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Polymorphism in Potassium Niobate, Sodium Niobate, and other ABO_3 Compounds*

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The first part of this paper presents the results of optical and X-ray studies of the perovskite-type crystals, potassium niobate and sodium niobate. Potassium niobate is orthorhombic at room temperature, changing to tetragonal at about 225° C. and cubic near 435° C. Sodium niobate is orthorhombic at room temperature, changing to tetragonal at about 370° C. and to cubic at about 640° C.

The second part of the paper discusses relations among the structures of the ABO_3 compounds.

Introduction

In the course of a search for new ferroelectric materials, B. T. Matthias has grown potassium niobate† ($KNbO_3$) and sodium niobate ($NaNbO_3$) crystals and found them to be ferroelectric (Matthias, 1949). The results of X-ray and optical work on these crystals, although in agreement with the original determinations of the structures as perovskite-type (Barth, 1925; Goldschmidt, 1926), were in conflict with the more recent published literature (Quill, 1932; Lapitskii, 1946),‡ and they are therefore reported herewith in the first part of this paper. It is expected that dielectric data on the same crystals will soon be published by B. T. Matthias and J. P. Remeika. The reason for the conflict with earlier crystallographic data is not known. Both our work and the earlier work seem to have been done on pure $KNbO_3$ and $NaNbO_3$. Quill describes in detail the precautions taken to ensure the purity of his material. Although only 'C.P.' grade material was used in Matthias's melts, spectroscopic analysis shows that no impurity is present in the crystals studied in amount greater than 0·005 % (except for potassium and sodium in amount 0·005–0·03 %), which probably would not be sufficient to cause the crystallographic difference reported.

There remains the question of the state of oxidation of the niobium. On this point the evidence is not as clear, but the fact that melt compositions with weight proportions ranging from 1·00 K_2CO_3 : 1·28 Nb_2O_5 to 1·00 K_2CO_3 : 2·14 Nb_2O_5 all produced crystals giving the same $KNbO_3$ X-ray powder picture as crystals made from 1·00 KOH : 2·38 Nb_2O_5, and that somewhat narrower ranges in the $NaNbO_3$ melts produced the same $NaNbO_3$ picture, indicates that the composition of the crystals in all cases is the same. Since the structure is perovskite type, ABO_3 is the most likely formula.

The second part of the paper suggests a diagrammatic representation of polymorphism in the perovskite group and other ABO_3 compounds. No new data are presented, but the suggestion is offered with the intent of aiding and stimulating further research on these compounds.

1. Potassium niobate and sodium niobate

Both potassium niobate ($KNbO_3$) and sodium niobate ($NaNbO_3$) have distorted perovskite-type structures. The prototype, undistorted perovskite structure (Fig. 10), is cubic with cations at 0, 0, 0, other cations at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and oxygen ions at $0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0$. It is the $G5$ structure of the *Strukturbericht* (Ewald & Hermann, 1931).

The crystals investigated by the writer were grown from high-temperature melts of K_2CO_3 and Nb_2O_5 by B. T. Matthias and J. P. Remeika. Both the potassium niobate and sodium niobate crystals are orthorhombic at room temperature, with higher-temperature tetragonal and cubic modifications. The orthorhombic modification may be thought of as derived from the $G5$ cube of Fig. 10 by a very small shear in the plane of (100), resulting in a slight elongation of [011] and shortening of $[0\bar{1}1]$. The direction that was [100] in the cube thus becomes a c direction of the orthorhombic crystal, and in both potassium niobate and sodium niobate this direction is appreciably shorter than the two other 'cube edges'. The tetragonal modification may be thought of as derived from the $G5$ cube of Fig. 10 by a small elongation in the [001] direction.

Nearly all of the crystals grown were composed of laminated twinned units such as that shown in Fig. 1, with (001) the twin plane. These laminae are extremely thin in the actual crystals; one of the thickest was 0·011 mm. thick. The enlarged detail of Fig. 1 shows the

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* The part of this paper dealing with potassium niobate and sodium niobate was presented at the first meeting of the American Crystallographic Association, State College, Pa., 10 April 1950.

† The Nomenclature Commission of the International Union of Chemistry agreed in September 1949 to recommend that element 41 be called *niobium* rather than *columbium*.

‡ Quill reports $KNbO_3$ as cubic with $a_0 = 4{\cdot}005 \pm 0{\cdot}002$ A. and $NaNbO_3$ as cubic with $a_0 = 3{\cdot}889 \pm 0{\cdot}002$ A. Lapitskii reports $NaNbO_3$ as cubic with $a_0 = 3{\cdot}892$ A.

orientation of the optic plane. Composite optic figures observed on each face of such a unit are indicated in Fig. 1 as they appear at the extinction position. Extinction directions are indicated by the radial lines outside the field-of-view circles. Fig. 2 shows how the figures on faces *e* and *f* result from the combination of two biaxial figures from optic planes lying at 45° to the line of sight. An isogyre of the composite figure exists only when isogyres of the two separate figures are superposed. The figure on face *g* is a composite of two obtuse-bisectrix figures.

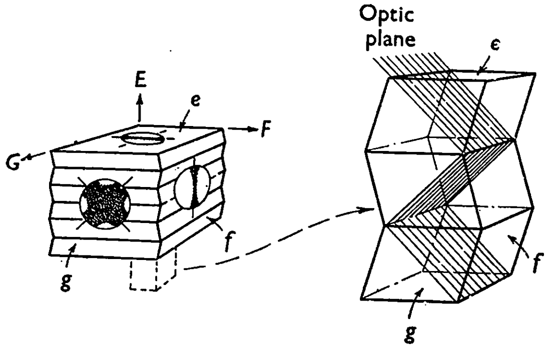

Fig. 1. Laminated twinned unit. Optical interference figures indicated diagrammatically.

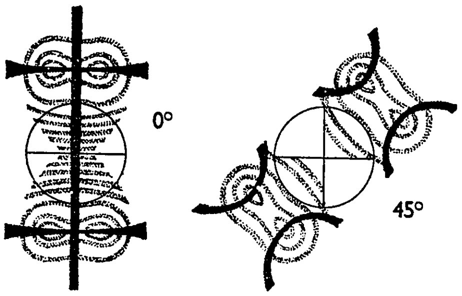

Fig. 2. Diagrammatic explanation of composite interference figures observed on faces *e* and *f* of the unit in Fig. 1.

Most crystals were composed of several laminated units, related to each other by a '(110)'* twin plane. The composition face between two such units could be translated uniformly by applying pressure on the sides of the crystal as illustrated in Fig. 3. The nature of this change is indicated by the orientation of the optic figure on either side of the boundary; it was always such as to enlarge the region in which the composite isogyre was normal to the applied pressure. Since the normal to the isogyre is the short (*c*) direction of the orthorhombic cell, this shift of the twin boundary results in the shortening of the crystal in the direction of applied pressure in accordance with Le Chatelier's principle. This effect was so readily produced in the potassium niobate crystals that they could hardly be picked up with the forceps without a resulting shift of twin boundaries. In sodium niobate, however, it was produced only by pressure nearly great enough to break the crystal. The difference of behavior may result from the fact that the angle between '(001)' and '(010)' differs from 90° by more in sodium niobate than in potassium niobate.

Similar changes were effected in potassium niobate with an applied electric field of the order of 3800 V.cm.$^{-1}$, but could not be achieved in sodium niobate with a field of 15,000 V.cm.$^{-1}$. With an applied field the boundary does not shift simply, as with applied pressure, but fine bands of the favored orientation appear within the unfavored region. The bands are parallel to the twin boundary.

Crystallographic data for the two substances are given in Table 1. Properties which they have in common have been discussed above. Their different properties will be discussed below.

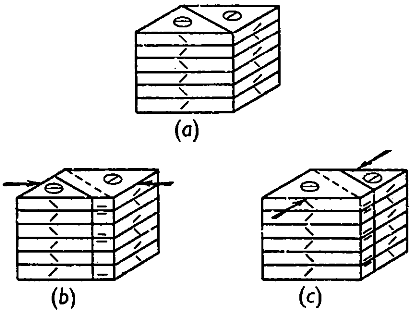

Fig. 3. Effect of application of directed pressure on laminated twinned crystal.

Potassium niobate

The potassium niobate crystals were grown from a mixture of 3·20 g. K_2CO_3 and 5·34 g. Nb_2O_5 held at 1000° C. in a platinum crucible for 30 hr. At the end of this period the furnace was turned off and cooled at a rate of approximately 100° C. per hour. Stock material was used with no special purification.

The crystals were cube-shaped, water-clear, vitreous and colorless, about 1–2 mm. on an edge with one dimension usually about two-thirds the other two. Most crystals showed cleavage-like '(110)' planes which could be translated uniformly by pressure. These are the '(110)' twin boundaries described above. Under extreme pressure the crystals cleaved parallel to '(100)'.

The average index of refraction is high, but was not determined, except to confirm that it is greater than 1·64. Maximum birefringence could not be measured, since it was impossible to look along the optic normal because of the twinning shown in Fig. 1. A rough measurement of partial birefringence along the *c* orthorhombic axis (*G* direction in Fig. 1) was obtained, however, where a 45° wedge with suitable orientation was available. Because of the laminated character of the crystal this involved counting orders and fractions

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* The indices of this type of plane on the orthorhombic axes proper to these crystals at room temperature would not be (110), but the description is clearer if cubic axes are used for these pseudocubic crystals. Where this is done, the indices will be enclosed in quotation marks.

Table 1. *Potassium niobate and sodium niobate: crystallographic data*

Potassium niobate

Spectrochemical qualitative analysis:		Estimated range
Major components:	K, Nb	> 1·0 %
Trace:	Na	< 0·03 %
Slight trace:	Ca, Cr, Cu, Pb, Pt	< 0·005 %
Very slight trace:	Mg, Ag	< 0·001 %

At 500° C. Cubic: $a_0 = 4{\cdot}024 \pm 0{\cdot}001$ A. (by Bradley–Jay extrapolation)

At 260° C. Tetragonal: $a_0 = 4{\cdot}00 \pm 0{\cdot}02$, $c_0 = 4{\cdot}07 \pm 0{\cdot}02$ A.

At 25° C. Orthorhombic cell containing 2 molecules:

$a_0 = 5{\cdot}702$, $b_0 = 5{\cdot}739$, $c_0 = 3{\cdot}984 \pm 0{\cdot}010$ A.

Pseudotetragonal cell containing 1 molecule:

$a_0 = 4{\cdot}045$, $c_0 = 3{\cdot}984 \pm 0{\cdot}010$ A.

On monoclinic axes:

$a_0 = 4{\cdot}045$, $b_0 = 3{\cdot}984$, $c_0 = 4{\cdot}045$ A., $\beta = 90° \, 21'$

Sodium niobate (see also Table 2)

Spectrochemical qualitative analysis:		Estimated range
Major components:	Na, Nb	> 1·0 %
Trace:	K	< 0·03 %
Slight trace:	Ca, Cr, Cu	< 0·005 %
Very slight trace:	Mg, Sn	< 0·001 %

At 490° C. Tetragonal: $c_0 = 4 \times$ pseudocubic-a_0, $a_0 = 2 \times$ pseudocubic-a_0*; pseudocubic-$a_0 = 3{\cdot}93 \pm 0{\cdot}01$ A. (by Bradley–Jay extrapolation)

At 425° C. Tetragonal: $c_0 = 4 \times$ pseudocubic-a_0, $a_0 = 2 \times$ pseudocubic-a_0*; pseudocubic-$a_0 = 3{\cdot}928 \pm 0{\cdot}003$ A. (by Bradley–Jay extrapolation)

At 300° C. Orthorhombic:

pseudotetragonal-$a_0 = 2 \times 3{\cdot}91$, $c_0 = 4 \times 3{\cdot}94 \pm 0{\cdot}02$ A.*

At 25° C. Orthorhombic cell containing 8 molecules:

$a_0 = 5{\cdot}512$, $b_0 = 5{\cdot}577$, $c_0 = 4 \times 3{\cdot}885 \pm 0{\cdot}010$ A.

Pseudotetragonal cell containing 16 molecules:

$a_0 = 2 \times 3{\cdot}921$, $c_0 = 4 \times 3{\cdot}885 \pm 0{\cdot}010$ A.

On monoclinic axes:

$a_0 = 2 \times 3{\cdot}921$, $b_0 = 4 \times 3{\cdot}885$, $c_0 = 2 \times 3{\cdot}921 \pm 0{\cdot}010$ A., $\beta = 90° \, 40'$

* Since rotation photographs were taken only at room temperature, these statements are made on the assumption that the 'extra lines' on the high-temperature films have the same significance as the same 'extra lines' on the room-temperature film.

of orders in a band about 0·01 mm. wide. The figure thus obtained for the birefringence was 0·20, representing four orders in a lamina 0·011 mm. wide.

X-ray diffraction powder photographs of these crystals showed lines not sharp enough for accurate measurement. Other crystals, bluish in color, made from a melt of KOH and Nb_2O_5 in weight proportions 1 : 2·38, gave sharper diffraction photographs not measurably different in spacing or relative intensities from those of the crystals described above; these crystals were therefore used for the photographs taken at 25, 260 and 500° C. shown in Fig. 4. Because of the pseudocubic character of these crystals $(h^2+k^2+l^2)$ numbers are easily assigned to the powder-photograph lines. Attention should be especially called to line 24, which, coming from (422), gives only a single $K\alpha_1 K\alpha_2$ doublet for cubic crystals (Fig. 4 (*a*)), two doublets (422 + 242, 224) for tetragonal crystals (Fig. 4 (*b*)), and four doublets for orthorhombic crystals, some of which overlap in Fig. 4 (*c*). These photographs agree with conclusions drawn from observations with the polarizing microscope, namely, that potassium niobate is orthorhombic at room temperature, changing to tetragonal at 225 ± 5° C. and to cubic at 435 ± 5° C. With decreasing temperature, the reverse changes occur at 200 ± 5 and 420 ± 5° C. respectively.*

The 'orthorhombic distortion', i.e. the departure from orthogonality of the room-temperature form, is measurable only from the high-angle lines. The lower lines are those of a tetragonal crystal. When this pseudotetragonal crystal becomes tetragonal at about 225° C. optical observations have shown that it does not retain the pseudotetragonal *c* axis for its tetragonal *c* axis but chooses one of the other pseudocubic axes. These changes are shown schematically in Fig. 6.

No optical change was observed between 25 and −50° C.

Sodium niobate

The sodium niobate crystals were grown from a mixture of 7·4 g. Na_2CO_3, 18·6 g. Nb_2O_5 and 12·5 g. NaF held at 1500° C. in a platinum crucible for 1 hr. At the end of this period the furnace was turned off and cooled at

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* These measurements were made with a high-temperature stage which permits observation of crystals with the polarizing microscope at temperatures as high as 800° C. Its construction is described in a note in the *American Mineralogist* (in the Press).

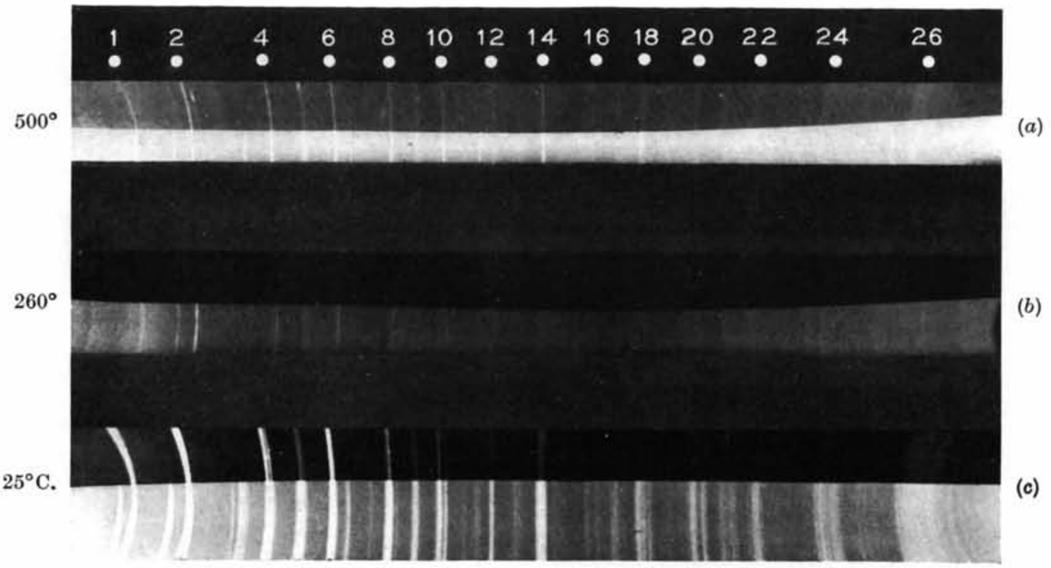

Fig. 4. X-ray diffraction powder photographs of potassium niobate at various temperatures.

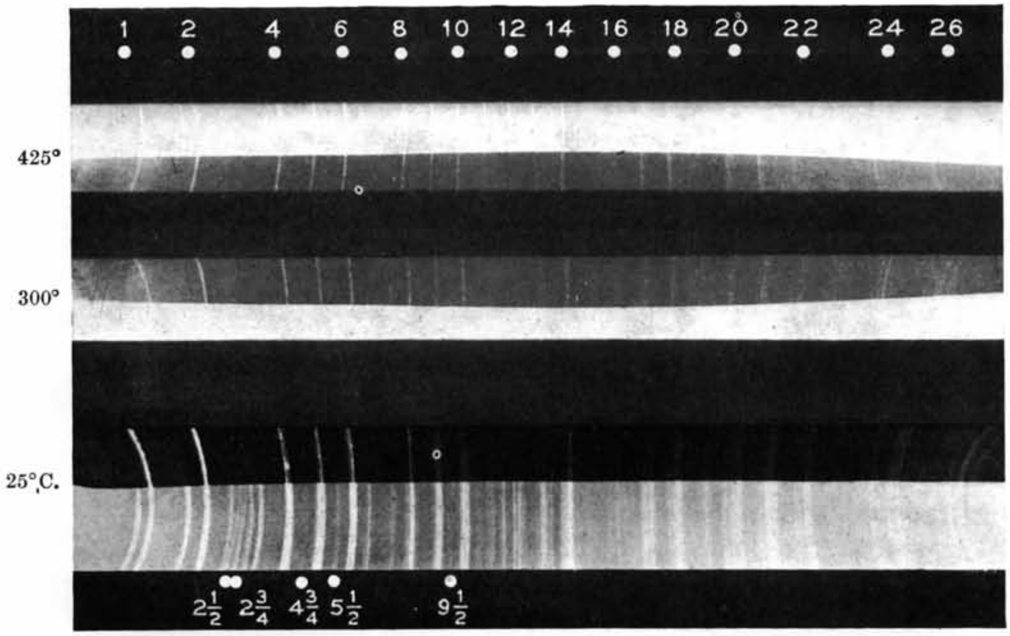

Fig. 5. X-ray diffraction powder photographs of sodium niobate at various temperatures.

a rate of approximately 100° C. per hour. Stock material was used with no special purification.

The crystals were pale tan, vitreous, in part water-clear, cube-shaped. According to J. P. Remieka, these crystals are colorless when first grown, but rapidly become colored owing to photosensitivity. Most of the crystals, however, showed fractures and inclusions with one or more of their faces recessed, stepped, curved, or irregular. The largest crystal from this melt was 1 × 2 × 3 mm., but they were commonly approximately 1 × 1 × 1 mm.

As in the case of potassium niobate, the index of refraction is known to be greater than 1·64, but was not determined. The partial birefringence along the *c* orthorhombic axis (*G* direction in Fig. 1), measured as for potassium niobate, was found to be 0·13, representing two orders in a lamina 0·008 mm. wide.

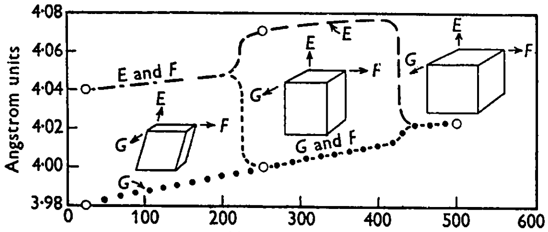

Fig. 6. Polymorphism in potassium niobate. Circled points are from X-ray diffraction data from the photographs of Fig. 4.

X-ray diffraction powder patterns of these crystals taken at 25, 300 and 425° C. are shown in Fig. 5. In its X-ray diffraction patterns, sodium niobate differs from potassium niobate in two important ways: first, the patterns show 'extra lines', indicated by fractional $(h^2+k^2+l^2)$ numbers in Fig. 5, and secondly, the symmetry indicated by the X-ray patterns differs from that indicated by the optical work. These two features will now be discussed in that order.

When $(h^2+k^2+l^2)$ numbers are assigned to the room-temperature powder pattern for sodium niobate, it is found that, in addition to the splitting of these lines due to the slightly non-cubic distortion of the lattice (*sic*), there are also lines at simple fractional values of $(h^2+k^2+l^2)$, some of which are labelled[*] in Fig. 6. These extra lines persist even in the photograph taken at 500° C., but they are too faint for detection in the print here reproduced. Since no fraction smaller than $\frac{1}{4}$ is found, multiplication of one or more cell edges by 2 would restore the integrality of the $(h^2+k^2+l^2)$ values. However, a rotation photograph around the *c* orthorhombic axis (*G* of Fig. 1) showed three faint layer lines between the zero layer line and the first strong layer line with the simple cell spacing, whereas, with the rotation axis along a pseudocubic edge normal to this, only one additional faint layer line appeared.[†] This, with the orthorhombic symmetry, indicates that the edge of the true cell is four times that of the simple monomolecular cell along the *c* orthorhombic axis (*G* of Fig. 1) and twice that of the simple cell in the other two pseudocubic directions (*E* and *F*, Fig. 1).[‡] The existence of this multiple cell means that one or more of the ions are displaced to non-special positions. The nature of these displacements has not been determined.

A comparison of the optical observations and the X-ray data is given in Table 2. Briefly, at a temperature where the crystal is behaving like a tetragonal crystal in diffracting X-rays, it is behaving like an orthorhombic crystal in transmitting light; and where it is behaving like a cubic crystal in diffracting X-rays it is behaving like a tetragonal crystal in transmitting light. It seems likely that the X-ray diffraction pictures indicate the symmetry of the niobium array while the optical properties indicate the symmetry of the oxygen–sodium array. Further structural work at elevated temperatures is necessary before these observations can be fully interpreted.

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[*] Compare similarly labelled photographs of $CaTiO_3$, $CaZrO_3$ and $CdTiO_3$ (Megaw, 1946, p. 136).

[†] On two crystals (*c.* 0·12 × 0·04 × 0·004 mm.), each consisting predominantly of one twin individual whose orientation was determined optically.

[‡] It was stated at the American Crystallographic Association meeting that the cell dimensions along *E* and *F* also had to be multiplied by 4. This was on the basis of a photograph of a crystal with a 0·02 mm. twin band at the base which apparently contributed spots, though precautions were taken to keep it out of the beam. When a crystal with a much smaller twin band was used, the results reported here were obtained.

Table 2. *Comparison of optical and X-ray evidence of polymorphism in sodium niobate* ($NaNbO_3$)

Temperature (° C.)	Optical	X-ray
25 ± 5	Extinction at 0° and 45° (orthorhombic)	Line 24: 4 doublets (orthorhombic); 'extra lines' indicate multiple cell
150 ± 10	(Orthorhombic)	Line 24: 4 doublets (orthorhombic); 'extra lines' indicate multiple cell
300 ± 15	Birefringence decreasing gradually (orthorhombic)	Line 24: 2 doublets (tetragonal); 'extra lines' indicate multiple cell
370 ± 5 (reverse change at 350° C. on cooling)	45° extinction changes to 0° (tetragonal)	—
425 ± 15	Birefringence decreasing (tetragonal)	Line 24: 1 doublet (cubic); 'extra lines' indicate multiple cell
480 ± 5 (reverse change at 470° C. on cooling)	Sudden drop of about 0·001 in birefringence (tetragonal)	—
640 ± 5 (reverse change at 635° C. on cooling)	Crystal becomes isotropic (cubic)	—

2. Other ABO_3 compounds

The ABO_3 compounds constitute a large group of substances on which much work has been done and much more remains to be done. We have found it helpful to indicate graphically on a grid some of the crystallographic information already available for these compounds (Fig. 7). The co-ordinates of the grid are the ionic radii of the A and B ions. The ionic radii given in Wyckoff's *Crystal Structures* (1948) were used with no correction for co-ordination. If co-ordination corrections had been applied, all of the perovskite group would be raised slightly on the diagram, and the calcite and aragonite group lowered slightly. Four structure types include the structures of most of the ABO_3 compounds: aragonite,* calcite* (Zachariasen's Class I), perovskite, and ilmenite (Zachariasen's Class IV). A few ABO_3 compounds lying outside these structural fields have other structures.

The structures of the same ABO_3 compounds are indicated diagrammatically on the same co-ordinate system in Fig. 8.* The cube root of the volume of a single molecule is indicated wherever it is known.

The data from which these charts were compiled were taken from the publications marked with an asterisk in the list of references.

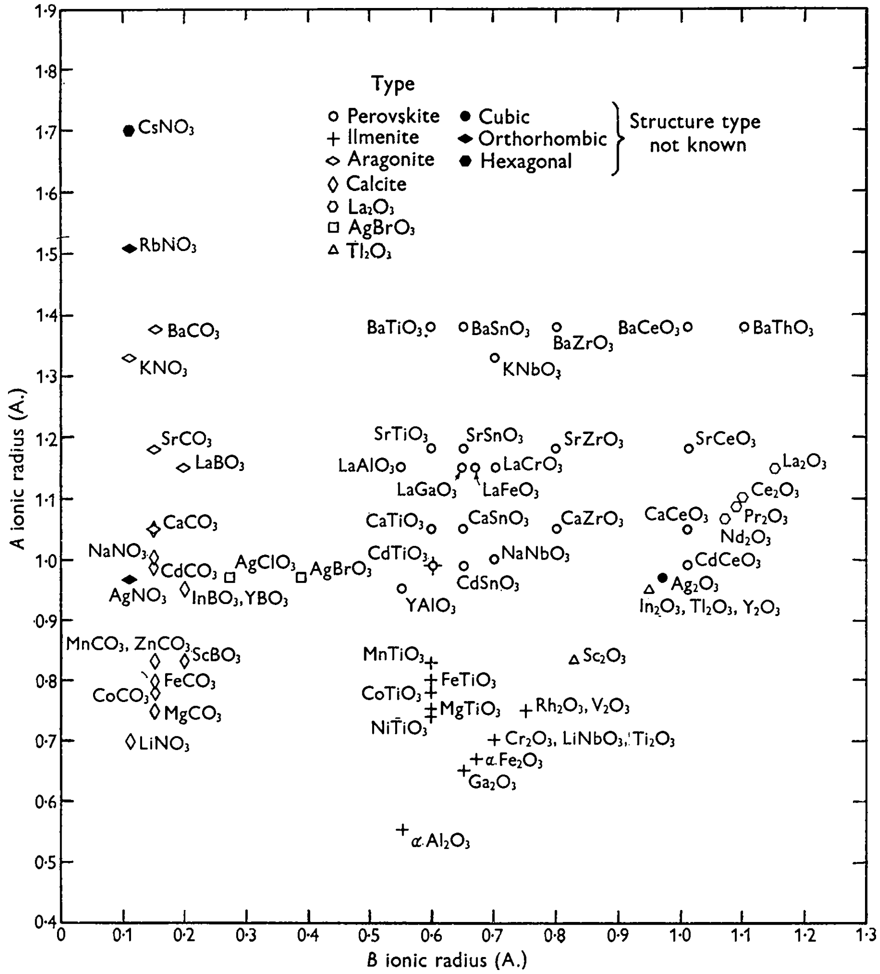

Fig. 7. ABO_3 compounds arranged according to A and B ionic radii.

An attempt has been made in Fig. 8 to draw isovols, lines connecting points with equal molecular volume, but a great many anomalies exist. Probably the most important reason for this is that the compounds have been plotted in accordance with ionic radii, which are not valid for cases where the bonding is partly covalent, i.e. for those elements without a rare-gas configuration. In most cases a single radius adjustment will not

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* R. W. G. Wyckoff has called these 'KNO_3' and '$NaNO_3$' structures respectively, after the compounds which lie well within each structural field, rather than use the terms which refer to the border-line substance $CaCO_3$. Inspection of Figs. 7 and 8 suggests that Wyckoff's terms are better terms for these structures, though 'aragonite' and 'calcite' are more familiar.

* A similar diagram, with the names of the various structure types qualitatively distributed on a chart whose unscaled co-ordinates are R_A/R_B and R_B/R_O, has been given by Zachariasen (1928, p. 156).

improve the situation. Consider, for example, the cerates, plotted with a *B*-ion radius of 1·01 A. The two lower ones, cadmium cerate ($CdCeO_3$) and calcium cerate ($CaCeO_3$), with molecular volumes 3·83 and 3·85 A.^{3} respectively, lie anomalously between isovols 4·1 and 4·2. They properly belong much farther to the left with a *B*-ion radius of about 0·65 A.; but if this radius were assigned to cerium, then the two upper cerates, strontium cerate ($SrCeO_3$) and barium cerate ($BaCeO_3$), with molecular volumes 4·27 and 4·38 A.^{3} respectively, would be moved from satisfactory to anomalous volumetric positions. On the other hand, the position of all the stannates, here plotted with a *B*-ion radius of 0·65 A., would be improved if this radius were increased to about 0·76 A., as indicated at the bottom of Fig. 8. This has therefore been done in Fig. 9, which is a similar diagram, but restricted to the perovskite and ilmenite structure fields.

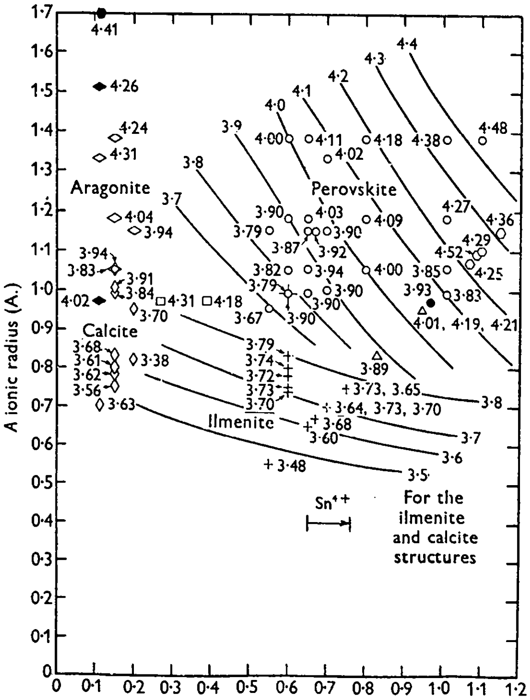

Fig. 8. Monomolecular volumes and isovols for the compounds of Fig. 7.

The perovskite and ilmenite* structures, with which the writer has been especially concerned, are shown on a larger scale in Fig. 9 as circles with various modifications symbolic of the modified perovskite structures. Only a few substances have the 'simple cubic' perovskite structure, shown in Fig. 10. It is the *G*5 structure of the *Strukturbericht*. The cell may be elongated or shortened along a cube axis, i.e. tetragonal; or along a face diagonal, i.e. orthorhombic; or along a cube diagonal, i.e. rhombohedral. According to Megaw (1946), the departures from the *G*5 structure that have been described as monoclinic have monoclinic a_0 equal in length to monoclinic c_0, within the limits of experimental error, and are therefore probably orthorhombic.

In addition to the variations described above, the oxygen ions or the metal ions may occupy non-special positions which result in one or more edges of the true unit cell being two or more times that of the simple *G*5 cell. For example, in calcium titanate itself, the nominal prototype of the perovskite group, the oxygen octahedra are thought to be tilted with respect to all three crystallographic (Náray-Szabó, 1943*a*) axes. As a result all the edges of the true unit cell are twice the length of the simple-cell edges. Such multiplications of one or more edges of the simple cell are indicated in Fig. 9 by doubled circles. All such cases so far reported in the literature belong to crystals having the orthorhombic modification of the perovskite structure at room temperature. In sodium niobate, as reported in the first part of this paper, the larger cell persists in the higher-temperature, more symmetrical modifications.

Since the identification of the larger cell in some cases depends on the detection of very faint 'extra lines', it is likely that further work will show that some of the orthorhombic crystals hitherto described as having a monomolecular unit cell have, in fact, a multiple unit cell.

These deviations from the *G*5 perovskite structure have been discussed by Megaw (1946), who calls them homotypic structures, by Náray-Szabó (1943*b*), who calls them sister-structures, and by Rooksby (1945), who prefers the term pseudo-isomorphous. Their presentation in the array shown in Fig. 9 simply facilitates the orderly consideration of the effect of the sizes of the ions on the structures. Structure-field boundaries can be drawn for the various modifications of the perovskite structure in Fig. 9 in the same way that structure-field boundaries could be drawn for the various structure-types in Fig. 8. The strictly cubic structure field is bounded by the lines $R_A = 1·2\,R_B + 1·07$, $R_A = 1·155$, and a third line not well defined by the available data. The fact that cadmium titanate ($CdTiO_3$) can be grown so as to have either perovskite structure or ilmenite structure suggests, as Posnjak & Barth (1934) pointed out, that the cadmium radius marks the *A* ionic radius boundary between the perovskite type and the ilmenite type. If Wyckoff's radii are used, yttrium aluminate ($YAlO_3$), orthorhombic perovskite type, falls below cadmium titanate and therefore in the ilmenite structure field, but with Goldschmidt's radii (see Table 3) these positions would be reversed.

Goldschmidt (1926) states that the Y_2O_3 from which the $YAlO_3$ was made for these data was impure. The likely impurities, as pointed out in the *Strukturbericht* (Ewald & Hermann, 1931, p. 334), would be other rare earths of the yttrium series (Gd–Lu) which probably have larger ionic radii, thus giving the impure com-

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* With 'ilmenite structures' are included Cr_2O_3-type structures which differ from ilmenite structures only in having the *A* and *B* ions the same as each other.

pound an average A ionic radius larger than that for pure yttrium. This might well raise it into the perovskite structure field. It would be of interest to know the structure of pure $YAlO_3$.

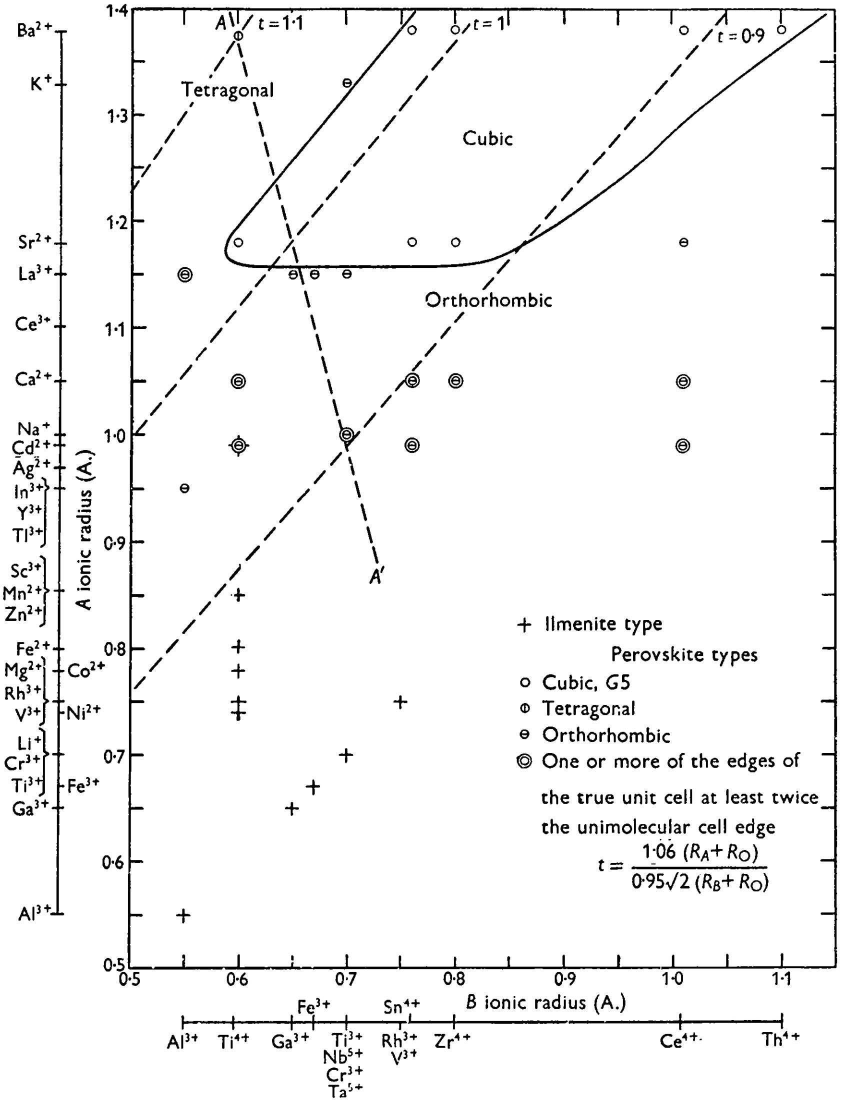

Fig. 9. Perovskite and ilmenite structure fields.

The distribution of these structure fields should be considered with respect to Goldschmidt's tolerance factor which is widely quoted as a test for the perovskite structure. An ideal $G5$ perovskite structure made up of rigid spheres, each of which just touched its nearest neighbors, would have $R_A+R_O=\sqrt{2}\,(R_B+R_O)$. Goldschmidt, Barth & Lunde (1925) found that in real perovskite structures the value of $(R_A+R_O)/\{\sqrt{2}\,(R_B+R_O)\}$ lay between 0·77 and 0·99, and they called the value of the ratio, t, the 'tolerance factor'. Zachariasen (1928, p. 152) applied corrections for co-ordination by multiplying the numerator by 1·06 and the denominator by 0·95. Lines representing $t=1$, $t=0{\cdot}9$ and $t=1{\cdot}1$, calculated with Zachariasen's correction factors and Wyckoff's oxygen radius (1·35 A.), are shown on Fig. 9. According to Zachariasen, if t is precisely 1·0 the structure is precisely cubic; if it falls below 0·9, the

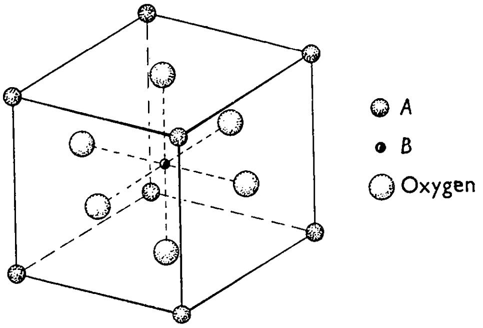

Fig. 10. Simple, cubic perovskite-type structure, $G5$.

ilmenite structure obtains; and if it falls above 1·1 structures that are neither perovskite nor ilmenite result. If B is too small, a structure in which B has a lower co-ordination number than 6 is formed.

Table 3. *Comparison of selected ionic radii*

	Wyckoff (A.)	Goldschmidt (A.)
Al^{3+}	0·55	0·57
Ba^{2+}	1·38	1·43
Ca^{2+}	1·05	1·06
Cd^{2+}	0·99	1·03
Ce^{4+}	1·01	1·02
La^{3+}	1·15	1·22
O^{2-}	1·35	1·32
Sr^{2+}	1·18	1·27
Th^{4+}	1·10	1·10
Y^{3+}	0·95	1·06

Fig. 9 shows wide departures from these rules, which the use of Goldschmidt's radii instead of Wyckoff's (see Table 3) will not greatly lessen. For example, if 1·43 A. were used for barium instead of 1·38 A. the cubic crystals barium cerate ($BaCeO_3$) and barium thorate ($BaThO_3$) would be brought a little closer to $t=1$, but the cubic crystals barium stannate ($BaSnO_3$) and barium zirconate ($BaZrO_3$) would be removed by the same amount, and similarly with the strontium compounds. The positions of the two crystals farthest from the prescribed field, cadmium cerate ($CdCeO_3$) and calcium cerate ($CaCeO_3$), would be virtually unchanged.

If we imagine that the ions are rigid spheres and consider the case where the A ion is the same size as the oxygen ion, we see that the A ions and oxygen ions together form a cubic close-packed structure. For any A ion smaller than this the structure must be 'held apart' by the oxygen ions, and on the basis of such a picture the A ionic radius *should* have no influence until it becomes so small that the structure collapses into some non-cubic arrangement. Further, in the close-packed oxygen octahedron, the center space will only admit a B ion with a radius of 0·55 A., using Wyckoff's radius of 1·35 A. for oxygen. Since all of the B ions (except Al) in the perovskite structures are larger than this the oxygen octahedra are not close-packed, but stretched apart, allowing even less influence on the part of the A ion. In spite of this, the A ionic radius does affect the size of the cell when A is smaller than the oxygen ion, showing that the simple rigid-sphere picture is inapplicable.

It thus seems that the consideration of the structure-field distribution of variations of the perovskite structure is a more satisfactory approach than the use of the tolerance factor. Jonker & van Santen (1950) have made mixed crystals between $A^{3+}Mn^{3+}O_3$ and $A^{2+}Mn^{4+}O_3$ compounds with resulting crystals lying along lines which traverse not only the boundaries between modifications of the perovskite structure but also the boundaries between the perovskite structure field and neighboring structure fields. Examples of the first are the series $LaMnO_3$–$BaMnO_3$ and $LaMnO_3$–$SrMnO_3$, both of which are cubic only in the middle range of compositions. This is shown in Fig. 11. An example of mixed crystals with wider structural variation is the series $YMnO_3$–$SrMnO_3$, in which the end-members do not crystallize in the perovskite structure but mixed crystals of intermediate composition do (see Fig. 11).

The series of polymorphic transformations observed when a crystal of the perovskite group is heated is broadly the same for the different members of the group: namely (with decreasing temperature), cubic, tetragonal, orthorhombic, rhombohedral modifications of the perovskite structure. We thus have the same group of modifications occurring with fixed composition at different temperatures as with fixed temperature at different compositions. This immediately suggests the construction of a three-dimensional diagram in which temperature is plotted on the third rectilinear coordinate, normal to the plane of Fig. 9. Above and below each point plotted on Fig. 9 (the room-temperature level) one would plot the temperatures at which the polymorphic transformations of the substance represented by that point occurred.

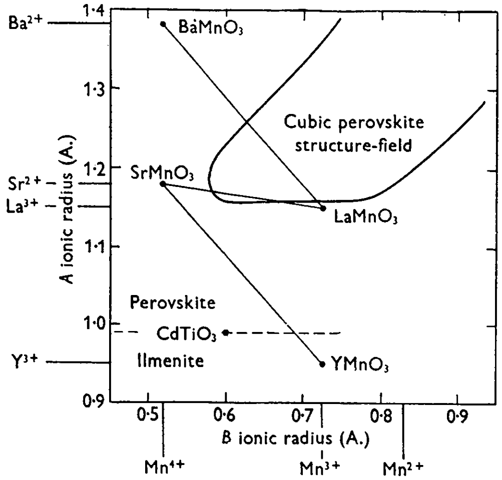

Fig. 11. Structural variations in $A^{3+}Mn^{3+}O_3$–$A^{2+}Mn^{4+}O_3$ mixed crystals. Data from Jonker & van Santen (1950).

Among the questions to be explored with the aid of such a diagram are: (1) Can all the points representing a particular type of polymorphic transformation be connected by a smooth surface which cuts the plane of Fig. 9 at the boundary between the two structure fields in question? (2) Does the introduction of mixed-crystal data necessitate marked changes in the shape of these surfaces? (3) Can polymorphic transformation temperatures be predicted with the aid of the diagram? (4) How do other properties vary over the diagram?

Obviously a large amount of data is necessary for the answers to these questions, and much of it is still to be collected. Some suggestion as to what may be expected, however, can be found in some more data-rich sections through the three-dimensional figure.

One such section, A–A' (see Fig. 9), is shown in Fig. 12. In this section the cubic–tetragonal transition* curve plunges steeply through the room-temperature surface on both sides of the cubic structure field. One might have predicted from this that efforts to reach this transition in strontium titanate by cooling the crystals with liquid air would fail, as, in fact, they did (Hulm, 1950). According to Jonker & van Santen (1947) the strontium titanate transition is in the neighborhood of the absolute zero. Part of the cubic–tetragonal transition curve between barium titanate and strontium titanate has been determined from mixed-crystal data.

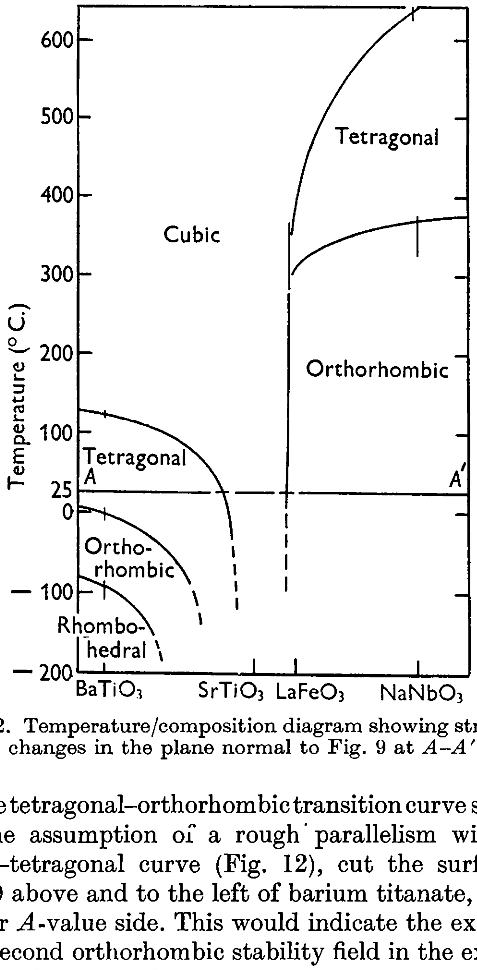

Fig. 12. Temperature/composition diagram showing structural changes in the plane normal to Fig. 9 at A–A'.

The tetragonal–orthorhombic transition curve should, on the assumption of a rough parallelism with the cubic–tetragonal curve (Fig. 12), cut the surface of Fig. 9 above and to the left of barium titanate, on the higher A-value side. This would indicate the existence of a second orthorhombic stability field in the extreme upper left corner of Fig. 9. No points lie in this region as the diagram is drawn, but if Zachariasen's ionic radii† for barium and potassium had been used, potassium niobate would have lain on this side of barium titanate on the border of the high-A orthorhombic field instead of in the tetragonal field where its slightly orthorhombic distortion makes it anomalous.

Megaw (1946) has pointed out that the orthorhombic modification of the perovskite structure observed in calcium titanate, for example, is a result of the inadequate size of the A ion, whereas the tetragonal modification seems to result, for obscure reasons, when the A ion is too large. The above discussion of potassium niobate indicates that there may be a second orthorhombic stability field for still larger A ions.

The three-dimensional polymorphic diagram for other than the perovskite structures will not be considered in detail in this paper, but it should be pointed out that similar relationships might be observed with the aid of such a diagram in, for example, the calcite–aragonite field. Lander (1949) has shown, for example, that barium carbonate changes from the aragonite structure to the calcite structure at 803° C., and to a cubic (sodium chloride) structure at 976° C. The lower transition was also observed in strontium carbonate at 912° C. and in mixed crystals at various temperatures.

Lander has pointed out (in a personal communication) that comparable transitions occur at higher temperatures in carbonates and lower temperatures in nitrates because the strength of the divalent carbonate–A-ion bond is twice that of the univalent nitrate–A-ion bond. Although the transitions in the perovskite group do not involve molecular rotation, as in these carbonates and nitrates, the effect of bond strengths on the temperatures of polymorphic transitions may make it impossible to include on the proposed three-dimensional diagram such a wide range of compounds as that shown in Fig. 9.

A second consideration, mentioned earlier in this paper, which may further limit the number of compounds that can be plotted on a single diagram, is the question of the nature of the bonding. The bonding is truly ionic only in the case of the ions with inert-gas configuration. Therefore ionic radii may not properly be used for the others without applying some correction proportional to the amount of covalent character of the bond, which in most cases is not known. It may be that, as further high-temperature and mixed-crystal data become available, it will be found that smooth transition surfaces can only be drawn among substances with the same bond strength and character.

Summary

The first part of this paper reports the results of preliminary optical and X-ray work on potassium niobate and sodium niobate. Both have a distorted perovskite structure and are orthorhombic (pseudotetragonal) and polysynthetically twinned at room temperature. Optical and X-ray work both show that potassium niobate becomes tetragonal at about 225° C. and cubic at about 435° C. The X-ray evidence indicates that sodium niobate is tetragonal at 260° C. and cubic at 500° C., but the optical evidence indicates lower symmetry at these temperatures (see Table 2). One of the edges of the pseudocubic unit cell of sodium niobate is four times the length of that of the simple mono-

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* 'Curie temperature' in the case of such ferro-electric crystals as barium titanate.

† Presented at the American Crystallographic Association meeting, 11 April 1950 .

molecular cell, and the other two are each twice the simple cell edge so that the cell contains 16 molecules.

The second part of this paper deals with the crystallographic variations in the perovskite group and other ABO_3 structure types, presenting them diagrammatically for orderly consideration. Plotting temperature along a third co-ordinate is suggested as an aid in comparing polymorphic transformations in related compounds and mixed crystals. Such a diagram invites prediction of properties as yet unmeasured and may serve to indicate fields of special interest for investigation.

The writer wishes to express her gratitude especially to Philip W. Anderson, W. L. Bond, Alan N. Holden and J. J. Lander for discussions that were helpful in the preparation of this paper and to B. T. Matthias and J. P. Remeika for providing the crystals on which the work was done.

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* Sources of data for Figs. 7 and 8.

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The Calculation of Structure Factors by Fourier Summation

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A method is described by which the structure factors of a proposed crystal can be calculated by sampling of the proposed unit cell followed by harmonic (Fourier) rather than non-harmonic summation. It is suggested that rapid computing devices may be used more advantageously with this than with the present methods, and that the advantage would be particularly great for structures with many atoms or with non-spherical atoms. The nature of the inherent error is discussed and a method for eliminating it is presented; an example of the use of the method is given, with a comparison of the results with those obtained by the ordinary method; and strips for 'hypothetical' two-dimensional carbon, nitrogen and oxygen atoms are given.

1. Introduction

The reduction of structure-factor calculation to Fourier-series summation would make it possible to perform the two principal types of computation in X-ray crystal-structure analysis by a single method which is particularly suited to such rapid computing devices as the electronic Fourier-summation computer X-RAC (Pepinsky, 1947) and Hollerith or IBM punched-card machines (Cox & Jeffrey, 1949; Donohue & Schomaker, 1949; Grems & Kasper, 1949; Cox, Gross & Jeffrey, 1949). The purpose of this paper is to show how this reduction can be effected, and to point out the nature of the inherent error and a procedure by which it can be eliminated.

The Fourier transform of the unit cell of a crystal is a continuous function in reciprocal space which constitutes a complete description of the X-ray scattering properties of the unit cell, standing in exactly the same relation to the unit cell as the familiar atomic scattering function does to a single atom. It includes a description of the scattering properties of the crystal which results when the unit cell is repeated on the crystal lattice, for the structure factors of the crystal are merely the values which the unit-cell transform assumes at the points of