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Structural Phase Transitions in Sodium–Potassium Niobate Solid Solutions by Neutron Powder Diffraction

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The structures of (Na,K)NbO$_3$ solid solutions have been determined by using the neutron powder-profile refinement technique: phases K and L at room temperature, and G and F at higher temperatures. In each case approximate values have been found for position parameters and temperature factors. The structural models proposed by Ahtee & Glazer [*Acta Cryst.* (1976), A**32**, 434–446] based on the lattice parameters and intensities of difference reflexions have been found to be substantially correct. Indications of vibrational modes have been found in the sequential phase transitions of Na$_{0\cdot90}$K$_{0\cdot10}$NbO$_3$.

1. Introduction

Recently Ahtee & Glazer (1976*a*,*b*) have studied the different phases of Na$_{1-x}$K$_x$NbO$_3$ both at room temperature and above. From the lattice parameters and the intensities of certain difference reflexions they have proposed structural models for each phase. Their preliminary interpretations are marked in the phase diagram shown in Fig. 1 and also compiled in Table 1.

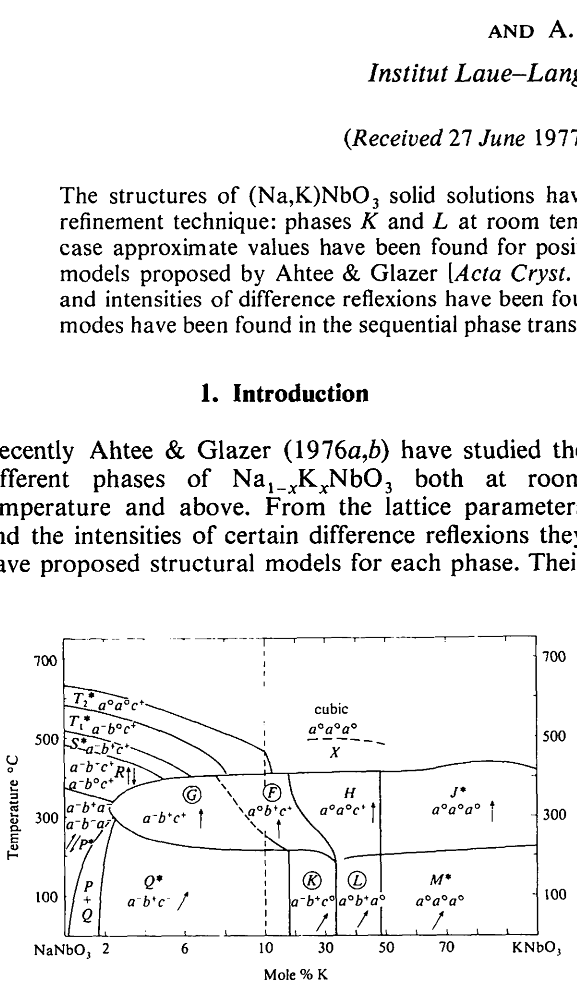

Fig. 1. Phase diagram of Na$_{1-x}$K$_x$NbO$_3$. In each phase the tilt system is indicated according to the scheme of Glazer (1972). Vertical arrows indicate one-corner displacements and inclined arrows two-corner displacements of the cations. The phases with known structures are marked with asterisks. The circled letters show the phases studied in this work.

The purpose of this paper is to give a more detailed picture of what is really happening in structural phase transitions by determining the magnitudes and directions of the atomic displacements. Since the growth of single crystal is difficult, this is most conveniently achieved by using the neutron powder profile refinement technique originally proposed by Rietveld (1969); lated modified by Hewat (1973) to include also the refinement of the anisotropic temperature factors. We have used this technique earlier to determine the structural details of phase Q at room temperature (Ahtee & Hewat, 1975).

It was suggested by Ahtee & Glazer (1976) that phases K and L are formed from phase Q just by the loss of one tilt at a time but all of them having parallel two-corner displacements of cations:

$$\begin{array}{ccccc} Q(a^-b^+c^-) & \rightarrow & K(a^-b^+c^0) & \rightarrow & L(a^0b^+c^0) \\ \mathrm{FE}\,(\nearrow) & & \mathrm{FE}\,(\nearrow) & & \mathrm{FE}\,(\nearrow)\,. \end{array}$$

At higher temperatures phase Q changes to phase G. Phases Q and $G(a^-b^+c^+;\ \uparrow)$ are the ferroelectric (FE) equivalents of the antiferroelectric phases of pure sodium niobate, namely $P(a^-b^+a^-;\ a^-b^-a^-;\ \swarrow\!\nearrow)$ and the structure suggested for R by preliminary work of

Table 1. *Summary of the structural models proposed by Ahtee & Glazer* (1976) *based on pseudocubic cell*

Phase	Space group	Multiplicities	Lattice parameters	Tilt system	Cation displacement
Q	Pm	2 × 2 × 2	$a_p \neq c_p > b_p$	$a^-b^+c^-$	2-corner [10$\bar{1}$]
K	Pm	2 × 2 × 2	$a_p \neq c_p > b_p$	$a^-b^+c^0$	2-corner]10$\bar{1}$]
L	Pm	2 × 1 × 2	$a_p \neq c_p > b_p$	$a^0b^+a^0$	2-corner [10$\bar{1}$]
G	$P2mm$	2 × 2 × 2	$a_p \geqslant b_p \neq c_p$	$a^-b^+c^+$	1-corner [100]
F	$P2mm$	2 × 2 × 2	$a_p \geqslant b_p \neq c_p$	$a^0b^+c^+$	1-corner [100]
T_2	$C4/mmb$	2 × 2 × 1	$a_p = b_p < c_p$	$a^0a^0c^+$	–

Sakowski-Cowley (1969) ($a^-b^+c^+$; $a^-b^0c^+$; ↑↓). We have now determined the structure of phase G with two different compositions x = 0·02 and 0·10 at temperatures 320 and 220 °C respectively. We have also refined the structure of ferroelectric phase F at 320 °C and of paraelectric (PE) phase T_2 at 450 °C with x = 0·10 to get a full sequence of phase transitions:

$$\begin{array}{ccccccc} \text{RT} & & 220\,^\circ\text{C} & & 320\,^\circ\text{C} & & 450\,^\circ\text{C} \\ Q(a^-b^+c^-) & \rightarrow & G(a^-b^+c^+) & \rightarrow & F(a^0b^+c^+) & \rightarrow & T_2(a^0a^0c^+) \\ \text{FE}\ (\nearrow) & & \text{FE}\ (\uparrow) & & \text{FE}\ (\uparrow) & & \text{PE} \end{array} .$$

2. Experimental

Compositions of 20 and 35 mole % K, well inside the phase boundaries, were chosen to represent the phases K and L, respectively. The samples were prepared from high-purity NaNbO$_3$ and KNbO$_3$ powders (Johnson Matthey Chemicals Ltd, England). The pure components were first carefully mixed in proper compositions and then sintered together at 1050 °C for 200 h to form single-phase solid solutions. When X-ray diffraction powder patterns were taken using monochromated Cu radiation, the resolution of the lines into indentifiable components indicated the specimen to be of single phase. For the high-temperature phases the same specimens of compositions of 2 and 10 mole % K were used as for the structure determination of phase Q (Ahtee & Hewat, 1975). Neutron diffraction measurements were made on a powder diffractometer (D1A) at the high-flux reactor of the ILL, Grenoble, using a wavelength at 1·509 Å. The 20 g powder samples were packed in thin-walled vanadium cans. The diffractometer was programmed to make steps of 0·05° in 2θ, the counting time being half a minute, so that 2θ range from 10 to 140° was covered in about 24 h. At the time when the measurements were carried out D1A consisted of only one counter and in order to get more experimental data for statistical use the specimens were measured twice and the counts added.

3. Starting models and the profile refinement

3.1. *Room-temperature phases K and L*

According to Ahtee & Glazer (1976) the space group of the ferroelectric phases Q, K and L is the same, Pm, even though they may have different tilt systems, namely $a^-b^+c^-$, $a^-b^+c^0$ and $a^0b^+a^0$ respectively. This is because if the cation displacements are antiparallel the structure is centrosymmetric and the space group is the same as that for the tilt system alone. But if they are parallel, the structure is noncentrosymmetric and the space group is a subgroup of that for the tilt system.

In the refinement of the structures of phases K and L the procedure used earlier for phase Q (Ahtee & Hewat, 1975) was followed very closely. The same additional constraints were used: (1) for oxygen atoms

Table 2. *Structural parameters in room-temperature* Na$_{0\cdot20}$K$_{0\cdot80}$NbO$_3$ (*phase K*)

Standard errors in brackets do not include error in the neutron wavelength

Isotropic temperature factor refinement:

	x	y	z	B
Na/K(1)*	0·255 (3)	0	0·232 (2)	1·67 (11)
Nb(1)	0·0151 (5)	0·258 (3)	−0·0151	0·83 (4)
O(1)	−0·006 (2)	0	−0·0125 (15)	1·68 (4)
O(5)	0·0294 (3)	0·2375	$\frac{1}{4}$	1·68

$R_{\text{NUC}} = 10{\cdot}3$, $R_{\text{PROF}} = 21{\cdot}7$, $R_{\text{EXP}} = 16{\cdot}4\%$

Anisotropic temperature factor refinement:

	x	y	z
Na/K(1)	0·256 (3)	0	0·228 (2)
Nb(1)	0·0155 (5)	0·252 (4)	−0·0155
O(1)	−0·004 (2)	0	−0·0146 (14)
O(5)	0·0291 (4)	0·2354	$\frac{1}{4}$

$R_{\text{NUC}} = 8{\cdot}6$, $R_{\text{PROF}} = 20{\cdot}6$, $R_{\text{EXP}} = 16{\cdot}3\%$
$a_p = 7{\cdot}9162\ (9)$, $b_p = 7{\cdot}8350\ (4)$, $c_p = 7{\cdot}8993\ (9)$ Å
$\beta = 90{\cdot}325\ (5)^\circ$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Na/K(1)	1·87 (23)	1·10 (27)	1·87	−0·53 (216)	0	0
Nb(1)	0·90 (9)	0·79 (17)	0·90	−0·18 (38)	0·03 (12)	−0·50 (68)
O(1)	1·83 (36)	0·83 (17)	2·92 (44)	−1·93 (45)	0	0
O(5)	2·19 (17)	2·92	0·70 (12)	−0·68 (45)	0·20 (10)	0·05 (52)

* For the notation see the refinement of phase Q (Ahtee & Hewat, 1975).

the regular octahedra were assumed to tilt as rigid units, (2) the two independent Nb atoms were put equal and the displacements were required to be strictly two-corner, and (3) for Na/K atoms, the restrictions caused by the regular oxygen octahedral environments were taken into account, *i.e.* the displacements u and w from the cubic perovskite positions were:

$$u_{A1} = u_{A3} = -w_{A2} = -w_{A4};\, u_{A2} = -w_{A1} = -w_{A3}.$$

The trial values for the tilt angles in phase K were: $\alpha = 5$, $\beta = 7$, $\gamma = 0°$, and in phase L: $\alpha = 0$, $\beta = 6$, $\gamma = 0°$. The tilts are proportional to the displacements u, v, w of the oxygen atoms from the ideal perovskite potions as follows: $\alpha \propto w(\mathrm{O1}) = v(\mathrm{O5})$, $\beta \propto u(\mathrm{O5})$ and $\gamma \propto u(\mathrm{O1})$. The trial values of the cation displacements in both phases were: $u_{\mathrm{Nb}} = -w_{\mathrm{Nb}} = 0{\cdot}02$; $u_{A1} = u_{A2} = 0{\cdot}02$.

These models refined very quickly in both cases but there were some indications of small antiphase γ-tilt in phase K and of both α and γ tilts in phase L. The correlation between the oxygen parameters giving α and γ tilts was 0·90. This high correlation value is due to the overlapping and partly common reflexions caused by the α and γ tilts. This means that without very good experimental data it is impossible to distinguish whether there are only γ tilts or both α and γ tilts contributing to phase K. The structural parameters are given in Tables 2 and 3.

To study this further we also refined the structure of phase K by setting additional restriction $\gamma = 0$. The other structural parameters changed by much less than their statistical errors. The same was true in phase L when we set both $\alpha = \gamma = 0$. It may be noted that the condition $\alpha = \gamma = 0$ (*i.e.* the tilt system $a^0b^+a^0$) would allow the multiplicity of the pseudocubic cell to be $2a_p \times b_p \times 2c_p$, whereas if $\alpha \neq 0$ and/or $\gamma \neq 0$ one must have $2a_p \times 2b_p \times 2c_p$.

A careful search for reflexions with k odd was made in the original data. Two types of reflexion came into question, namely odd–odd–odd and even–odd–even. The odd–odd–odd reflexions, indicating the existence of antiphase (–) tilts (see, for example, Glazer, 1975) were within the variation of the background. With even–odd–even type difference reflexions the conclusion is vaguer as these reflexions were often overlapped by the big main reflexions.

In any case we may conclude that $\gamma = 0$ in phase K, and $\alpha = \gamma = 0$ in phase L. The small deviations from the zero values merely indicate the uncertainty resulting from the limitations of the experimental evidence. We also tried to include the same kind of distortion within the oxygen octahedra caused by the size of a big A cation in $\mathrm{KNbO_3}$, (Hewat, 1973) but the data were not good enough to reveal any differences.

3.2. *Phase G at* 320°C ($x = 0{\cdot}02$) *and at* 220°C ($x = 0{\cdot}10$)

The plan of the trial structure of phase G, showing the tilting of the oxygen octahedra is drawn in Fig. 2. In addition to the Nb displacements the probable directions of the Na/K displacements deduced from the arrangement of nearest-neighbour oxygen atoms are marked in the figure. The origin is on the undisplaced Na/K(1).

There are eight independent Na/K atoms per unit cell, lying on twofold axes, each having its own u parameter. There are two independent Nb atoms in

Table 3. *Structural parameters in room-temperature* $\mathrm{Na_{0{\cdot}35}K_{0{\cdot}65}NbO_3}$ (*phase L*)

Isotropic temperature factor refinement:

	x	y	z	B
Na/K(1)	0·262 (2)	0	0·229 (2)	1·61 (10)
Nb(1)	0·0167 (3)	0·264 (12)	–0·0167	0·58 (4)
O(1)	–0·002 (4)	0	0·005 (4)	1·24 (3)
O(5)	0·0133 (3)	0·2455	¼	1·24

$R_{\mathrm{NUC}} = 8{\cdot}3$, $R_{\mathrm{PROF}} = 17{\cdot}4$, $R_{\mathrm{EXP}} = 14{\cdot}0\%$

Anisotropic temperature factor refinement:

	x	y	z
Na/K(1)	0·260 (2)	0	0·226 (2)
Nb(1)	0·0171 (4)	0·2483 (13)	–0·0171
O(1)	–0·004 (3)	0	–0·003 (2)
O(5)	0·0128 (6)	0·247	¼

$R_{\mathrm{NUC}} = 9.2$, $R_{\mathrm{PROF}} = 18{\cdot}0$, $R_{\mathrm{EXP}} = 14{\cdot}0\%$
$a_p = 7{\cdot}9751\ (7)$, $b_p = 7{\cdot}8620\ (4)$, $c_p = 7{\cdot}9565\ (6)$ Å
$\beta = 90{\cdot}340\ (4)°$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Na/K(1)	1·69 (26)	1·87 (31)	1·69	2·95 (74)	0	0
Nb(1)	0·65 (11)	0·52 (14)	0·65	0·12 (31)	0·14 (13)	–0·44 (30)
O(1)	0·82 (23)	0·65 (14)	1·77 (31)	5·13 (541)	0	0
O(5)	1·90 (16)	1·77	0·79 (12)	–0·15 (44)	0·12 (14)	1·03 (28)

general positions, each with three parameters. Of the independent oxygen atoms, eight are in special positions on each of the mirror planes, and two in general positions, giving 22 parameters. There are thus altogether 36 position parameters to be refined. This number can be reduced by making restrictions as follows.

For the oxygen atoms we assumed, as in the refinement of phases Q, K and L that the octahedra are undistorted and that they are tilting as rigid units; this replaces their 22 parameters by the three tilt parameters α, β, γ.

The two niobium atoms were constrained to have the same displacements as each other.

For the Na/K atoms there are four different types of surroundings. By considering the effect of the nearest-neighbour oxygen atoms it seems obvious (Fig. 2) that Na/K(1) and Na/K(5) are displaced along a in the negative direction and the Na/K(4) and Na/K(8) on the second layer in y are displaced by the same amount in the opposite direction. On the other Na/K atoms the effects of the nearest neighbours cancel each other and it is impossible by simple inspection to predict even the approximate directions of the displacements. Unfortunately the experimental data were not good enough to give reasonable results when Na/K atoms were allowed to vary freely. So in addition to the restriction (see Fig. 2)

$$-u_{A1} = u_{A4} = u_{A5} = u_{A8},$$

the following further restrictions were made:

(1) $-u_{A2} = u_{A3} = -u_{A6} = u_{A7}$ with $|u_{A1}| = |u_{A2}|$

or

(2) $u_{A2} = -u_{A3} = u_{A6} = -u_{A7}$ with $|u_{A1}| = |u_{A2}|$.

Many other possibilities were tried, *e.g.* $|u_{A2}| = \frac{1}{2}|u_{A1}|$. If u_{A1} and u_{A2} were allowed to vary independently the absolute values grow unreasonably large as a result of the high correlation between them.

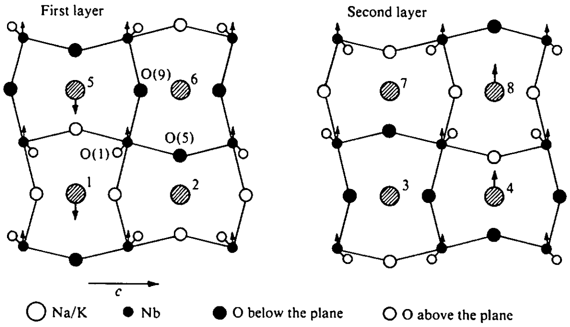

Fig. 2. Plan of the structure of phase $G(a^-b^+c^+)$ showing the tilting of the octahedra. The predicted directions of the Na/K and Nb displacements are indicated by arrows.

The trial values for the tilts were: $\alpha = 7, \beta = 8, \gamma = 7°$ ($x = 0{\cdot}02$); $\alpha = 5$, $\beta = 7$, $\gamma = 5°$ ($x = 0{\cdot}10$). The displacements u, v, w of the oxygen atoms from the ideal positions were affected by the tilts as follows: α: $w(\mathrm{O1}) = v(\mathrm{O5})$; β: $u(\mathrm{O5}) = w(\mathrm{O9})$; γ: $v(\mathrm{O9}) = u(\mathrm{O1})$; and $u(\mathrm{O9}) = 0$, when the rigidity of the octahedra is assumed. The trial values for the cation displacements were: $u_{A1} = 0{\cdot}015$, $u_{A2} = 0$; $u_{\mathrm{Nb}} = 0{\cdot}017$, $v_{\mathrm{Nb}} = 0$, $w_{\mathrm{Nb}} = 0$.

The anisotropic temperature factors of the oxygen

Table 4. *Structural parameters in phase G of* Na$_{0\cdot98}$K$_{0\cdot02}$NbO$_3$ *at* 320°C

Isotropic temperature factor refinement:

	x	y	z	B
Na/K(1)	−0·0040 (31)	0	0	2·74 (14)
Nb(1)	0·2636 (10)	0·2541 (17)	0·2435 (50)	0·87 (4)
O(1)	0·2270 (12)	0	0·2300 (3)	1·72 (4)
O(5)	0·2165 (10)	0·2300	$\frac{1}{2}$	1·72
O(9)	0·5	0·2270	0·2839	1·72

$R_{\mathrm{NUC}} = 12{\cdot}52$, $R_{\mathrm{PROF}} = 24{\cdot}51$, $R_{\mathrm{EXP}} = 20{\cdot}44\%$

Anisotropic temperature factor refinement:

	x	y	z
Na/K(1)	−0·0099 (32)	0	0
Nb(1)	0·2659 (8)	0·2466 (15)	0·2529 (64)
O(1)	0·2185 (19)	0	0·2307 (4)
O(5)	0·2255 (24)	0·2307	$\frac{1}{2}$
O(9)	0·5	0·2185	0·2745

$R_{\mathrm{NUC}} = 10{\cdot}72$, $R_{\mathrm{PROF}} = 23{\cdot}39$, $R_{\mathrm{EXP}} = 20{\cdot}36\%$
$a_p = 7{\cdot}9004\ (4)$, $b_p = 7{\cdot}8362\ (7)$, $c_p = 7{\cdot}9376\ (10)$ Å

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Na/K(1)	2·19 (45)	5·17 (102)	0·83 (54)	0	0	0
Nb(1)	0·65 (11)	1·72 (54)	0·29 (40)	−0·69 (57)	0·25 (58)	−0·20 (25)
O(1)	1·57 (34)	0·39 (38)	2·33 (14)	0	1·21 (33)	0
O(5)	3·64 (56)	2·33	0·88 (43)	−2·10 (37)	0	0
O(9)	1·32 (19)	1·57	3·64	1·16 (51)	0·32 (42)	0·24 (21)

atoms were constrained according to the possible vibrations of the rigid octahedron. Furthermore, the first four, the next four and the last two oxygen atoms were constrained to have the same thermal parameters as each other respectively. The same was done with the eight Na/K atoms and the two Nb atoms. In this way, we were left with ten positional (including the cell constants). 20 thermal and five instrumental parameters to be refined.

For the two models with different senses of Na/K displacements, the position parameters as well as the thermal parameters refined to the same values inside the error limits. The sense of the Na/K displacements given in Table 4 is that of model (1), which gave slightly better R values than model (2).

3.3. *Phase F with* $x = 0\cdot10$ *at* 320 °C

In phase F, the change of space group from $P2mm$ to $I2mm$ means that in the absence of restraints there are fewer independent parameters to be found; similar restraints as in phase G were however used where necessary.

For oxygen rigid octahedra were again assumed, with tilts $\alpha = 0$, $\beta = 0\cdot5$, $\gamma = 8°$ for the trial structure.

For Nb there is only one independent displacement to be found, with three components, given trial values $u = 0\cdot015$, $v = 0$, $w = 0$.

For Na/K, there are now only four possible values for u_A. The oxygen surroundings do not suggest any preferable direction for Na/K displacements. We tried two different models, as follows:

(1) $u_{A1} = u_{A2} = u_{A3} = u_{A4}$. This resembles model (1) of phase G except that in the second layer (along y) in phase F all the u_A's are parallel to those in the first layer whereas in phase G they are antiparallel.

(2) $u_{A1} = -u_{A2} = u_{A3} = -u_{A4}$. This coincides with model (2) of phase G.

No difference was found between the two models. The values corresponding to model (2) are given in Table 5.

We also refined the structure of phase F starting from phase G. The displacements of the atoms and also the temperature factors were as in the first refinement, within the error limits, except the displacements of oxygen atoms which gave the corresponding tilt angles as: $\alpha = 1\cdot04$ (4), $\beta = 1\cdot3$ (1·0) and $\gamma = 6\cdot6$ (2)° (see Table 10).

3.4. *Phase* T_2 *with* $x = 0\cdot10$ *at* 450 °C

The structure of phase T_2 in pure $NaNbO_3$ at 600 °C has been determined by Glazer & Megaw (1972). Its space group is $P4/mbm$ when conventional tetragonal axes $[(2a_p)^{1/2}, (2b_p)^{1/2}, c_p)]$ are used.

In the refinement only the space-group symmetry constraints were used. A slightly more reasonable result was, however, obtained by restricting the oxygen octahedron to vibrate as a rigid unit. It is clear from Table 6, where the atomic positions and the anisotropic temperature factors are listed, that the refinement was not fully successful, as indicated in particular by the negative values of B_{33} (Nb) and B_{33} (O1). This was first thought to be caused by the secondary extinction which especially affects the strong reflexions of low

Table 5. *Structural parameters in phase F of* $Na_{0\cdot90}K_{0\cdot10}NbO_3$ *at* 320 °C

Isotropic temperature factor refinement:

	x	y	z	B
Na/K(1)	0·014 (5)	0	0	3·12 (26)
Nb	0·2306 (15)	0·2505 (18)	0·2400 (35)	0·59 (11)
O(1)	0·2326 (17)	0	0·25	2·12 (34)
O(3)	0·2701 (20)	0·25	0	2·50 (40)
O(5)	0	0·2674	0·2299	2·52 (21)

$R_{\text{NUC}} = 16\cdot80$, $R_{\text{PROF}} = 27\cdot80$, $R_{\text{EXP}} = 18\cdot73\%$

Anisotropic temperature factor refinement

	x	y	z
Na/K(1)	−0·022 (66)	0	0
Nb	0·2274 (12)	0·2517 (21)	0·2489 (38)
O(1)	0·2321 (15)	0	0·25
O(3)	0·2599 (41)	0·25	0
O(5)	0	0·2679	0·2401

$R_{\text{NUC}} = 12\cdot07$, $R_{\text{PROF}} = 24\cdot92$, $R_{\text{EXP}} = 18\cdot66\%$
$a_p = 7\cdot9127$ (7), $b_p = 7\cdot8474$ (9), $c_p = 7\cdot8666$ (4) Å

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Na/K(1)	4·06 (93)	1·80 (67)	3·05 (86)	0	0	0
Nb	0·82 (25)	0·70 (32)	0·85 (38)	0·79 (39)	−0·72 (58)	0·24 (49)
O(1)	2·73 (61)	0·21 (31)	3·63 (44)	0	−0·281 (117)	0
O(3)	6·43 (81)	3·63	0·38 (44)	−0·21 (147)	0	0
O(5)	0·20 (32)	2·73	6·43	1·09 (58)	−0·26 (120)	3·63 (102)

Bragg angle; but correction for extinction did not improve the situation. Also the possibility of ordering of Na/K atoms was taken into account. However, the observed intensities of the difference reflexions did not support any simple ordering model. Therefore it was concluded that the negative values of the anisotropic temperature factors were due to the inadequate experimental information.

4. Discussion

4.1. *Assessment of results*

It is worth noting that each structure refinement described here is based on a very large number of statistically independent observations; for phase *G*, for example, there were about 3000, and the angular range investigated included about 650 reflexions. This is sufficient to give confidence in the validity of the results as a whole – subject to two qualifications. One is that we cannot yet distinguish fine differences between position parameters of atoms of the same general type. The other is an uncertainty about the anisotropic temperature factors, which are affected seriously by uncertainty in determining the background diffracted intensity and by the relatively low-angle cut-off of the data. In spite of this the results as they stand represent good enough approximations to the structures to serve as a useful basis for discussion.

4.2. *Comments on results*

The tilts of the oxygen octahedra cause doubling of the unit-cell axes perpendicular to the tilt axes and thus affect the reflexions on half-integral reciprocal lattice layers. Ahtee & Glazer (1976) measured the relative intensities of such $\{\frac{3}{2}0\frac{1}{2}\}$ and $\{\frac{3}{2}\frac{1}{2}\frac{1}{2}\}$ reflexions – indexed with respect to the pseudocubic cell – for all phases of $Na_{1-x}K_xNbO_3$. From these values they estimated the angles of the corresponding inphase (+) and antiphase (–) tilts. These are compared with our values in Table 7. The values based only on the intensities of the difference reflexions are bigger for two reasons: first, this experimental technique gives results on the high side if accurate intensity measurements including all corrections are not made; secondly, the relative intensities are affected by other contributions, especially by the thermal effect at higher temperatures.

Phases *Q*, *K* and *L* resemble each other in the structural details as can be seen from Table 8 where some of the structural parameters are collected. The only obvious differences are in the tilt angles. Their decrease with composition is needed to give more space for the larger potassium atom. In KNbO$_3$ where there are no tilts the K atom can be in contact with twelve neighbours and it is even large enough to push the oxygen atoms slightly apart. In phases *L*, *K* and *Q* the effect of the size of the *A* cations on their environments agrees with the qualitative considerations of Darlington & Megaw (1973).

In considering the absolute magnitudes of the anisotropic temperature factors in phases *K* and *L* collected in Tables 2 and 3 one has to be careful. From their relative sizes some conclusions can be made, *e.g.* the heavy niobium atoms do not vibrate much inside the oxygen octahedra at room temperature. The high anisotropy of the temperature factors of the oxygen atoms suggests the presence of the zone-boundary

Table 6. *Structural parameters in phase* T_2 *of* $Na_{0\cdot90}K_{0\cdot10}NbO_3$ *at* 450 °C (*conventional tetragonal orientation*)

Isotropic temperature factor refinement:

	x	y	z	B
Na/K	0	$\frac{1}{2}$	$\frac{1}{2}$	3·80 (19)
Nb	0	0	0	1·76 (9)
O(1)	0	0	$\frac{1}{2}$	6·58 (49)
O(2)	0·2381 (5)	0·7381	0	1·73 (9)

$R_{NUC} = 14\cdot3$, $R_{PROF} = 24\cdot6$, $R_{EXP} = 16\cdot5\%$

Anisotropic temperature factor refinement:

	x	y	z
Na/K	0	$\frac{1}{2}$	$\frac{1}{2}$
Nb	0	0	0
O(1)	0	0	$\frac{1}{2}$
O(2)	0·2361 (7)	0·7361	0

$R_{NUC} = 9\cdot7$, $R_{PROF} = 22\cdot0$, $R_{EXP} = 16\cdot5\%$
$a_0 = 5\cdot5783$ (4), $c_0 = 3\cdot9443$ (2) Å

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Na/K	2·00 (77)	2·00	6·30 (171)	−0·19 (47)	0	0
Nb	2·68 (26)	2·68	−0·24 (34)	0	0	0
O(1)	4·02 (29)	4·02	−1·01 (52)	0	0	0
O(2)	3·14 (27)	3·14	4·02	0·09 (41)	0	0

vibrational modes R_{25} corresponding to the antiparallel rotation of the rigid oxygen octahedra around the x and z axes and M_3 corresponding to the parallel rotation around the y axis. If the values of the anisotropic temperature factors in phase Q are also taken into account, the vibrations of the octahedra seem to have their highest values in phase K and the vibration around the z axis has clearly decreased in phase L.

In phase G, in contrast to phases K and L, the large anisotropy of the temperature factors affects the fractional coordinates of the atoms, *e.g.* for composition $x = 0{\cdot}02$ the u values of O(1) and O(5) corresponding to the tilt angles β and γ are almost exactly interchanged in the two refinements in Table 4. The change of the tilt system from $a^-b^+c^+$ (phase G) to $a^-b^+c^-$ (phase Q) can be assumed to occur through the large vibrations connected with the β tilts of the oxygen octahedra. The large changes in the Na/K environments in the [100] and [001] directions (Fig. 2) force the Na/K atoms then to find new equilibrium states. This new arrangement in its turn demands a change in the tilt direction around the z axis. The high anisotropy of the temperature factors of the Na/K and heavy Nb atoms – for composition $x = 0{\cdot}02$, $B_{22}(\text{Na/K}) = 5{\cdot}2$ Å^2 and $B_{22}(\text{Nb}) = 1{\cdot}7$ Å^2 – probably accounts for the change from one-corner-type displacements of these atoms in phase G to two-corner-type displacements in phase Q.

4.3. *Theoretical considerations*

Following Landau's theory of continuous phase transitions, Darlington (1975) has developed an expression for the free energy of the perovskite crystals as an expansion in terms of polarization and the tilting of the octahedra, produced respectively by the condensation of the zone-centre mode and the octahedral rotational modes R_{25} and M_3. Darlington applied this phenomenological theory on the $NaNbO_3$–$KNbO_3$ system and reconstructed the phase diagram using coefficients deduced from those of the end members, assuming a linear dependence on composition. In a later paper Darlington (1976) has added extra terms caused by the condensation of X modes to the free-energy expansion. These extra terms make possible the inequalities not predicted by the earlier simpler theory,

Table 7. *Comparison of the tilt angles obtained by Ahtee & Glazer* (1976) (A & G) *from the intensities of the reflections* $\{\frac{3}{2}0\frac{1}{2}\}$ *and* $\{\frac{3}{2}\frac{1}{2}\frac{1}{2}\}$ *with those of this work* (A & H)

Tilt angle	Phase K ($x = 0{\cdot}20$)		Phase L ($x = 0{\cdot}35$)		Phase G ($x = 0{\cdot}02$)	
(°)	A & G	A & H	A & G	A & H	A & G	A & H
α	4·2	3·3 (3)	0	0	7·5	4·4 (1)
β	7·4	6·6 (1)	5·0	2·9 (1)	9·5	5·6 (5)
γ	0	0	0	0	7·5	7·2 (4)
Tilt angle	Phase G ($x = 0{\cdot}10$)		Phase T_2 ($x = 0{\cdot}10$)		Phase F ($x = 0{\cdot}10$)	
(°)	A & G	A & H	A & G	A & H	A & G	A & H
α	4·0	2·0 (2)	0	0	0	0.
β	7·5	0·5 (6)	6·0	2·0 (9)	0	0
γ	6·5	7·0 (1)	6·0	4·2 (3)	8·0	3·2 (3)

Table 8. *Comparison of structural parameters in phases Q, K, L,* $KNbO_3$ *and* $NaNbO_3$

	$NaNbO_3$*	Phase Q†		Phase K	Phase L	$KNbO_3$‡
	$x = 0$	$x = 0{\cdot}02$	$x = 0{\cdot}10$	$x = 0{\cdot}20$	$x = 0{\cdot}35$	$x = 1{\cdot}00$
Lattice parameters (Å)						
$2 \times a_p$	7·8292	7·8567	7·8782	7·9162	7·9751	8·0691
$2 \times b_p$	2 × 7·7600	7·7670	7·7920	7·8350	7·8620	7·9420
$2 \times c_p$	7·8292	7·8478	7·8632	7·8993	7·9565	8·0691
β (°)	90·621	90·586	90·479	90·325	90·340	90·267
Displacements (Å)						
Nb	0·13	0·18	0·19	0·17	0·19	0·20
Na/K	0 or 0·18	0·22	0·23	0·18	0·21	0·10
Tilt angles (°)						
α	6·7	6·8	5·2	3·3	0	0
β	8·0	7·8	7·3	6·6	2·9	0
γ	6·7	6·8	5·2	0	0	0

* Sakowski-Cowley, Lukaszewicz & Megaw (1969).
† Ahtee & Hewat (1975).
‡ Katz & Megaw (1967).

e.g. of the lattice parameters, $a_p \neq c_p$, and the tilt angles, $\alpha \neq \gamma$, in phase Q. However, even the inclusion of X modes does not explain the inequality of all the lattice parameters, $a_p \neq b_p \neq c_p$, in phase L — one would expect $a_p = c_p \neq b_p$. This may indicate that there is another condensed mode that lowers the symmetry as the X-mode does.

In the refinement of phase G described in Table 4 the oxygen octahedra are supposed to tilt as rigid units. Darlington (1976) argues, however, that in phases which have two or more octahedral tilts the static displacements of the atoms cannot be accounted for by the linear superposition of R- and M-type rotational modes alone, but that there will be additional displacements of the atoms associated with one or more normal modes at the X point. This has been found true, for example in phases III and IV of CsPbCl$_3$ (Fuiji, Hoshimo, Yamada & Shirane, 1974), phase III of CsPbBr$_3$ (Hirotsu, Harada, Iizumi & Gesi, 1974) and SrZrO$_3$ at 760°C (Ahtee, Glazer & Hewat, 1978). Accordingly in phase G there would be two doubly degenerate transverse modes one involving the displacements of Na/K atoms the other the displacements of oxygen atoms along the x axis (see Fig. 3). Unfortunately no definite conclusion could be drawn from the present results.

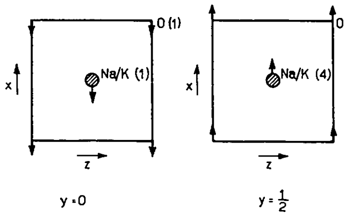

Fig. 3. The two normal modes at the X point. One of the modes involves the movement of A atoms, the other movement of oxygen atoms.

4.4. *Structural phase transitions in* $\mathrm{Na_{0\cdot90}K_{0\cdot10}NbO_3}$

The sequence of phase transitions in $\mathrm{Na_{0\cdot90}K_{0\cdot10}Nb_3}$ is compiled in Table 9 and the values of the lattice parameters, cation displacements and tilt angles for phases G, F and T_2 in Table 10. The behaviour of the lattice parameters (Fig. 8 in Ahtee & Glazer, 1976*a*) indicates that the transitions from T_2 to F and from G to Q are first order, whereas the transition from F to G is second order. The difference between phases F and G lies in fact mostly in the observation that in phase F there are no *uuu*-type difference reflexions. Also the *eue*-type reflexions (at the X point) which indicate the

Table 9. *Summary of the sequence of the phase transitions in* $\mathrm{Na_{0\cdot90}K_{0\cdot10}NbO_3}$

Phase	Space group	Multiplicity	Transition temperature	Tilt system	B-cation displacement	Condensed modes
Cubic	*Pm*3*m*	1 × 1 × 1		$a^0a^0a^0$	None	
			510°C			
Tetragonal (T_2)	*P*4/*mbm*	2 × 2 × 1		$a^0a^0c^+$	None	M_3
			390°C			
Orthorhombic (F)	*I*2*mm*	2 × 2 × 2		$a^0b^+c^+$	One corner parallel	M_3, Γ_{15}
			250°C			
Orthorhombic (G)	*P*2*mm*	2 × 2 × 2		$a^-b^+c^+$	One-corner parallel	M_3, R_{25}, Γ_{15}, (X)
			220°C			
Monoclinic (Q)	*Pm*	2 × 2 × 2		$a^-b^+c^-$	Two-corner parallel	M_3, R_{25}, Γ_{15}, (X)

Table 10. *Lattice parameters, cation displacements and tilt angles in phases G, F and T_2 from isotropic* (*a*) *and anisotropic* (*b*) *refinements*

	Phase G				Phase F		Phase T_2
Lattice parameters (Å)	$x = 0\cdot02$		$x = 0\cdot10$		$x = 0\cdot10$		$x = 0\cdot10$
$2 \times a_p$	7·9004 (4)		7·9185 (4)		7·9127 (7)		7·8889 (6)
$2 \times b_p$	7·8362 (7)		7·8296 (7)		7·8474 (9)		7·8889
$2 \times c_p$	7·8376 (10)		7·8418 (6)		7·8666 (11)		3·9443 (2)
Displacements (Å)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*)	(*b*)	(*a*/*b*)
Nb	0·11 (1)	0·13 (1)	0·12 (1)	0·12 (1)	0·15 (1)	0·17 (1)	0
Na/K	0·03 (3)	0·08 (3)	0·10 (5)	0·04 (4)	0·11 (4)	0·17 (52)	0
Tilt angles (°)							
α	4·6 (1)	4·4 (1)	2·2 (2)	2·0 (2)	0	0	0
β	7·6 (2)	5·6 (5)	3·3 (3)	0·5 (6)	4·6 (5)	2·0 (9)	0
γ	5·3 (3)	7·2 (4)	7·4 (2)	7·9 (1)	4·0 (4)	4·2 (3)	3·2 (3)

displacements of antiparallel A cations (Glazer, 1975) are either absent or very small in phase F. Cochran & Zia (1968) have identified among others the following modes in ferroelectric $NaNbO_3$ (phase Q): $W[(\frac{1}{2}\frac{1}{2}\frac{1}{2})R_{25}] = 2{\cdot}31$, $W[(\frac{1}{2}\frac{1}{2}0)\ M_3] = 1{\cdot}64$, $W[(000)\Gamma_{15}] = 1{\cdot}45$, $W[(00\frac{1}{2})M'_5] = 0{\cdot}36$, and $W[(\frac{1}{2}\frac{1}{2}0)M'_5] = 0{\cdot}19$. Here W is the strength or importance of the condensed mode, the wave vector is given in the round brackets and the label follows. Modes M_3 and R_{25} correspond to the inphase and antiphase tilts respectively, and Γ_{15} the ferroelectric mode at the centre of the Brillouin zone.

The anisotropy of the temperature factors indicates that some of the vibrational modes become unstable and may condense in the next lower phase. In phase T_2 the values $B_{11}(Nb) = B_{22}(Nb) = 2{\cdot}7$ Å^2 are exceptionally high for the heavy niobium atom, indicating that Nb is vibrating along the [101] or the [10$\bar{1}$] direction, *i.e.* along one of the pseudocubic axis a_p and c_p. In phase F the ferroelectric mode has condensed giving the displacement of niobium along a_p. Again, in phase G the value of $B_{22}(Nb) = 1{\cdot}7$ Å^2 is large and in phase Q niobium atoms have two-corner displacements. For the oxygen atoms in phase T_2 the anisotropic temperature factors include all the different tilts of the oxygen octahedra around the pseudocubic axes; the values $B_{11}(O1) = B_{22}(O1) = B_{33}(O2) = 4{\cdot}0$ Å^2 contain the tilts around the a_p and c_p axes and $B_{11}(O2) = B_{22}(O2) = 3{\cdot}1$ Å^2 the tilt around the c_p axis.

5. Summary and conclusion

The structures of phases K, L, G and F in the $Na_{1-x}K_xNbO_3$ system have been investigated in more detail and are shown to be substantially those previously suggested by Ahtee & Glazer (1976) from X-ray-powder diffraction evidence. Though some caution is needed in arguing from the anisotropic temperature factors, it is tempting to correlate their large observed values with the instability of certain vibrational modes, which in turn are associated with the sequence of positional changes at the phase transitions.

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