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The Field-Induced Ferroelectric Phase of Sodium Niobate

By E. A. Wood, R. C. Miller and J. P. Remeika

Bell Telephone Laboratories, Murray Hill, New Jersey, U.S.A.

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Antiferroelectric sodium niobate ($a=5\cdot57$, $b=15\cdot54$, $c=5\cdot51$ Å) can be changed into ferroelectric sodium niobate ($a=5\cdot57$, $b=7\cdot77$, $c=5\cdot51$ Å) by the application of an electric field perpendicular to the b axis. The 'transition field' is about 50 kV. per cm. When the field is removed, the field-induced structure may then coexist in a single crystal with the unaltered part, not subjected to the field. With crystals of a particular orientation, changes in orientation of the field-induced area can be observed both by X-ray diffraction techniques and with the polarizing microscope.

The combination of two related types of twinning in the ferroelectric crystal makes possible the optical detection of the ferroelectric direction.

In the potassium niobate–sodium niobate system there are three phases, most readily distinguished by the length of the b axis which is successively 15·54, 7·77 and 3·89 Å (4 ×, 2 × and 1 × the edge of the perovskite-type unit) with increasing potassium content. The relation of these phases to the field induced phase in potassium-free sodium niobate is discussed.

Introduction

Antiferroelectric sodium niobate with a unit cell containing eight formula units can be changed into ferroelectric sodium niobate with a unit cell containing four formula units by the application of an electric field. This result was first reported by Wood & Miller (1961) after which more detailed electrical data were published by Miller, Wood, Remeika & Savage (1962). The purpose of this paper is to discuss the crystallography of this and related phase changes.

Crystals of sodium niobate ($NaNbO_3$) have been investigated by various workers for more than ten years. The crystal has a distorted perovskite-type structure in which the 'monomolecular' unit approximates a cube with $a=4$ Å. There have been disagreements in the literature concerning its structure and the presence of ferroelectricity in the material. In the interest of brevity and clarity, the literature as it pertains to the present paper, will be reviewed in outline form.

1949. B. T. Matthias (*Phys. Rev.* **75**, 1771).
$NaNbO_3$ reported ferroelectric. Crystals grown from a mixture of Na_2CO_3, NaF and Nb_2O_5 heated to 1500 °C., and cooled at 100°/hr. Stock materials. Water clear parallelepipeds.

1951. C. Kittel (*Phys. Rev.* **82**, 729).
Suggested the existence of the antiferroelectric state.

1951. E. A. Wood (*Acta Cryst.* **4**, 353).
Reported Matthias' crystal orthorhombic with $a=5\cdot512$, $b=5\cdot577$, $c=4\times3\cdot885\pm0\cdot01$ Å.
Detailed study of twin relationships.

1951. P. Vousden (*Acta Cryst.* **4**, 545).
Acicular crystals 'prepared by dissolving the polycrystalline material in NaCl flux' at 1100°. Application of d. c. field near breakdown (~ 10^4 v./cm.) caused motion of twin boundaries. Determined structure, finding small antiparallel displacements of Nb atoms along a as well as displacements of Na and O atoms along the a and c orthorhombic axial directions by his nomenclature, in which
$a=5\cdot5682$, $b=4\times3\cdot8795$, $c=5\cdot5052$ Å.
Remarked about the existence of ferroelectricity in what he found to be a non-polar structure. Space group $P22_12$.

1952. P. Vousden (*Acta Cryst.* **5**, 690).
Suggested that the discrepancy between his structure and Matthias' results might be resolved if we 'assumed that the crystal changes from a non-polar to a polar state by the sudden reversal of atomic displacements when the field reaches a certain critical value. The substance must possess two distinct, though closely related structures with different space groups but nearly the same free energy'. (Pointed out that Dr H. D. Megaw had made the same suggestion independently by private communication.)

1954. G. Shirane, R. Newnham & R. Pepinsky (*Phys. Rev.* **96**, 581).
Crystals grown by same method as those described in Matthias' 1949 paper found to exhibit no electrical evidence of ferroelectricity. Fields only as high as 20 kV. per cm. were used. Crystal 'seems to be antiferroelectric' in accordance with Vousden's structure. 'Small additions of $KNbO_3$ to pure $NaNbO_3$ produce a new ferroelectric phase, the existence of which suggests a possible explanation of the conflicting dielectric and structural properties previously reported' for sodium niobate. The phase line, according to their dielectric measurements, lies between $(Na_{0.90}K_{0.10})NbO_3$ and

$(Na_{0.95}K_{0.05})NbO_3$. They agree with Vousden and Megaw that a strong electric field might induce a ferroelectric phase in $NaNbO_3$.

1954. L. E. Cross & B. J. Nicholson (*Research*, Vol. **7**, p. s36) quoted by H. D. Megaw, *Ferroelectricity in Crystals*, 1957, p. 100).
Found that no hysteresis loops were developed at low fields, but double loops with fields greater than 90 kV./cm. applied perpendicular to the *y* axis (Vousden's *b* axis). Concerning these results, H. D. Megaw points out, 'this implies the existence of a ferroelectric structure of only slightly greater energy than the antiferroelectric'.

1956. H. D. Megaw (The Chemical Society, London) *Annual Reports on the Progress of Chemistry*, Vol. LIII, p. 401.
Postulated that the phase which Cross & Nicholson induced with a high field was probably not the same as the ferroelectric phase induced by a field at low temperature which has its polar moment along the direction corresponding to *b* in Vousden's structure.

1958. H. D. Megaw & M. Wells (*Acta Cryst.* **11**, 858).
Disagreed with Vousden concerning space group of $NaNbO_3$. Stated that it is *Pbma* or one of its subgroups $Pb2_1$ or $P2_12_12$. This is now agreed to by Vousden (private communication, 1961).

1958. L. E. Cross (*Nature, Lond.* **181**, 178).
Reported that the field required to initiate double hysteresis loops (cf. Cross & Nicholson, 1954) is continuously reduced with increasing additions of potassium in place of sodium 'and the halves of the loop commence to overlap'. He found that 'with compositions containing more than 0·6 mol.% potassium niobate mixed crystals give ferroelectric hysteresis loops'.

1960. C. F. Pulvari (*Phys. Rev.* **120**, 1670).
Reported that $Na(V_xNb_{1-x})O_3$ is one of a class of new ferroelectric materials made up of two or more antiferroelectric compounds. He interpreted the ferroelectricity as due to the interaction of unbalanced dipoles of the two antiferroelectric components making up the crystals.

1960. M. Wells & H. D. Megaw (*Acta Cryst.* **13**, 1072).
Distinguished Phase I, $NaNbO_3$, antiferroelectric with lattice constants essentially as given by Vousden (although they disagree with his space group); Phase II, $Na_{0.975}K_{0.025}NbO_3$ with (Vousden's) *b* axis twice that of the perovskite cubic unit instead of 4 times. 'It is probable that Phase II is identical with the "forced ferroelectric" structure found when large fields are applied to $NaNbO_3$'.

1961. M. Wells & H. D. Megaw (*Proc. Phys. Soc.* **78**, 1258).
Published a revised structure of 'Phase I' $NaNbO_3$ with space group *Pbma* and the structure of 'Phase II', $Na_{0.975}K_{0.025}NbO_3$ with space group $P2_1ma$.
The small displacements of atoms from special positions result in a non-polar structure of Phase I and a polar structure of Phase II.

Experiments and results

The present study was begun for the purpose of investigating the effect described by Pulvari. Crystals of $Na(Nb_{1-x}V_x)O_3$ and $NaNbO_3$ grown from the appropriate oxides in an excess of sodium carbonate were similar in appearance and twin relationships to those $NaNbO_3$ crystals described by Wood (1951). These are laminated twins as shown in Fig. 1. The '*e*, *f*, *g*' nomenclature is useful since, because of the polysynthetic twinning, the different types of surfaces of the crystal are not satisfactorily described by ordinary crystallographic symbols.

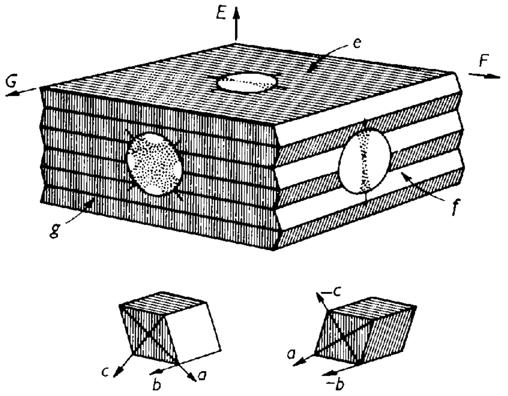


Fig. 1. Perspective view of idealized $NaNbO_3$ crystal, showing optical interference figures.

The electrical effects produced when a field is applied to these crystals have been described elsewhere (Miller, Wood, Remeika & Savage, 1962). It is the purpose of this paper to discuss the crystallographic changes produced by the field.

In virgin sodium niobate the structure (Wells & Megaw, 1961) is based on a unit cell containing eight somewhat distorted perovskite-type units. If undistorted, these would be cubes with sodium at the corner, oxygen at the face centers and niobium at the body center. Small displacements from these ideal positions make it necessary to choose an orthorhombic cell in which *a* and *c* are approximately $\sqrt{2}$ times the perovskite cube edge and *b* 4 times the perovskite cube edge, conveniently called '$4a_c$', about 15·5 Å.

In the present investigation, fields of approximately 50 kV./cm. along *E* or *F*, Fig. 1 (i.e., normal to the *b* axis) resulted in halving the length of the *b* axis. Fig. 2 is a first layer precession photograph with the precession axis normal to (101). The composition of

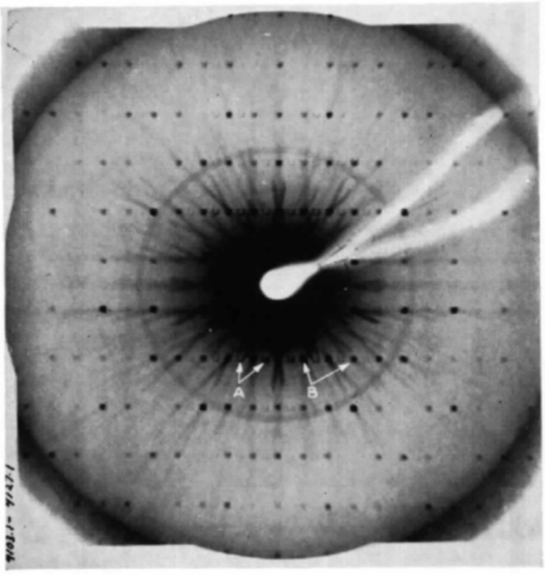
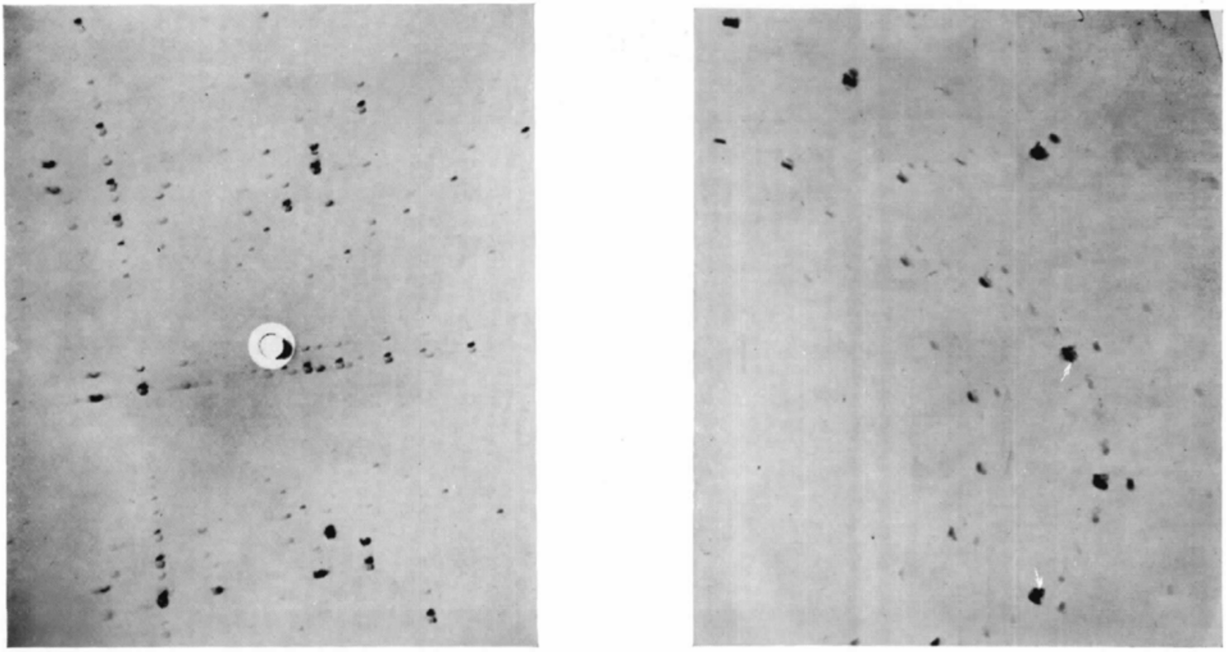


Fig. 2. First layer precession photograph of the crystal shown in Fig. 5. Precession axis normal to (101).



(*a*) (*b*)

Fig. 3. (*a*) Back-reflection Laue photograph of the crystal shown in Fig. 5. (*b*) Part of a forward Laue of the same crystal.

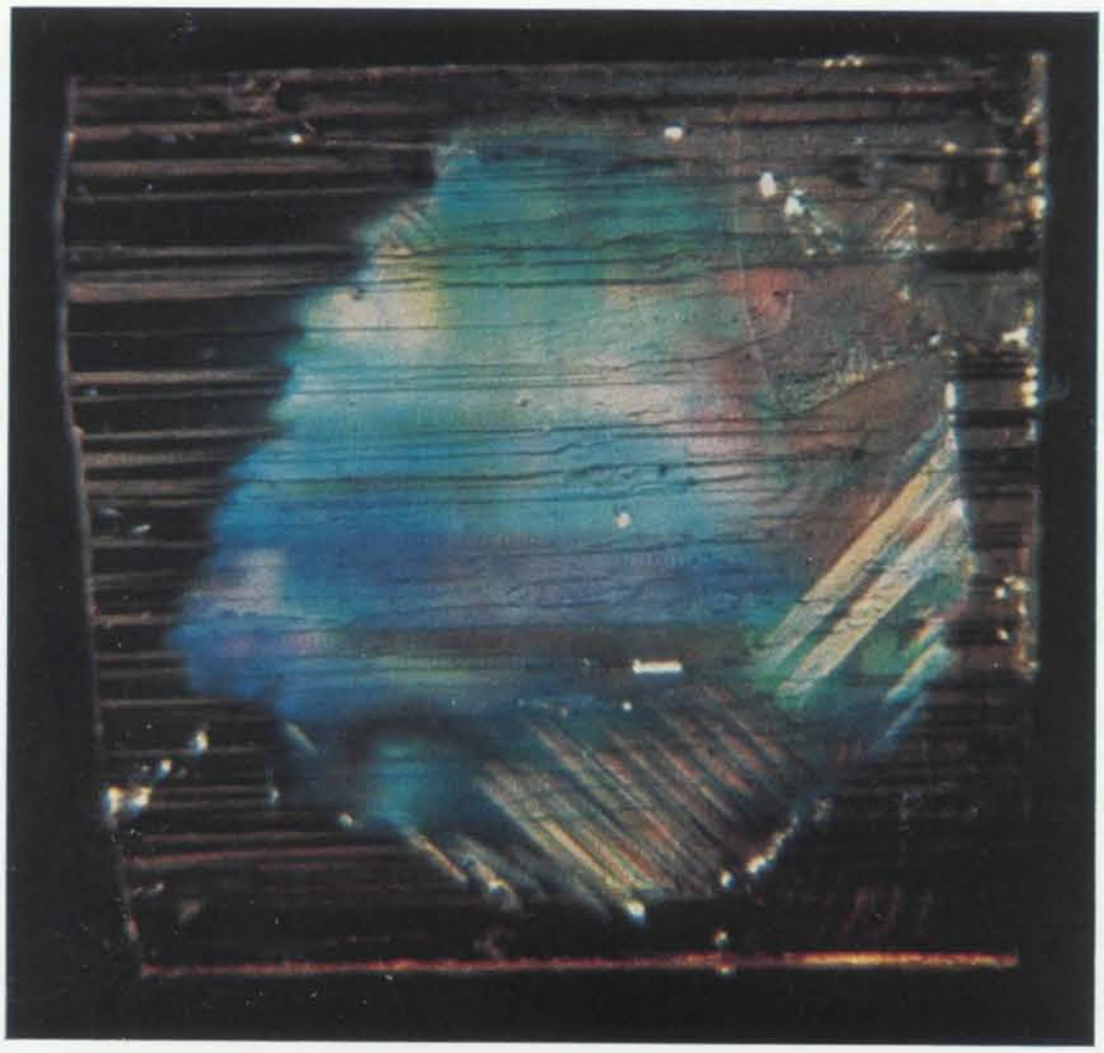


Fig. 5. Photomicrograph of cleaved crystal plate, *f* orientation (see Fig. 1) with central region changed to *e* by the application of a field of approximately 50 kV. cm.$^{-1}$. Between crossed polarizers. The prominent dark lines in the *e* region are cleavage steps. X-ray patterns in Figs. 2 and 3.

this crystal was $NaNb_{0\cdot996}V_{0\cdot004}O_3$. The results to be described were also observed with pure $NaNbO_3$ crystals. The crystal was a thin rectangular plate with its largest faces (*f*, Fig. 1) normal to the precession axis, along which the field was applied. Fig. 5 is a photograph of this crystal in crossed polarized light. The *f* face has been changed to *e* by the field, an effect which has been discussed by Miller, Wood, Remeika & Savage (1962). Since the circular liquid[*] electrodes were slightly smaller than the area covered by the X-ray beam, those reflections which are missing in the field-induced structure appear as spots with missing circular areas.[†] See *A*, Fig. 2. These are the spots due to the $4a_c$ (15·5 Å) length of the *b* axis. These are also missing on the zero layer of course. The pattern from the first layer is illustrated in order to show the presence of the spots in the $2a_c$ ($b =$ ca. 7·75) positions which are extremely weak on the zero layer. See *B*, Fig. 2.

Since Wells & Megaw (1960) have pointed out the probability that Cross & Nicholson's (1957) high-field phase is identical with the Phase II found by them for $Na_{0\cdot975}K_{0\cdot025}NbO_3$, it is desirable to compare our diffraction data with intensities calculated on the basis of their Phase II structure. In order to do this the diameter of the X-ray beam was made smaller by the insertion of a bushing in the collimator so that the beam encountered only that region of the crystal (Figs. 2 and 5) which had been changed by the applied field. It is impossible to cover the whole surface of the crystal with the electrode and apply the high fields needed to induce the transition (the so-called 'transition field' of Miller, Wood, Remeika & Savage, 1962) because of break-down across the edges of the crystal. An attempt to remove the outer (unchanged) portions of the crystal and leave only the part to which the transition field had been applied resulted in the reversion of the metastable altered phase to its original condition with $b = 4a_c$ (ca. 15·5 Å).

A second difficulty in obtaining reliable intensity data from the field-induced phase arose because of the lamellar twinning (Fig. 1) always present in this phase. The structures in the two sets of lamellae are related by a rotation of 180° around the *E* axis, $[101]^*$, as shown in Fig. 1, not by a mirror parallel to the composition plane since this would bring the positive ends of neighboring polar *a* axis together at the composition plane between the lamellae, an energetically unfavorable situation.

As a result of the twinning, reflections from planes of the type $(h_1k_1l_1)$ fall on top of reflections from planes of the type $(l_1k_1h_1)$. There is, however, a way of getting around this difficulty if we make one assumption. In both the structures determined by Wells & Megaw, as well as from our own diffraction data on untwinned fragments of sodium niobate (Phase I), *hk*0 reflections with *h* odd are missing. If we assume that these reflections are also systematically missing from the field-induced phase then a comparison of reflections indexed as *hk*0 (*h* odd) with reflections indexed as 0*kl* (*l* odd) will tell us the volume proportions of the two contributing, twin-related parts. We can then apply the appropriate weighting factor to F_clkh to give an F_c for each (composite) spot for the particular crystal in question. The intensity ratios of *hk*0 (*h* odd) to 0*kl* (*l* odd) are constant for any given crystal, but vary from crystal to crystal.

In Table 1 the F_c column represents *F*'s calculated with contributions from both twin-related parts determined as just described. Thus, for example, the F_c's listed for '*hk*0' reflections are due entirely to the contribution from the 0*kl*, twin-related, reflections. The values in the F_o column were determined in the usual manner from visually estimated intensities. Although the agreement is good for many reflections it is poor for many and the *R* factor is 42%. However, because of the nature of the crystal as discussed below, no conclusions as to the structure of the field-induced phase should be drawn from these data.

A back-reflection Laue photograph of this crystal (Fig. 3(*a*)) shows that in addition to the twinning shown in Fig. 1 which results in an angle of 1° 20′ between twin related {101} planes there is another type of twinning, not previously reported, resulting in a displacement angle of 14′ ± 3′ in a direction normal to the first. A diagram of a single spot of Fig. 3(*a*) is shown in Fig. 4 along with a diagram of the crystal whose photograph is Fig. 5. The *f* part of the crystal would of course be the only part that would show the 1° 20′ displacement of lamellar parts (cf. Fig. 1) in a back reflection Laue photograph, since, in the *f* part, it is the planes nearly parallel to the surface which make this angle with each other whereas in the

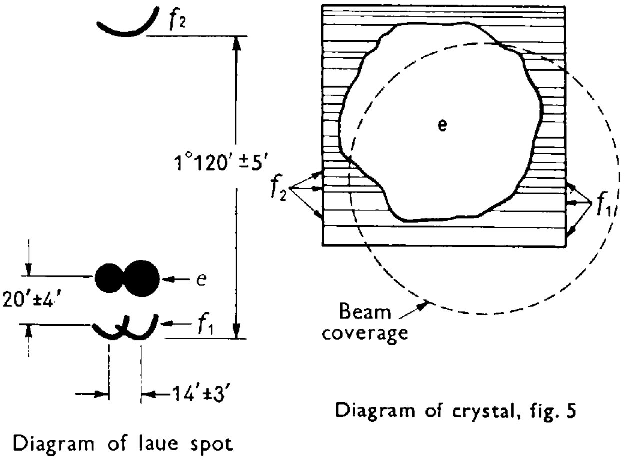


Diagram of laue spot

Diagram of crystal, fig. 5

Fig. 4. Diagram of Laue spot from Fig. 3(*a*), showing its relation to the crystal.

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[*] Aqueous solution of lithium chloride, E. A. Wood patent number 2, 785, 322.

[†] A small strip was broken from the upper edge of the crystal after the photograph in Fig. 5 was made and before the pattern of Fig. 2 was taken.

Table 1. *Observed and calculated structure factors, first layer normal to* [101]*

hkl	F_o	F_c	*hkl*	F_o	F_c
110	n.o.	6	374	n.o.	17
120	39	14	384	15	24
130	130	42	405	28	9
140	n_o	2	415	n_o	7
150	62	32	425	31	17
160	12	6	435	29	8
170	70	34	445	33	8
180	n_o	2	455	n_o	7
190	26	26	465	28	15
1,10,0	n_o	2	201	71	52
021	37	7	211	49	47
031	65	21	221	59	46
041	n_o	1	231	32	40
051	31	16	241	42	32
061	n_o	3	251	43	39
071	32	17	261	18	23
081	n_o	1	271	19	30
091	15	13	281	20	19
0,10,1	n_o	1	291	26	27
102	69	47	2,10,1	n_o	14
112	55	37	302	31	38
122	69	50	312	26	21
132	35	35	322	39	44
142	36	30	332	60	36
152	86	42	342	23	28
162	22	25	352	n_o	23
172	33	33	362	29	30
182	n_o	17	372	52	36
192	43	33	382	15	15
1,10,2	n_o	16	392	n_o	21
203	51	43	403	35	39
213	19	27	413	25	38
223	41	43	423	23	47
233	42	36	433	n_o	27
243	39	32	443	30	34
253	n_o	19	453	41	39
263	23	27	463	19	36
273	28	33	473	n_o	19
283	18	18	483	30	27
293	n_o	15	504	12	36
304	27	39	514	12	21
314	25	31	524	33	52
324	68	61	534	22	28
334	n_o	21	544	42	31
344	28	32	554	n_o	16
354	34	36	564	38	44
364	39	45			

e part the {101} planes of adjacent lamellae are parallel to each other and to the surface.

The unexpected features of Fig. 3(*a*) are the 20′ displacement of the *e* part of the spot (from the central, field-induced region) and the 14′ displacement of both the *e* and f_1 (see Fig. 4) spots in a direction 90° to the previously known twinning. In a forward Laue of the same crystal, part of which is shown in Fig. 3(*b*), the 1° 20′ displacement now is seen in the *e* part of the crystal since now the planes nearly *normal* to the surface are the reflecting planes. In addition there are details of the structure of the spots (indicated by arrows) which indicate twinning or misorientation through still smaller angles.

In view of this substructure no conclusions can be drawn from the intensity data.

Back reflection Laue photographs of a number of other crystals show a variety of displacements of spots, many of which have not yet been satisfactorily interpreted.

The 1° 20′ displacement is found repeatedly and is understood on the basis of the lamellar twinning. The smaller displacements do not always show the same angular separation and in most cases these spots are less well defined, indicating inhomogeneous strain.

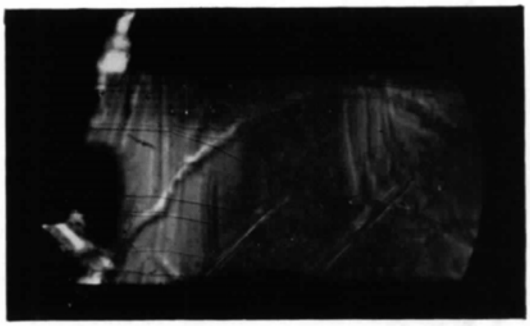
Changes of orientation associated with the production of the field-induced phase

When the *transition field* i.e., the field necessary to cause the transition to the new phase (Miller, Wood, Remeika & Savage, 1962), is applied to an *e* face of the crystal (Fig. 1) the face is still an *e* face after the transition to the field-induced phase. When the transition field is applied to an *f* surface, it changes to an *e* face when the transition takes place. Fig. 5 is a photograph of a crystal plate showing an outer *f* area and a central *e* area resulting from the application of a field. A plausible explanation for this change as being necessitated by an intolerable charge concentration on the twin boundaries if the *f* orientation is retained has been given in detail by Miller, Wood, Remeika & Savage (1962).

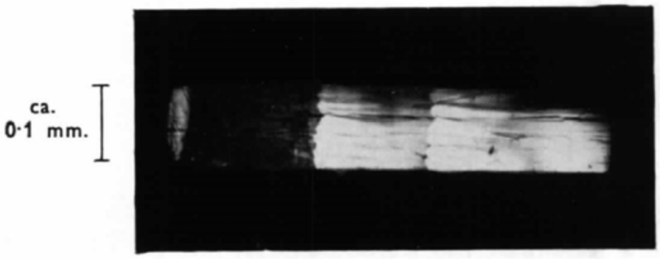
Commonly new sets of twin lamellae are formed in the changed area (which always has the *e* orientation after the change) with the twin boundary (i.e., composition plane) approximately 45° to the edges of the crystal and sloping down into the crystal at an angle which cannot be accurately measured from this view of the crystal (see Fig. 5).

If the angle made by the twin planes with the surface were 54° 44′ and if the crystal were the simple perovskite cube, these planes would be {111} planes. If they are the equivalent planes in the distorted structure, they are either {120} planes or {021} planes. The second alternative seems more probable since *a* is parallel to these planes. The polar direction as indicated by the niobium displacements (assumed to be along the same direction as the antiparallel net displacements of the atoms) is along *a* and composition planes parallel to *a* would not result in the unfavorable charge concentration on the twin boundary that would otherwise occur.

In the central area of Fig. 5, where the crystal has been altered by the field, *e* (Fig. 1) is parallel to the plane of the paper. Along a direction normal to the paper the various lamellae shown in Fig. 1 are traversed and the *a* axis of one lamella makes an angle of 89° 20′ with the *a* axis of the next, in the *ac* plane. Since the twin boundary described above is energetically unfavorable if it is not parallel to *a* it must zig-zag back and forth from lamella to lamella. A photomicrograph of a crystal showing such twins, viewed along both the *E* and the *b* axes, is shown in Fig. 6. The direction of the twin boundary (which



»Plan view« (*e* surface)



»Front elevation« (*g* surface)

Fig. 6. Photomicrograph of *g* surface (010) showing reversal of slope of '45° twin' composition plane in alternate 'lamellar twin' individuals.

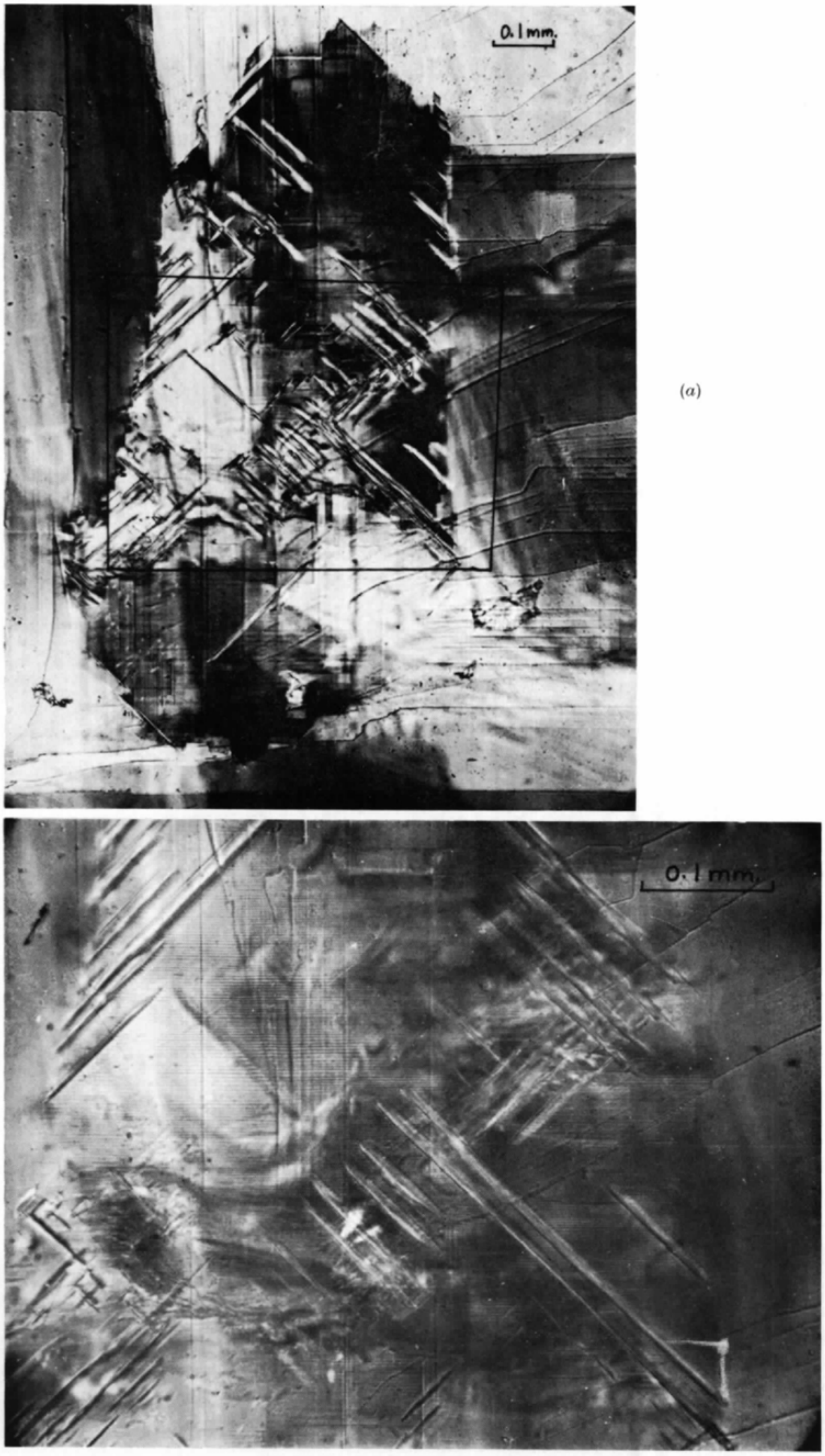


Fig. 7. Photomicrograph of $NaNbO_3$ crystal grown in 1949, cleaved in 1961, and altered by the application of a field of about 50 kV. cm.$^{-1}$. (*a*) Lower magnification. (*b*) Higher magnification.

must be parallel to *a*, by the above reasoning) indicates the polar direction in each lamella.

Fig. 7(*a*) is a photomicrograph (in transmitted light) of a crystal plate cleaved from one of the crystals grown by J. P. Remeika in 1949. The area covered by the liquid electrode when the transition field was applied is marked by a contrast in shade, by the '45° twinning' that has been described above, and by very fine banding parallel to the *b* axis which is better seen in the more enlarged photograph in Fig. 7(*b*).

Such bands have been observed in many crystal plates to which the transition field has been applied. By continuous observation of the crystal in an applied field it has been found that the bands begin at the negative electrode and progress through the crystal with increasing field toward the positive electrode. They have been tentatively interpreted as ferroelectric domains separated by non-ferroelectric septa. In the crystal shown in Fig. 7, the transformation to the field-induced phase has not progressed through the entire thickness of the crystal so that the far side appears like the unaltered periphery of Fig. 7(*a*).

Examination in polarized light

Fig. 5 was taken with the crystal plate between crossed polarizers. The peripheral area of the plate, unaltered by the field, still shows the *f* banding (Fig. 1). A given band which appears dark near one edge of the field is light at the other end. If the transmitted rays were perfectly parallel, we would be looking along a symmetry plane of the optic figure in both sets of lamellae and they would extinguish simultaneously between crossed polarizers. In other words, the traces of the optic planes on the *f* surfaces for the two sets of lamellae are parallel as shown in Fig. 8. The contrast between adjacent lamellae is therefore unexpected and was either not noticed or not explained in the previous study of twinning in sodium niobate (Wood, 1951). The explanation of it can be deduced from Fig. 8 (after Wood, 1951).* The traces of the optic planes on face *g* for the two sets of lamellae are nearly normal to each other, and there is every gradation of angle between this and the zero angle between their traces on face *g*. Therefore, since the light by which Fig. 5 was taken was in fact convergent, the rays at opposite ends of the plane were traveling not along *F* but along a direction slightly rotated toward *G*, giving a slight non-parallelism of the optic plane traces for the ray in question. Since the deviation of the light beam is of opposite sense at the opposite ends of the *f* bands, the extinction angle differs from zero in opposite senses at the two ends.

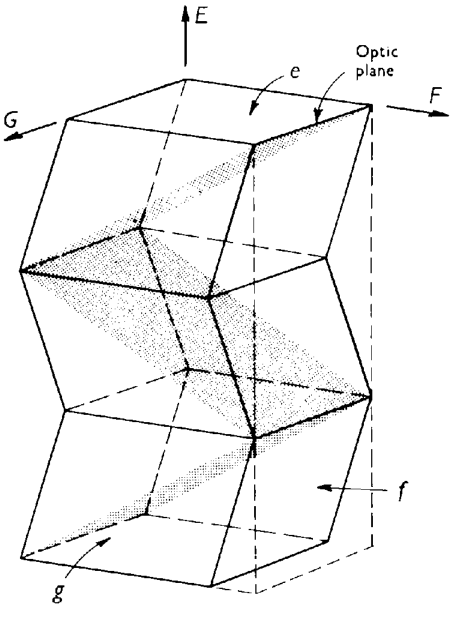


Fig. 8. Orientation of the optic plane in $NaNbO_3$.

Imperfect extinction of *e* plates

The center part of Fig. 5 has been altered to *e* orientation by the application of the transition field (see Miller *et al.*, 1962). All *e* orientation crystal plates between crossed polarizers transmit light in a mottled irregular pattern of colors that are not pure interference colors when they are in what should be the total extinction position. This is difficult to explain since, in any individual lamella the face exposed on the *e* surface (see Fig. 8) is crystallographically equivalent to the face exposed on the *f* surface. Any distortion that would destroy extinction for observation along *E* would destroy extinction for observation along *F*. The only tenable hypothesis seems therefore that the birefringence comes from strain along very thin layers, presumably at the twin boundaries. Light traveling nearly parallel to these thin boundary layers, i.e., in the *F* direction, suffers low angle reflection from the optical discontinuity and too little light travels within the strained layer to be observed. In contrast, light traveling normal to the twin boundaries, i.e., along the *E* direction, Fig. 8, would travel through a succession of such optically anisotropic strained boundary layers and the small retardation at each boundary layer would contribute to a total retardation great enough to give the effect shown in Fig. 5. The closely spaced dark bands indicated by the arrows in Fig. 3(*b*) and visible also in some of the other spots of that figure might be due to the higher reflection intensity from such thin layers of strained material. Such bands are seen throughout the spot with shorter exposure.

The argument against this hypothesis is that if the boundary strain is great enough to produce bire-

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* Optic plane formerly shown parallel to (100) since either diagonal plane could be chosen on the basis of observations by Wood. Subsequently refractive index measurements by Jona, Shirane & Pepinsky (1955) have shown (001) to be the correct orientation.

fringence one would not expect the crystals to contain such large numbers of these boundaries as they do, nor would one expect that they could be shifted by approximately 90° without rupture of the crystal as shown in Fig. 5 and described by Miller, Wood, Remeika & Savage (1962).

The system $NaNbO_3$-$KNbO_3$

Earlier in this paper it was pointed out that Shirane, Newnham & Pepinsky (1954) reported that small additions of potassium niobate to sodium niobate resulted in a ferroelectric phase. They thought the critical amount required lay between 5 and 10 mol.% $KNbO_3$. Cross (1958) found that any crystals containing more than 0·6 mol.% $KNbO_3$ showed ferroelectric hysteresis loops. Since Wells & Megaw (1960) have shown that the b axis of ferroelectric $Na_{0{\cdot}075}K_{0{\cdot}025}NbO_3$ is half that of pure sodium niobate, i.e., is $2a_c$ (ca. 7·75 Å) in length, it seems likely that the crystals reported as ferroelectric, by Shirane *et al.* (1954) and by Cross (1958) had the $2a_c$ b axis (ca. 7·75 Å) as well and therefore that the $4a_c$–$2a_c$ boundary lies between zero and 0·6 mol.% $KNbO_3$.

Pure $KNbO_3$ has a distorted perovskite-type structure with only two formula weights per cell, a '$1a_c$' cell with one dimension approximately 4 Å and the other two approximately $\sqrt{(2)} \times 4$ Å. Therefore it was obvious to the present authors that there must be a second phase division in the system somewhere between 2·5% $KNbO_3$ and 100% $KNbO_3$. Reisman & Banks (1957) have made differential thermal analyses, density and X-ray studies of the system $KNbO_3$–$NaNbO_3$. They used powder diffraction techniques and assumed the presence of 'extra lines' (at $\sqrt{(h^2+k^2+l^2)} = 2\frac{1}{2}$, $2\frac{3}{4}$, $4\frac{3}{4}$, $5\frac{1}{2}$, and $9\frac{1}{2}$) to be indicative of the $4a_c$ cell (b ca. 15·5 Å). Actually, since all of these lines can be given integral *hkl* values with a b axis approximately equal to 7·75 Å ($2a_c$), they are not proof of the $4a_c$ cell, but since this was the only larger cell which had been reported at that time, the interpretation seemed reasonable. The 'superlattice' lines from the 15·5 Å b axis are apparently too weak to show in a powder pattern. They would require fractional $h^2+k^2+l^2$ values with the number sixteen in the denominator. It is therefore necessary to take a single crystal photograph to determine the length of the b axis.

As the result of their interpretation, Reisman & Banks state 'a critical examination of the mixed system unequivocally shows the persistence of the 'extra lines' down to at least 75 mol.% $NaNbO_3$. Since the 'extra lines' could arise only from the alternate displacement of pairs of Nb atoms' (the $4a_c$ structure with b ca. 15·5 Å) 'which is characteristic of the antiferroelectric state, it is inconceivable that the mixed phases are ferroelectric in concentration greater than 75 mol.% $NaNbO_3$'. Since the 'extra lines' referred to are all possible lines for the ferroelectric $2a_c$ phase with b about 7·75 Å, Reisman & Banks' statement is now interpreted to mean that they saw X-ray evidence for the $2a_c$ phase up to a $KNbO_3$ content of 25%, but not beyond that.

The diagram given by Reisman & Banks for density versus composition in this system shows a broad minimum (about 4·50 g.cm.$^{-3}$) at about 35 mol.% $KNbO_3$. Its significance is not discussed by Reisman & Banks, but the closeness of this minimum to the composition at which the 'extra lines' disappear may indicate that it marks the boundary between the $2a_c$ (b about 7·75 Å) structure and the $1a_c$ structure (b about 3·9 Å).

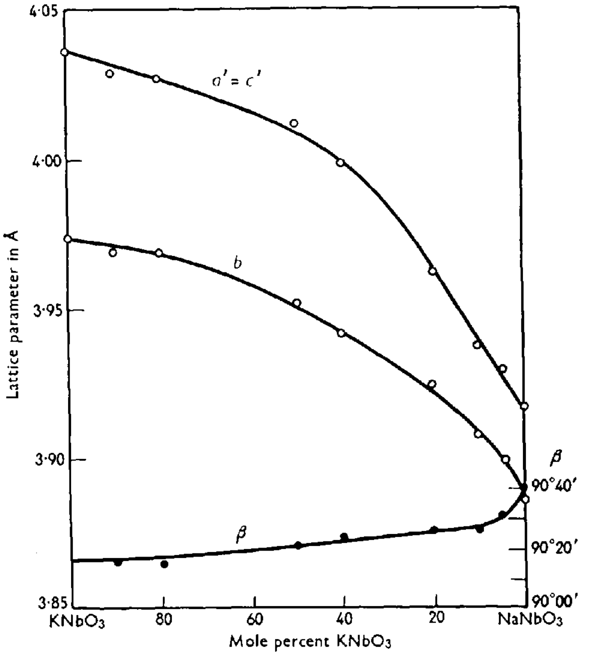

Fig. 9. Lattice parameters versus composition in the $KNbO_3$–$NaNbO_3$ system, disregarding multiplicity of the b axis after Shirane *et al.* (1954).

In this connection Fig. 9 from Shirane, Newnham & Pepinsky (1954) is of interest. It is a plot of the dimensions of the monomolecular perovskite-type unit as a function of composition in this system, disregarding the multiplicity in the b direction. There is a noticeable break in the $a' = c'$ curve in the vicinity of 30–35% $KNbO_3$. The curves for b and β do not show this, but a reasonable curve for each could be drawn, using their experimental points which would show a break at this composition.

Fig. 10 shows the lattice constant curve that can now be drawn including the multiplicity of the b axis as now known. The variations shown in Fig. 9 cannot very well be seen on this scale.

The structure of $KNbO_3$ has not been published, but some work has been done on it by H. D. Megaw and her students. Since the relationship of the $2a_c$

(b ca. 7·75 Å) structure of (Na, K)NbO_3 to the $1a_c$ (b ca. 3·9 Å) structure of $KNbO_3$ must involve small displacements that are *different* in the two halves of the cell in the $2a_c$ structure and the *same* in the $1a_c$ structure, the interesting possibility is suggested of again producing the phase change from one of these to the other by the application of a field. Preliminary efforts to achieve this have failed, perhaps due to the poor quality of the crystals of appropriate composition.

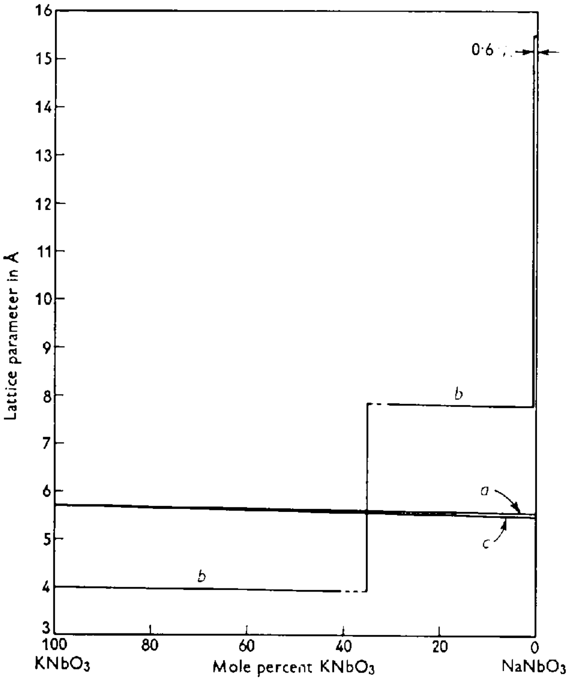

Fig. 10. Lattice parameters versus composition in the $KNbO_3$-$NabO_3$ system.

We wish to thank M. Wells and H. D. Megaw for making available to us a prepublication copy of their paper on the structures of $NaNbO_3$ and $Na_{0\cdot975}K_{0\cdot025}NbO_3$ and both Megaw and Vousden for discussion of their work by letter. We are grateful to Vera B. Compton for taking the X-ray diffraction pictures and performing some of the calculations for this work and to R. G. Treuting for the computer programs used.

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