Acta Cryst. (1958). **11**, 858

The Space Group of $NaNbO_3$ and $(Na_{0.995}K_{0.005})NbO_3$

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(*Received* 11 *March* 1958)

A method is described for the determination of possible space groups for pseudosymmetric structures, i.e. structures derived from an idealised structure of higher symmetry by small displacements of the atoms from special positions. Conventionally, systematic absences are used to infer the presence of symmetry operators; this method is difficult to apply in the case of a pseudosymmetric structure where the space group absences occur among a set of systematically weak reflections. The new method uses systematic variations of intensity among these weak reflections to infer the sense and magnitude of the displacements of atoms from their idealised positions; symmetry operators are then introduced in a manner consistent with the displacements. The detailed application of the method to $NaNbO_3$ is described and the possible space groups are shown to be *Pbma* or one of its subgroups $Pb2_1a$ or $P2_12_12$.

Introduction

We have recently undertaken single-crystal studies on a material of composition $(Na_{0.995}K_{0.005})NbO_3$, kindly supplied to us by Dr L. E. Cross. Its structure belongs to the perovskite family, i.e. it is derived from that of ideal perovskite by small displacements of the atoms.

There has been considerable interest in compounds of this group because of their ferroelectric and antiferroelectric properties. The structure of pure $NaNbO_3$ has been studied by Vousden (1951). Electrical and optical evidence (Cross, 1958) suggested that there was no phase boundary between 99·5% Na and 100% Na; but our results for the former material differed in detail from those of Vousden for the latter. It therefore became desirable to re-examine pure $NaNbO_3$. We were unfortunately unable to obtain untwinned crystals of this; nevertheless it was possible to index the high-angle reflections unambiguously, and to show that the significant features were identical with those of the 99·5% material.

It is not easy to determine the space group of a pseudosymmetric structure with certainty by conventional methods, because of the large number of systematically weak reflections. It is possible, however, to use the experimentally determined intensities in a qualitative way to draw conclusions about the atomic positions, and from these to deduce the space group. Because of the importance of perovskite-type structures, and because the general line of approach may be useful with other pseudosymmetric structures, it seemed worth recording the experimental evidence and nature of the argument. This has been done for the 99·5% material rather than pure $NaNbO_3$, because the existence of untwinned crystals allowed more complete evidence to be obtained.

$(Na_{0.995}K_{0.005})NbO_3$: experimental

The material consisted of rectangular plates and needles. With care, it was possible to pick out untwinned crystals about 0·1 mm. square × 1·0 mm. long. The cell dimensions were found from oscillation photographs, with Cu $K\alpha$ radiation, of twinned and untwinned crystals about the axes [10$\bar{1}$], [010], and [101]. Weissenberg photographs, using Cu $K\alpha$ and Mo $K\alpha$ radiation, were taken of the *hkh* and *h*0*l* zones and the *h*1*l* and *h*2*l* layers; of these only *hkh*, *h*0*l* and *h*1*l* were used in deducing the space group, but the others provided confirmation.

Unit cell and symmetry

The material was believed, from optical evidence, to be orthorhombic. This was confirmed by X-ray work, which showed (i) no detectable departure from 90° angles (confirming Vousden's results), (ii) no difference in spacing or intensity (after correction for absorption) between pairs of reflections *h*0*l* and *h*0$\bar{l}$, *hk*0 and *h*$\bar{k}$0, 0*kl* and 0*k*$\bar{l}$.

Table 1. *Cell dimensions*

		$(Na_{0.995}K_{0.005})NbO_3$	Pure $NaNbO_3$ (Vousden, 1951)
Orthorhombic Axes	*a*	5·563 ± 0·003 Å	5·568 Å
	b	15·508 ± 0·010	15·518
	c	5·514 ± 0·003	5·5052
Monoclinic Axes	*a*, *c*	2 × 3·916 ± 0·002 Å	2 × 3·885 Å
	b	4 × 3·877 ± 0·002	4 × 3·879
	β	90° 33′ ± 1′	90° 40′

Figures given for errors are not standard deviations but estimated limits of error,

The cell dimensions are given in Table 1; they are close to those for pure $NaNbO_3$. For convenience, dimensions are also given in terms of the 'monoclinic' cell, i.e. a non-primitive true unit cell so chosen that its axes correspond in direction with those of ideal perovskite. Throughout the text of this paper, however, we use the primitive true cell chosen with its axes along the orthorhombic symmetry

directions. If the ideal perovskite structure were referred to these axes, it would be face-centred on B, and have four identical layers within the height b of the unit cell.

Intensities

For the present purpose, rough qualitative estimates of intensity are adequate. The facts used as evidence for the space group are recorded below. It should be noted that the strong reflections are those characteristic of the ideal perovskite structure, and have $h+l = 2m$, $k = 4n$ (where m and n are integers). All others are systematically weak or absent; they are the *difference reflections* ('superlattice reflections').

1. In the $h0l$ zone,
   (*a*) reflections with $h+l$ odd are absent altogether if l is small (e.g. 700, 601), but appear, though they are very weak, if l is large (e.g. 007, 106).
   (*b*) the strong reflections $h00$ fall off steadily with h.
2. In the hkh zone,
   (*a*) reflections with $k = 4n+2$ are completely absent.
   (*b*) reflections with $k = 4n\pm1$ are weak if h is small, and increase in intensity rapidly with h.
   (*c*) neither within the class $k = 4n$ nor within the class $k = 4n\pm1$ is there any apparent dependence on k.
3. In the $h1l$ layer,
   (*a*) reflections with h small are weak,
   (*b*) reflections with $h+l$ odd are weak,
   (*c*) reflections with $h+l$ even increase in intensity quite rapidly with h,
   (*d*) reflections $h10$ are absent if h is odd,
   (*e*) reflections $01l$ are all absent.

Deduction of atomic positions

We make the following postulates: (i) the structure is close to that of ideal perovskite, (ii) all intensities are preponderantly due to the contribution of Nb atoms (except possibly those near the origin in reciprocal space).

The unit cell contains 8 Nb atoms, each close to its ideal position at the corner of a sub-cell. We may write its coordinates with respect to this corner as x_i, y_i, z_i (these being all small quantities). We may conveniently divide the atoms into two sets, x_{jp}, y_{jp}, z_{jp} and x_{jq}, y_{jq}, z_{jq}, where the suffix $j (j = 0, 1, 2, 3)$ indicates the height of the ideal position as a multiple of $b/4$ (the origin being taken at an ideal Nb position) and the suffix p or q distinguishes whether it is at $x = 0$, $z = 0$, or $x = \frac{1}{2}$, $z = \frac{1}{2}$.

The geometrical structure factor for all the Nb's is then

$$\Sigma_j i^{jk}\left\{\exp 2\pi i(hx_{jp}+lz_{jp}) \exp 2\pi iky_{jp} + \exp 2\pi i(hx_{jq}+lz_{jq}) \exp 2\pi iky_{jq} \exp 2\pi i\frac{h+l}{2}\right\}. \quad (1)$$

We assume in the first instance that the magnitudes of all the x's are equal, and similarly of all the z's, but that they will have different signs. This is strictly true if the atoms are in general positions of orthorhombic holohedral symmetry (class *mmm*), but in any case it is a reasonable approximation, since the magnitudes are all small. Afterwards we shall consider what differences are to be expected in the alternative extreme case, when some of the magnitudes are allowed to be zero (corresponding to special positions).

Since the symmetry is orthorhombic (though not necessarily holohedral) the signs of each coordinate (x or z) of the four atoms associated with p are either all alike or half plus and half minus. Whichever condition holds for p holds also for q. Hence we can argue as follows.

Consider reflections $h0l$ with h small or zero. The structure factor is approximately

$$\Sigma_j\left\{\exp 2\pi ilz_{jp} + \exp 2\pi ilz_{jq} \exp 2\pi i\frac{h+l}{2}\right\}. \quad (2)$$

Since, for $h+l$ odd, these intensities are not zero, all the z_{jp}'s must have the same sign, opposite to that of all the z_{jq}'s. Since the intensities are only detectable for l large, $|z|$ must be small.

Consider reflections $h1l$, with l small. The structure factor is approximately

$$\Sigma_j i^j\left\{\exp 2\pi ihx_{jp}+\exp 2\pi ihx_{jq} \exp 2\pi i\frac{h+l}{2}\right\}. \quad (3)$$

Since these intensities increase fairly rapidly with h for $h+l$ even, $|x|$ must be moderately large, and x_{jp} must have the same sign as x_{jq} and the opposite sign from $x_{j+2,p}$. This conclusion is in agreement with the fact that $h1l$ reflections with l small remain weak for $h+l$ odd, and that $h0l$ reflections with l small are absent for $h+l$ odd.

To complete the set of signs of x, z, we may make an arbitrary choice of x_{0p}, z_{0p}, and x_{1p} as positive, thus fixing the positive senses of the x, z and y axes respectively. The set is now as shown:

	p		q	
	x	z	x	z
$j = 0$	+	+	+	−
1	+	+	+	−
2	−	+	−	−
3	−	+	−	−

Since the hkh intensities for $k = 4n$, $k = 4n\pm1$, or $k = 4n+2$ do not vary noticeably with n, $|y|$ must be small. The following argument suggests that it may be strictly zero. The structure factor for hkh reflections with $k = 4n+2$, which are experimentally zero, is

$$\Sigma_j(-1)^j\{\exp 2\pi i(hx_{jp}+hz_{jp}) \exp 2\pi iky_{jp} + \exp 2\pi i(hx_{jq}+hz_{jq}) \exp 2\pi iky_{jq} \exp 2\pi ih\}. \quad (4)$$

Since the signs of x and z are identical for layers $j = 0, 1$ and again for $j = 2, 3$, this becomes zero if

$y_{0p} = y_{1p}$, $y_{2p} = y_{3p}$, and similarly for terms in q. But there can be no symmetry element imposing these equalities unless the atoms are in special positions with y zero; and it is improbable that the equalities would occur for all four pairs of atoms without a symmetry requirement.

Estimate of magnitudes of displacements

It is worth while at this stage to estimate the magnitudes of x and z, using very rough visual comparisons of intensities.

Experimentally, 505 and 515 are roughly equal. The calculated intensities are in the ratio $64\cos^2 2\pi.5x : 32\sin^2 2\pi.5x$, or $2\cot^2 10\pi x$. Hence $x \simeq 0{\cdot}03$, i.e. the displacement is 0·17 Å. This is in agreement with the observed steady decrease of $h0l$ for $h+l$ even, and the steady increase of $h1h$, as h increases up to the limit of observation, $h = 7$ in the first case and $h = 5$ in the second.

Again, 007 is experimentally very much weaker than 107. From a preliminary rough estimate we may put the ratio as $\frac{1}{10}$ (concerning ourselves only with order of magnitude). The calculated ratio is $64\sin^2 2\pi.7z : 64\cos^2 2\pi.7z \times \cos^2 2\pi x$, or very nearly $\tan^2 14\pi z$. Hence $z \simeq 0{\cdot}007$, i.e. the displacement is 0·04 Å.

Vousden (1951) found, for pure $NaNbO_3$, x and z components of the displacement of 0·11 Å and 0·04 Å respectively. There is order-of-magnitude agreement with our results, which is all we are looking for at this stage.

Consideration of special positions

If any atoms are in special positions in the (010) projection, orthorhombic symmetry requires that they shall occur in pairs. Consider the case in which two pairs of atoms have an x-coordinate of exactly zero and the other two pairs have a non-zero x coordinate of magnitude $|x|$. From the greater rate of increase of intensity for $h1l$ when $h+l$ is even, compared with that for $h0l$ when $h+l$ is odd, we can still deduce that $|x| > |z|$. Then, if we approximate by putting $z = 0$ the calculated intensities of 505 and 515 are in the ratio $64\cos^2 \pi.5x : 32\sin^2 \pi.5x$, from which $x \simeq 0{\cdot}07$. If we use this value to calculate the $h00$ intensities we find that they fall to zero very rapidly: in fact they show a steady decrease up to $h = 8$, and 400, which on the above view should be weak, is in fact a very strong reflection. From this we conclude that no atoms have a zero x-coordinate.

Since the value of $|z|$ is already very small we cannot use a similar argument to exclude the possibility that certain atoms have a z-coordinate of exactly zero; however, our interest is to produce a working assumption on which to base a structure determination, and since $|z|$ is so small the distinction between zero and non-zero values becomes less important. Thus as far as we can see there is no evidence

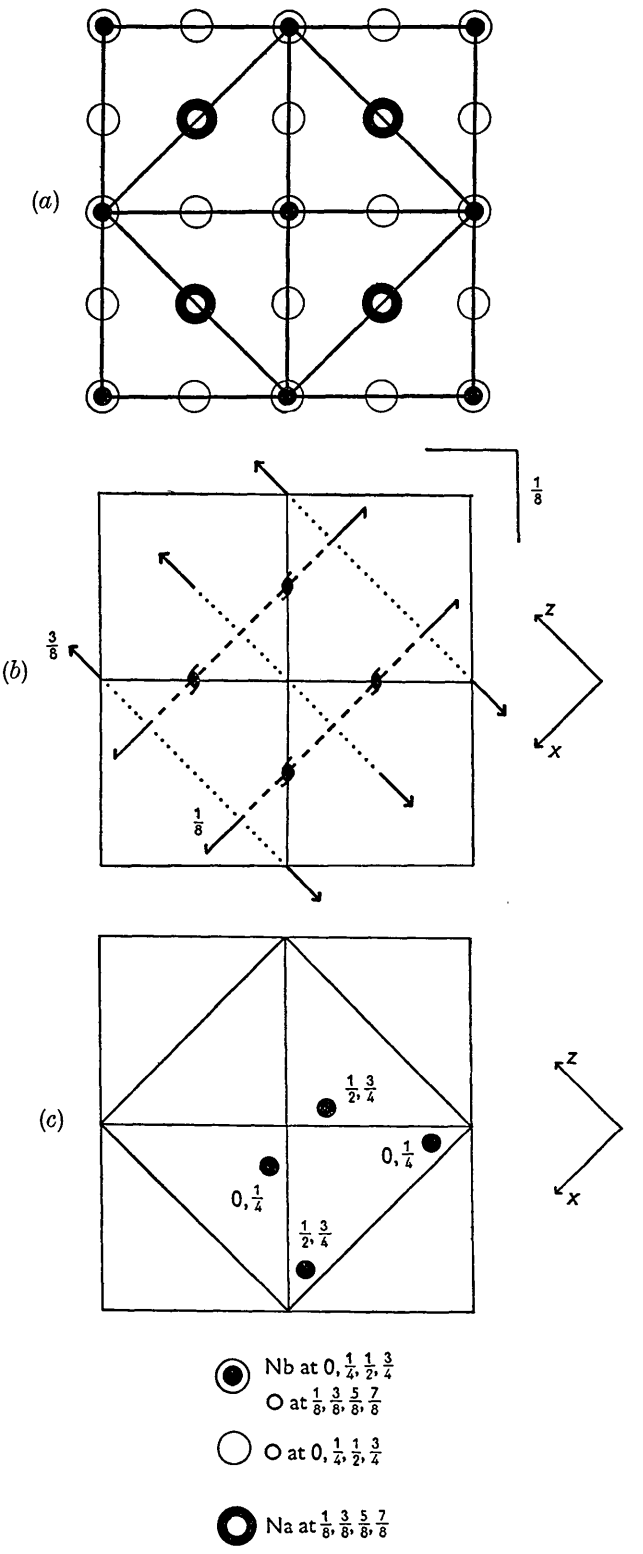

Fig. 1. Projection on (010): (*a*) positions of atoms in ideal perovskite structure, (*b*) symmetry elements of *Pbma*, (*c*) arrangement of Nb atoms deduced in the text (with magnitudes of displacements exaggerated).

to contradict the view that all the $|x|$ are equal, (ca 0·03) all the $|z|$ are equal, (ca 0·007) and all the $|y|$ are zero; we take this as our working assumption.

Deduction of space group

The arrangement of atoms deduced above is shown in plan in Fig. 1(*c*) with displacements x and z exaggerated. It has the symmetry *Pbma*, with the *b*-glide plane at $x = 0$, the m plane at $y = \frac{1}{8}$, and the *a*-glide plane at $z = \frac{1}{4}$, relative to the ideal Nb position as origin. Figs. 1(*a*) and 1(*b*) show that these symmetry planes (and the concomitant axes) are all possessed by an ideal perovskite structure with this size of cell; hence no new symmetry has been created in the pseudosymmetric structure.

We might have reached this conclusion about the space group directly, by conventional methods, if we had trusted our systematic absences. The required absences are $0kl$ for k odd, and $hk0$ for h odd, both of which we know to hold when $k = 1$. These, by themselves, give a choice between *Pbma* and $Pb2_1a$; adding the information that the y parameters are zero decides for *Pbma*.

This argument has taken only Nb atoms into consideration. We have to remember that when Na and O are included the true symmetry may be lower; it must then be a sub-group of *Pbma*. Work in progress on the detailed structure has, however, shown no need as yet for such lowering; neither does there seem to be any evidence for the occurrence of piezoelectricity (Cross, private communication), which would be expected if the class were not *mmm*.

Discussion of method

It is interesting to note the contrast between the conventional method and that used here. Conventionally we consider systematic *absences* only, deduce the symmetry elements, insert the atoms in a set of trial positions consistent with the symmetry, and compare calculated and observed intensities. In the new method we consider systematic *regularities* in difference intensities, deduce the sense and relative magnitude of the displacements of atoms from ideal positions, and insert the symmetry elements in positions consistent with them. It is to be noted that the position of the set of symmetry elements relative to the known array of atoms is found directly by the new method, whereas the conventional method left it still to be determined. On the other hand, the fact that approximate estimates of intensities are used means that the result remains an approximation; for example, we cannot be sure of the existence of a true mirror plane, but merely that the atoms are close to positions which they would occupy if such a plane existed. This is not wholly a disadvantage, for we are ultimately interested in atomic positions rather than in the space group, and it is better to be sure of a good approximation which can perhaps be refined later than to aim at rigour from the beginning with the risk of being grossly astray.

Experimental results for $NaNbO_3$

A Weissenberg photograph of a twinned crystal was taken about [010]. Like the 99·5% Na material, it showed hardly any $h0l$ reflections for $h+l$ odd; but the same reflections as before, with large l, were unmistakably present, notably 007 and 306, the latter being distinguishable from a twinned orientation of 603. All intensities were, to a preliminary inspection, the same as for the 99·5% Na material.

Comparison with Vousden's structure for $NaNbO_3$

There seems no reason for supposing that $NaNbO_3$ and $(Na_{0\cdot995}, K_{0\cdot005})NbO_3$ are different phases. The X-ray results give unit cells of very nearly the same size, and with very nearly the same magnitudes for the x and z components of the Nb displacements, since the intensities in the $h0l$ zone are closely alike. Vousden (1951) does not record any observation of the 007 and 306 reflections, but they might not have been noticeable against the background in his oscillation photographs. It is worth noting that 007 and 701 have almost exactly the same spacing and would overlap on an oscillation photograph of a twinned crystal. The evidence which Vousden publishes does not lead unambiguously to his space group, $P22_12$, and in fact we can find nothing in his work which would exclude the possibility of *Pbma* or its sub-groups $Pb2_1a$ or $P2_12_12$. (Vousden's reason for rejecting $P2_12_12$, that it is inconsistent with a perovskite structure, is not valid). It should be noted that the difference is not merely a matter of degree of approximation; $Pb2_1a$ and $P2_12_12$ are capable of giving approximately the same displacements as *Pbma*, while $P22_12$ is not. The diad axes in $P22_12$ are differently placed relative to the Nb atoms, and this will affect the whole system of displacements of Na and O. It is satisfying, however, to notice that the main features ascribed to $NaNbO_3$ remain unaffected even though the space group assigned to it has to be amended. These are the 4-layer unit cell, and the Nb displacements with large antiparallel components in the x-direction, arranged in a sequence of layers parallel to (010) such that a pair of layers with displacements in one sense is followed by a pair with displacements in the opposite sense.

Summary.

$NaNbO_3$ and $(Na_{0\cdot995}K_{0\cdot005})NbO_3$ are the same phase. As far as Nb positions are concerned the space group is *Pbma*, and this is probably the true space group of the structure, though the possibility of one of its subgroups, e.g. $Pb2_1a$ or $P2_12_12$, is not completely excluded. The new method of deriving the space group from

observed intensities ensures that there is at least a good approximation to the atomic positions. Further work is in progress.

We wish to express our thanks to Dr L. E. Cross for providing the crystals together with information about their electrical properties, and to Dr P. Vousden for the opportunity of discussing this note before publication. One of us (M. W.) thanks D.S.I.R. for financial support while this work was carried out.

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Acta Cryst. (1958). **11**, 862

On the Structure of Staurolite, $HFe_2Al_9Si_4O_{24}$

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(*Received* 26 *March* 1958)

A reinvestigation of the structure of staurolite has been made taking account of new chemical analyses leading to the chemical formula $HFe_2Al_9Si_4O_{24}$ or $4\,Al_2SiO_5.AlOOH.2\,FeO$ proposed by Hörner; the staurolite cell contains two of these molecules, whereas the old formula was $2\,Al_2SiO_5.Fe(OH)_2$, with four molecules in the unit cell. The two surplus Al^{3+} ions can be located reasonably and the Fe^{2+}–O^{-2} distance has been also improved. The agreement between measured and estimated intensities and measured and calculated F-values is satisfactory. The true space group is $C2/m$.

The structure of staurolite was determined long ago by one of us (Náray-Szabó, 1929), but since then some doubts have arisen about the chemical formula which had been idealized as

$$2\,Al_2SiO_5.Fe(OH)_2 = H_2FeAl_4Si_2O_{12}\,.$$

Analytical evidence available in 1929 was not enough to invalidate this formula, until Skerl, Bannister & Groves (1934) showed that the cell of lusakite, a cobalt-bearing staurolite, contains 18 aluminium ions. A similar result was obtained by Juurinen (1956) for common rock-forming staurolite crystals. Meanwhile Hurst, Donnay & Donnay (1956) made a thorough study of the morphology, twinning and the optical properties of staurolite. They conclude that 'the evidence provided by X-ray diffraction is completely in favour of orthorhombic symmetry'. Optical measurements, however, showed that the real symmetry is monoclinic. These authors also took precession X-ray photographs by the method of de Jong-Bouman (1938) with a camera of the Buerger type (1939) and found some very weak reflexions indicating that the space group *Ccmm* adopted by Náray-Szabó is only a pseudo-space-group and the real one is a sub-group of it, $C2/m$. Juurinen choose $C222_1$ which is in contradiction to the monoclinic symmetry.

The structure type of staurolite $S0_4$ is based on *Ccmm* which was also found by Cardoso (1928). No twofold positions exist in this space group and therefore the few chemical analyses were rounded off to the first formula given above a procedure which also takes account of the close relationship of staurolite with kyanite Al_2SiO_5, which exhibits frequently a parallel growth with staurolite.

In view of the contradictions of the papers mentioned we re-examined the structure of staurolite. A series of oscillation photographs has been taken from a small staurolite crystal but we failed to find any reflexions on them to which indices prohibiting *Ccmm* could unambigously be assigned. We are much indebted to Dr V. J. Hurst by whose courtesy we obtained a precession X-ray photograph of a minute staurolite crystal, showing $(0kl)$ reflexions only. No ambiguity can arise in the indexing of this diagram and in fact some very faint reflexions forbidden in *Ccmm*, e.g. (001), (021), (041) etc. occur on it. On our own oscillation photographs, taken with Mo K radiation, a few faint reflexions coinciding with the β-spots of other reflexions appeared and have therefore been regarded as doubtful. Our own unambiguously indexed reflexions and the spots appearing on the photograph obtained from Dr Hurst indicate that the real space group is a sub-group of *Ccmm* but not $C222_1$ in which (001) could not occur. Neither Hurst, Donnay & Donnay (1956) nor the present authors were able to find a piezoelectric effect; therefore the symmetry centre required by $C2/m$ is probable and so this must be adopted as the true space group.

The content of the unit cell which has been idealized in the original work to $H_8Fe_4Al_{16}Si_8O_{48}$, should be $H_2Fe_4Al_{18}Si_8O_{48}$ according to analyses of Hörner (1915) and Skerl, Bannister & Groves (1934) and