.

5. Discussion of method of structure analysis

Suppose for simplicity that only one atom, of scattering factor f_i, is displaced from its position in the ideal perovskite structure. The symmetry operations will mean that opposite displacements of similar atoms take place so that, for example, the unit-cell dimension along a is doubled. Rotation photographs about this axis will then show additional weak layer lines. It may be shown that to a first approximation the intensities of the original reflexions are thereby unchanged, and that the structure factors of the additional reflexions are proportional to $f_i \sin 2\pi h\delta_i$. Here δ_i is the fractional displacement of the atom along the a axis. The value of δ_i may therefore be immediately determined from the intensities of these reflexions.

The function $f_i \sin 2\pi h\delta_i$ is characteristic of the particular atom. It increases with $\sin\theta/\lambda$ from zero to a maximum value, and subsequently continuously decreases. With Cu $K\alpha$ radiation the maximum occurs for light atoms when $\theta \sim 40°$, and for heavier atoms when $\theta \sim 90°$. Additional weak reflexions due only to the displacement of, say, niobium atoms may thus be immediately distinguished from those due only to the displacement of sodium or oxygen atoms.

In the general case in which all the atoms are displaced it is found that to a first order the displacements of a given atom still contribute only to certain reflexion classes, and these relations may be calculated from a knowledge of the space group of the pseudosymmetric structure and of the relative phases of the undisplaced atoms. This results in a systematic dependence of the intensities of the weak reflexions upon the index, and from this dependence the relations between the displacements may be calculated. Certain ambiguities may arise in the more complicated cases, but these may always be stated in the final result. In particular, a superimposed polar displacement of the atoms may not be detected.

It is convenient to refer the indices to such a cell that they are the same for the structure in which the atoms are not displaced as for the pseudosymmetric structure. One or more of the indices of the additional weak reflexions are therefore fractional. Thus in $NaNbO_3$ the indices are subsequently referred to a monoclinic cell of approximate dimensions 4 × 4 × 4 A., which contains one formula unit, and is subsequently referred to as a subcell (Vousden, 1952).

It is very important to know the conditions under which this interpretation of the reflexions is valid. If an error of 10 % in the values of the structure factor is allowed, this means that with Cu $K\alpha$ radiation and displacements of 0·1 A. the approximation is valid up to $\theta \sim 60°$. However, an immediate practical test is the existence of the systematic relations between the intensities. This was a striking feature of the rotation photographs of $NaNbO_3$; in fact, a large number of reflexions were absent, and corresponding reflexions of different classes were of equal intensity. A direct interpretation of these absences and equalities in terms of particular displacement relations may be made, and the information so obtained is independent of the actual measurement of the intensities. Consequently, once the relations between the displacements have been obtained from this information, and the approximation has been shown to hold, it is strictly necessary to measure the intensities of only a comparatively small number of reflexions in order to determine the magnitudes of the displacements; thus cross-checking is often possible. In the subsequent description of the structure determination it is therefore possible to indicate the actual intensity information from which each result was calculated. A detailed exposition of the evidence and arguments is omitted for reasons of space.

6. Determination of the displacements

The classes of additional weak reflexions are

$$h,\tfrac{1}{4}k,l;\quad h,\tfrac{1}{2}k,l;\quad \tfrac{1}{2}h,\tfrac{1}{4}k,\tfrac{1}{2}l;\quad \tfrac{1}{2}h,\tfrac{1}{2}k,\tfrac{1}{2}l;\quad \tfrac{1}{2}h,k,\tfrac{1}{2}l,$$

where the indices are proper fractions. The dependence of the intensities upon $\sin\theta/\lambda$ clearly showed that the displacements of the niobium atom contribute only to the first class. The second class was absent. From this information it was conclusively and unambiguously shown that the arrangement of Nb atom displacements along the a axis is that drawn in Fig. 2. In the ideal perovskite structure the screw axes therefore pass through the Nb atoms, while the rotation axes pass through the Na and O_b atoms, and these atoms may be displaced only along these axes. (O_a, O_b, O_c are defined as the oxygen atoms with co-ordinates $0, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, 0, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, 0$, respectively, referred to the unit cell of the ideal perovskite structure.) The general position in the orthorhombic unit cell is fourfold, and only the Na and O_b atoms lie on special positions. Twenty-six parameters then define the displacements of the atoms.

The determination of the displacement of the Nb atom as $0{\cdot}11 \mp 0{\cdot}03$ A. provided a valuable check on the correctness of the space group and confirmed the conclusions deduced from the powder photographs (§ 1). The only other detectable displacement of this atom was parallel to b and was $0{\cdot}04 \mp 0{\cdot}02$ A. The displacements of the two crystallographically independent atoms in the same layer (Fig. 2) were equal within the experimental error, and there was no measurable displacement of this atom parallel to b.

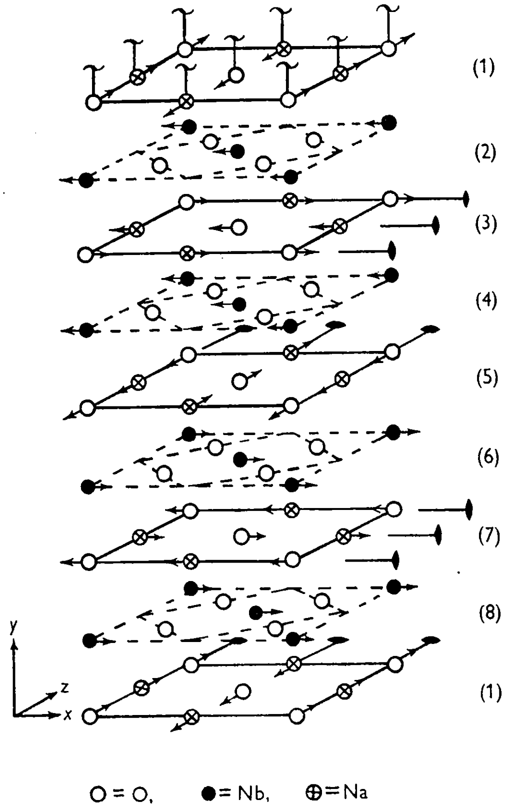

Fig. 2. The atom displacements in the orthorhombic unit cell of $NaNbO_3$. The shift of the O_a and O_c ions and the small z shift of the Nb atom have been omitted for the sake of clarity.

The displacements of the $Na+O_b$ atoms can contribute to a first approximation to the classes $\frac{1}{2}h{\cdot}\frac{1}{4}k{\cdot}\frac{1}{2}l$ and $h{\cdot}\frac{1}{4}k{\cdot}l$. The former corresponds to opposite and the latter to equal displacements of similar atoms in the same layer. Only the latter were found, and the intensities of the $\frac{1}{2}h{\cdot}\frac{1}{4}k{\cdot}\frac{1}{2}l$ class showed that the arrangement of displacements was that drawn in Fig. 3 (a). Here the displacements in the layers 1, 5 are equal to those in the layers 3, 7 within the limit of measurement (Fig. 2).

The reflexions $h{\cdot}\frac{1}{2}k{\cdot}l$ and $\frac{1}{2}h{\cdot}k{\cdot}\frac{1}{2}l$ result from the displacement of the O_a and O_b atoms. Eight independent parameters define the displacements in the ac plane. The former class required the arrangement drawn in Fig. 3 (b) or (c), where the oxygen displacement of about 0·2 A. may be either towards or away from the niobium atom. The latter class showed that superimposed upon this displacement was a twisting of the configuration of the four oxygen atoms surrounding the niobium. Here the displacement was about 0·1 A.

The displacements of the oxygen atoms along b may be conveniently divided into those in which all four atoms in the same ac plane move in the same direction, and those in which two adjacent pairs move in opposite directions. The former contribute to the reflexions $h{\cdot}\frac{1}{2}k{\cdot}l$ and the latter to the strong reflexions hkl. The absence of the former class showed that the magnitude of the first type of displacement was less than 0·05 A., but the latter displacements could not be determined because the proportional change in the intensities was too small.

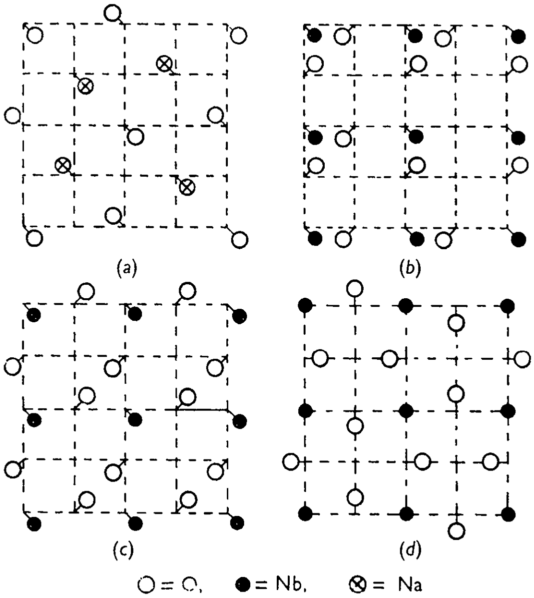

Fig. 3. (a) The displacement of the $Na+O_b$ atoms. (b), (c) The two possible displacements of the $Nb+O_a+O_c$ atoms. (d) The probable superimposed displacement of the O_a+O_c atoms.

So far the intensities of all the reflexions except the $\frac{1}{2}h{\cdot}\frac{1}{2}k{\cdot}\frac{1}{2}l$ class have been accounted for. However, none of the displacements contributes to a first order to these rather weak reflexions, but the dependence of the intensities upon $\sin\theta/\lambda$ clearly showed that they were due to the displacement of the sodium or oxygen atoms. These intensities agreed fairly well with the assumption that they were a second-order result of the displacement of the O_a+O_b atoms, but no detailed interpretation was made because of the large number of alternative solutions.

Fig. 2 shows the displacements of the Nb, Na and O_b atoms, and in Table 1 the values of the displacements are given. A large number of these are equal or zero within the experimental error, although the parameters

Table 1. *Atom displacements in the eight different layers of the structure*

Layer	Nb			O_a+O_c		Layer	Na			O_b		
	x	y	z	x, z	y		x	y	z	x	y	z
2 a	$-0{\cdot}11^{1}$	$<0{\cdot}04^{3}$	$+0{\cdot}04^{5}$	Eight independent parameters of about 0·2 A.	Four independent parameters all less than 0·05 A.	1 a	—	—	$+0{\cdot}15^{21}$	—	—	$+0{\cdot}2^{25}$
b	$-0{\cdot}11^{2}$	$<0{\cdot}04^{4}$	$+0{\cdot}04^{6}$			b	—	—	$-0{\cdot}15^{22}$	—	—	$-0{\cdot}2^{26}$
4 a	$-0{\cdot}11^{1}$	$<0{\cdot}04^{3}$	$-0{\cdot}04^{5}$			3 a	$-0{\cdot}15^{19}$	—	—	$-0{\cdot}2^{23}$	—	—
b	$-0{\cdot}11^{2}$	$<0{\cdot}04^{4}$	$-0{\cdot}04^{6}$			b	$+0{\cdot}15^{20}$	—	—	$+0{\cdot}2^{24}$	—	—
6 a	$+0{\cdot}11^{1}$	$<0{\cdot}04^{3}$	$-0{\cdot}04^{5}$			5 a	—	—	$-0{\cdot}15^{21}$	—	—	$-0{\cdot}2^{25}$
b	$+0{\cdot}11^{2}$	$<0{\cdot}04^{4}$	$-0{\cdot}04^{6}$			b	—	—	$+0{\cdot}15^{22}$	—	—	$+0{\cdot}2^{26}$
8 a	$+0{\cdot}11^{1}$	$<0{\cdot}04^{3}$	$+0{\cdot}04^{5}$			7 a	$+0{\cdot}15^{19}$	—	—	$+0{\cdot}2^{23}$	—	—
b	$+0{\cdot}11^{2}$	$<0{\cdot}04^{4}$	$+0{\cdot}04^{6}$			b	$-0{\cdot}15^{20}$	—	—	$-0{\cdot}2^{24}$	—	—
Probable error		$\mp 0{\cdot}03$	$\mp 0{\cdot}02$				$\mp 0{\cdot}05$			$\mp 0{\cdot}05$		

Values are in Ångström units. The divisions (a), (b) refer to the crystallographically different atoms in the same ac plane. Similar numerical suffixes indicate those displacements which are related by symmetry operations.

are crystallographically independent. With the possible exception of the one type of displacement of the $O_a + O_b$ atoms, the displacements are confined to the ac plane. The structure may thus be conveniently regarded as consisting of eight layers of displaced atoms. Within the same layer the adjacent Nb atoms move in the same direction and the $Na + O_b$ atoms move in opposite directions.

7. Ambiguities in the structure determination

It was stated in § 5 that the systematic method of interpretation of the intensity information enabled any ambiguities in the structure determination to be noted. Two ambiguities of this type do, in fact, arise. In the first place it is impossible to decide from the available intensity information whether the displacements of the oxygen atoms are towards or away from the niobium atom (Fig. 4 (*b*), (*c*)); and secondly, it is impossible to determine the magnitude of the opposite displacements of the $O_a + O_c$ atoms in the same layer along the y axis. This arrangement corresponds in the ideal perovskite structure to the opposite displacement along, say, the y axis of the adjacent oxygen atoms normally in the $0, \frac{1}{2}, 0$ plane. This does not involve any doubling of the cell dimensions, and thus only the intensities of the *hkl* reflexions are slightly altered.

The large scattering factor of niobium enabled the displacements of this atom greater than about 0·05 A. to be determined with certainty, and this could also be done for the Na and O_b atoms because these displacements are limited to the direction of the rotation axes. However, the magnitude of the total displacement of the $O_a + O_c$ atoms in the ac plane is such that the first-order approximation for the intensities is insufficient, and under these circumstances the displacements drawn in Fig. 4 (*b*)–(*d*) can only be regarded as probable. This is emphasized by the fact that the eight parameters defining the displacements are crystallographically independent, yet only two parameters are required to define the displacements in Fig. 4 (*b*), (*c*).

8. Discussion of the space group *P*2*mm*

In § 4 it was shown that the only possible alternative to the space group $P22_12$ was *P*2*mm*, if the symmetry is orthorhombic. Now the unambiguous displacements of the Nb atoms along the a axis (§ 1) would mean that in this case reflexion planes perpendicular to b would pass through the layers 3 and 7 and those perpendicular to c would pass through the Nb and Na atoms. Assuming this space group, one may again calculate the classes of reflexions to which the various displacements contribute, but it is then found to be impossible to account for the intensities. One important instance may be mentioned: the intensities of the reflexions $\frac{1}{2}h, \frac{1}{4}k, \frac{1}{2}l$ would be due to the displacement of the $O_a + O_c$ atoms instead of the $Na + O_b$ atoms, and it may be easily shown that the existence of the reflexion planes perpendicular to c would mean that the intensity would be greatest when $h = \mp l$. Instead, however, it is found that these reflexions are absent on the rotation photographs, though if $h \neq \mp l$ the intensities are quite strong. This alternative must therefore be rejected.

9. Discussion of the structure

This structure determination raises a serious problem in the theory of ferroelectricity because the space group of $NaNbO_3$ in the ferroelectric state is non-polar. The complex arrangement of atom displacements which is observed cannot be essential to the existence of the ferroelectricity, for such an increase in cell size does not occur in tetragonal barium titanate, in which compound a polar displacement of atoms along the tetrad axis has recently been reported (Kaenzig, 1950). In this paper only the experimental evidence for the non-polarity is discussed, and a possible cause of the atom displacements is suggested.

The causes of pseudosymmetrical structures can be discussed in terms of the free energy of the pseudo-structure and that of the corresponding ideal structure (Vousden, 1952). It is concluded that the space groups of such compounds will be non-polar because of short-range dipolar interaction between the displaced atoms, and because the free energy would then be independent of boundary conditions. The opposite atom displacements in $NaNbO_3$ can therefore be explained by such dipolar interaction, but in this case the structure would not be polar. If self-polarization were caused by some other short-range force then an orthorhombic polar space group should result and opposite displacements of atoms should not occur, while if the forces producing the polarization were long range, and of a dipolar nature, it would be necessary to suppose that although short-range dipolar interaction produced the non-polar displacements, the long-range dipolar forces produced a permanent polarization. The symmetry of the structure would be reduced because of the shear of one of the (100) planes, and this shear must be less than 0·1′ (§ 4). The accompanying atom shifts would be superimposed upon the non-polar shifts and would not be directly detectable by X-rays. This possibility seems highly unlikely, but cannot be conclusively rejected in the light of present evidence, particularly as the permanent polarization of these ferroelectric materials has previously been unquestioned.

No value of the spontaneous polarization has yet been published, but we have observed twin boundaries to move under an applied d.c. field of about 10^4 V.cm.$^{-1}$,* which is the same order of magnitude of field required to produce such changes in crystals of $BaTiO_3$ (see Kay, 1948). This result, taken in conjunction with the existence of a tetragonal phase in both compounds (Vousden, 1951 *a*), and the fact that the transition temperatures differ only by a factor of about two, strongly suggests that the order of magnitude of the saturation polarization of the two compounds is the same. The higher transition temperature of $NaNbO_3$, and its larger strain at room temperature, suggests perhaps that its value is rather higher than that of $BaTiO_3$. By analogy with $BaTiO_3$, the polar axis should then be *a* (see Forsbergh, 1949; Kay & Vousden, 1949), yet this is the axis along which the niobium atoms move in opposite directions by 0·11 A.

Kaenzig reports a shift of the titanium atom in tetragonal barium titanate at room temperature of about 0·06 A. Any polar displacement of the niobium atom along the *a* axis in $NaNbO_3$ must result in a shear of the *bc* plane because of the crystal symmetry. Using a typical value for the piezoelectric coefficient e_{14} (10^6 e.s.u.) the value of such a shear would be about 300′ if $P_s = 10^{-5}$ coulomb. The value of the coefficient in $NaNbO_3$ must be rather less than that of a normal piezoelectric crystal as the electromechanical coupling is due only to the small displacement of the atoms, but it would hardly be small enough to produce a shear of less than 0·1′, which the experimental evidence requires (§ 4). Measurement of this coefficient should conclusively settle the existence or absence of a permanent polarization in this material, but suitable crystals for this purpose have not yet been obtained.

The origin of the observed atom displacements in the unit cell will now be considered. The discussion falls into two sections: first, the cause of the particular geometrical relations of the displacements, that is, of the space group and unit-cell size; and secondly, the cause of the displacements within the subcell, or of the change of nearest-neighbour interatomic distances.

It can be shown that if the forces producing such a distortion are effectively nearest-neighbour forces between the atoms, then the space group will relate the displacements of similar atoms in all the different basic units within the unit cell (Vousden, 1952). The equal and opposite displacements of equivalent atoms in different basic units result from dipolar interaction, and in an increase in cell size.

If in the perovskite structure space groups which limit the displacement of atoms to along one axis only are ruled out, then the only possibilities are $P22_12$, $P2_12_12_1$ and *Pcmn*, in the orthorhombic crystal classes D_2, D_2 and D_{2h} respectively, and the monoclinic space group $P2_1c$. Structures with the first two space groups will have unit-cell dimensions of about 5·6 × 16 × 5·6 A., and the third will have a structure with the unit-cell dimensions of about 5·6 × 8·0 × 5·6 A. These cells will contain four and eight subcells respectively. Structures with the space group $P2_1c$ will have cell dimensions 4 × 8 × 8 A. and will contain four subcells. Mention may also be made of the rhombohedral space group $R\bar{3}m$, in which the unit-cell dimensions will be about 5·6 A. with $\alpha \doteqdot 60°$. However, in this case only three parameters are required to define the atom displacements because of the high symmetry, and consequently the possible changes in the interatomic distances are very limited.

The relation of the unit-cell size of $NaNbO_3$ to its space group thus follows from quite general considerations, and, therefore, it is only necessary to explain why of the three possible orthorhombic space groups $P22_12$ actually occurs. The difference between $P22_12$ and $P2_12_12_1$ in these circumstances is very slight; in fact, displacements of the niobium atom alone are consistent with either possibility within the accuracy of the determination. The important distinction between $P22_12$ and *Pcmn* is probably that only the former allows both the metallic atoms to be displaced. A movement of both the niobium and sodium atoms in the *ac* plane can be combined only in a unit cell about 16 A. in length along the *b* axis if the structure is to be non-polar. The remaining problem is thus to account

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* In view of the failure to obtain such movement with fields of 15,000 V. cm.$^{-1}$ by Wood (1951) some further details seem desirable. Fields were applied, by the apparatus previously described (Kay & Vousden, 1949), parallel to the pseudocubic axes of well-developed crystals of $NaNbO_3$ with linear dimensions of the order $10^{-1} \times 10^{-1} \times 10^{-2}$ cm. When the field nearly attained the electrical breakdown value migration of the twin boundaries parallel to the pseudocubic diagonals began. The value of the field required was not accurately measured, but was certainly not greater than $2{\cdot}5 \times 10^4$ V.cm.$^{-1}$; it depended very critically on the electrode contact. As the field was varied the whole of the crystal surface became covered by migrating twin boundaries, exactly as in $BaTiO_3$. One could not tell, however, whether the axis which tended to be aligned parallel to the field was *a* or *c*. In some crystals no migration was observed because electrical breakdown first occurred.

for the short-range forces causing an alteration of both the Nb–O and Na–O interatomic distances.

Now certain other non-ferroelectric compounds having the perovskite structure are orthorhombic with A–O distances (where A is the larger metallic atom) appreciably larger than the sum of the Goldschmidt radii corrected for co-ordination number. Megaw (1946) suggested that the orthorhombic distortion occurs in order that the oxygen atoms may be displaced towards the A atoms, and consequently that the misfit of packing of atoms may be reduced. In $NaNbO_3$ this misfit is very marked; in fact, the difference between the observed and ideal Na–O distances is 0·4 A. (see Vousden, 1951*b*). Consequently, on purely empirical grounds an orthorhombic distortion of this structure might be expected independently of its ferroelectric properties, and this suggests that when the orthorhombic phase results from the ferroelectricity atom displacements will occur which may be regarded as reducing the misfit. The additional lowering of the free energy of the crystal resulting from these displacements may be sufficient to prevent the rhombohedral phase occurring at lower temperatures (cf. $BaTiO_3$), since in this phase the additional restrictions imposed by the symmetry would severely limit the displacements. Such displacements would not be expected in the orthorhombic phase of $BaTiO_3$, or in that of $KNbO_3$, for in these compounds the A ion is too large.

These conclusions are at least consistent with the experimental facts known at present. For example, in $KNbO_3$ there are no anomalies in the intensities of the powder lines which would indicate a larger unit cell, and this has recently been confirmed by X-ray investigations on single crystals by other workers in this laboratory. No rhombohedral phase has been found in $NaNbO_3$ as low as −173° C. (Vousden, 1951*b*), but one might be expected from these arguments in $KNbO_3$. It may also be noted that it has been established in this laboratory that the space group of $CaTiO_3$ is *Pcmn*, in agreement with the previous conclusions of possible space groups of these perovskite pseudocubic compounds.

When, however, the displacements are considered in detail it is clear that simple ideas involving atomic radii are by themselves insufficient to account for the complex structure. From such considerations alone one would expect only a displacement of the O atoms towards the Na atoms which would be perpendicular to the Nb atoms. This occurs for the O_b atoms, but there is no evidence that it occurs for the O_a and O_c atoms. It might be argued that the probable increase in the Nb–O distance in the ac plane is a result of the Nb–O distance being too short, but unfortunately the relations of these displacements are uncertain, though the displacements certainly exist (Fig. 3). Some form of directed force is clearly required to account for the rather complicated displacement of these atoms in the ac plane, and the only likely cause of this is an appreciable homopolar bonding of the niobium to the oxygen atom. If such bonding resulted in these displacements, which reacted on the $Na+O_b$ plane of atoms above and below this plane, resulting in their displacement because of the large Na–O distance, then one would account for the general features of the structure. The opposite displacements of the Na atom in the same ac plane, and of the Nb atoms in different ac planes, could then be explained by dipolar interaction. It is very unlikely that a homopolar bond would come into existence at the transition, but more probable that semipolar bonding exists in all phases of the structure and at all temperatures. The arrangement in which the bond lengths are unequal, that is, in which the atom displacements occur, has always lower energy, but has lower free energy below the transition, when the reduced thermal vibration allows the displacements to take place. However, these speculations are likely to be of little value until further knowledge is obtained on the relation between the displacements and the ferroelectricity, and in particular of the problem of the non-polarity.

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