

## The Thermal Expansion of Interatomic Bonds, Illustrated by Experimental Evidence from Certain Niobates

BY HELEN D. MEGAW

*Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England*

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The thermal expansion of structures with frameworks of linked octahedra may be broken up into two parts: the changes in shape and size of individual octahedra, and their changes of tilt relative to one another. Expansion due to the second cause, when allowed by symmetry, is generally much greater than expansion of the octahedron itself, which is always small and may even be negative. Typical values of the average macroscopic expansion are  $16 \times 10^{-6} \text{ deg}^{-1}$  in  $\text{NaNbO}_3$  where change of tilt can occur,  $4 \times 10^{-6}$  in  $\text{KNbO}_3$ , where it cannot. At a first approximation, the octahedron may be treated as regular at all temperatures. At a second approximation, differences of shape can be associated with off-centre displacement of the Nb atom, of such a kind that the O–O edges associated with a ‘relaxed’ O–Nb–O link are on the average longer (typically by about 0.02 Å) than the other O–O edges. This extension  $e$  is independent of the tilt of the octahedron, its exact symmetry, the nature of the second cation, or the existence of ferroelectricity rather than antiferroelectricity, but is directly proportional to the Nb displacement. This empirical rule applies to all octahedral niobates examined (including  $\text{LiNbO}_3$ ), and when symmetry allows deduction of  $e$  from lattice parameters it can be used to predict the value of the Nb displacement, and does so correctly for  $\text{KNbO}_3$  (the only symmetrical structure about which sufficient information is available). A general consequence of the rule is that O–O edges parallel to a temperature-dependent Nb displacement (or having a component parallel to it) will tend to *contract* as the temperature rises. Geometrical relations are developed allowing easy calculation of O–O edge lengths and their thermal changes, both individual and mean values, from macroscopically measured data, for structures of different symmetries.

### 1. Introduction

#### 1.1. Outline of problem

Comparative studies of thermal expansion would be easier and more informative if it were possible to break up the macroscopic observed effects into parts associated with features which recur from one structure to another, though in different combinations and with different environments. For structures which can be described in terms of Goldschmidt coordination polyhedra, the obvious analysis is in terms of these polyhedra, irrespective of the degree of covalent character in the interatomic bonds. (The terms ‘cation’ and ‘anion’ will be used in this paper without any implications about this.) We shall be concerned with structures of niobates in which  $\text{NbO}_6$  octahedra share corners to form a three-dimensional framework. The macroscopic lattice parameters are dependent directly only on the size and shape of the octahedra and on their tilts relative to one another. Similarly, the thermal expansion can be expressed as a function of the changes in shape and size of the octahedra, and the changes of their tilts. This analysis prepares the ground for an attempted explanation.

The structures considered are potassium niobate  $\text{KNbO}_3$ , sodium niobate  $\text{NaNbO}_3$  and lithium niobate  $\text{LiNbO}_3$ . The three materials have in common a framework built from nearly regular  $\text{NbO}_6$  octahedra with each corner shared between two octahedra, the A cations (K, Na, or Li) occupying interstices of the frame-

work. In the idealized forms, which we may take as the zero order approximation, all octahedra are perfectly regular and parallel or antiparallel to one another. The important difference between the idealized form of the framework in  $\text{KNbO}_3$  and  $\text{NaNbO}_3$  (perovskite type) on the one hand, and  $\text{LiNbO}_3$  on the other, is that in ideal perovskite all the symmetry axes of the octahedron are retained as symmetry axes of the resulting cubic structure, whereas in  $\text{LiNbO}_3$  (ideally based on hexagonal close packing) only one triad axis and the three diads at right angles to it are retained; in the former, the two Nb–O bonds meeting at a corner are collinear, whereas in the latter their horizontal components are at  $120^\circ$ . The  $\text{NbO}_3$  framework of idealized  $\text{LiNbO}_3$  could be derived from that of idealized  $\text{KNbO}_3$  by allowing all octahedra to rotate  $30^\circ$  in alternate senses about the triad axis (Fig. 1). As they do so, the 12-coordinated interstice originally occupied by K is broken up into two 6-coordinated interstices, either of which can hold Li. (It is not implied, of course, that this derivation represents a physically possible sequence of structures).\*

Departures of the framework from the ideal involve tilts (or rotations) of the octahedra relative to one another as well as distortions of the octahedra. It is conceivable that both distortions and tilt magnitudes might differ from one octahedron to another, but such

\* For a more detailed discussion of the structural relationship, see Megaw (1968*b*).

further complexities do not occur in any of our actual examples.

The individual geometries of the various structures will be summarized later, in § 2.

Experimental data are taken mainly from the following papers:

$\text{NaNbO}_3$ : lattice parameters, Lefkowitz, Łukaszewicz & Megaw (1966); structural data, Sakowski-Cowley, Łukaszewicz & Megaw (1968), superseding preliminary note by Wells & Megaw (1961).

$\text{Na}_{0.975}\text{K}_{0.025}\text{NbO}_3$  ('Phase II'): lattice parameters and structural data, Wells & Megaw (1961); and Wells (1960).

$\text{KNbO}_3$ : lattice parameters, Shirane, Newnham & Pepinsky (1954); structural data, Katz & Megaw (1967).

$\text{LiNbO}_3$ : lattice parameters and structural data at room temperature, Abrahams, Reddy & Bernstein (1966); at high temperatures, Abrahams, Levinstein & Reddy (1966).

### 1.2. Theoretical approach

To simplify the problem, we proceed by successive approximations.

As a first approximation, we assume that the octahedra are all regular. In general they are freely hinged at the corners so that they can tilt relative to one another, but special cases are possible in which they are so placed relative to the symmetry of the structure that tilts are restricted to rotation about one axis or prohibited altogether. In practice, we shall have more examples of symmetry-clamped octahedra than of freely hinged octahedra.

The macroscopic expansion is the sum of the effects due to changes of tilt and changes of octahedron size. On general grounds we expect the changes of size (measured either by the octahedron edge length  $l_m$  or the Nb–O bond length) to be fairly small, and changes

of tilt (within a given phase) to be moderately large and in the direction which will increase the specific volume with increasing temperature.

At the second approximation we must consider changes in shape of the octahedron. A theory of this has been put forward (Megaw, 1968*a*) which associates the character and magnitude of the distortion with the direction and magnitude of the off-centre displacement of Nb. If there are no external faces on the octahedron, the predicted displacements are as follows:

one-corner displacement – tetragonal bipyramid elongated parallel to direction of displacement;

two-corner displacement – tetragonal bipyramid compressed perpendicular to plane of displacement, accompanied by an isotropic expansion;

three-corner displacement – no change of shape, but larger isotropic expansion.

Both Nb displacement and distortion of the octahedron are associated with relaxation of stress in one or more O–Nb–O diameters of the octahedron, which are under tension either from the octahedron itself (intrinsic effect) or from isotropic external forces; and the sequence of types in the above list is the order of increased tension.

The elongated edges are thus to be considered as relaxed, the shorter edges as unrelaxed. The difference between the long and short edges is called the relaxation extension, denoted by  $e$ . Thus the theory predicts an increase of  $e$  with increasing Nb displacement, whatever its direction. This is a simple rule which can easily be tested.

At the third approximation we consider the effect of non-isotropic external stresses on the octahedron. They will of course have an effect on the magnitude and perhaps the direction of the Nb displacement, and will affect different edges differently. However, we predict that the relationship already established between  $e$  and the Nb displacement will hold good (or be very

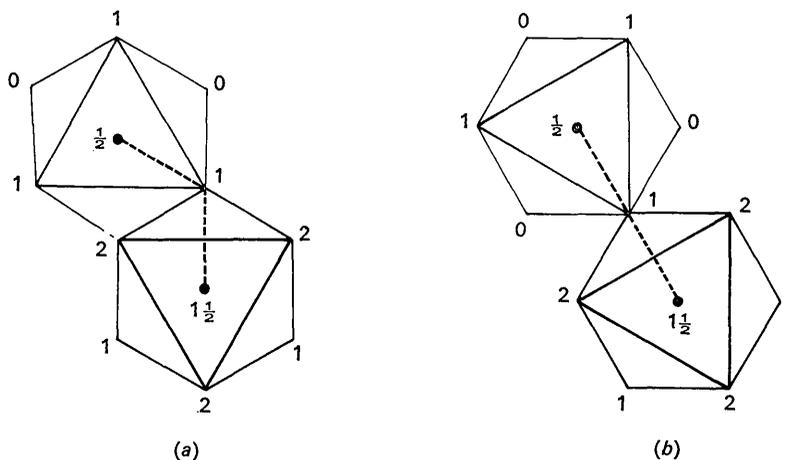


Fig. 1. Projection down triad axis of two octahedra sharing a corner at height 1. Heights in arbitrary units. Nb–O bonds to common O are shown dotted. (a) Part of  $\text{LiNbO}_3$  framework. (Atom at height zero coming vertically below atom at height 2 has been omitted, and the edge formed by it is left unfinished.) (b) Part of perovskite framework.

little altered) provided  $e$  is defined as the difference between the *mean* lengths of the relaxed and unrelaxed edges, the classification of edges as relaxed or unrelaxed being made in the same way as at the second approximation. This averaging procedure, initially adopted quite empirically, will be given some theoretical justification in § 1.3.

There will, as we have said, in general be a scatter of edge lengths within the relaxed and unrelaxed groups. In particular, we consider the effect of the symmetry of the structure on the relaxed edges. The external forces must have the symmetry of the structure, which (except in the perovskite aristotype) is less than the symmetry of the octahedron; hence they do not necessarily affect all relaxed edges equally. We describe the distortion in terms of a symmetry-clamping parameter  $s$ , the difference between the mean lengths of the relaxed edges most nearly perpendicular to the direction of the Nb displacement and those most nearly parallel to it. This definition allows us to give a numerical value to  $s$  even when the octahedron is not symmetrically situated in the structure, though we then expect it to be small.

Neither the symmetry-clamping difference nor other systematic differences within the relaxed or unrelaxed groups (whether or not their cause can be explained) affect the validity of the relations derived for  $e$ , the difference of *mean* lengths of the two groups.

### 1.3. *The role of polarization*

The qualitative statement of the theory is in terms of interatomic forces which are assumed to be central, so that we can deal with stresses in interatomic bonds as compressions or tensions in links between point atoms. A misfit in effective atomic size between Nb and O, in conjunction with the non-linear elasticity of the bonds, is the cause of off-centre displacement.

Actually, of course, interatomic forces are not central (unless purely ionic, which is an idealized extreme rarely encountered). The electron clouds round O are not spherical, but change shape according to the approach of neighbouring atoms. When, as a result of off-centring, Nb approaches one O more closely, such changes of polarization obviously occur, and would need to be allowed for in a quantitative theory. Qualitatively, however, so far as the isolated octahedron is concerned, they merely enhance the effects already discussed in terms of central forces.

It is when we turn to consider the linkage between octahedra, and the effects of structural stresses external to the octahedra, that we need to think about polarization. Without attempting calculation, we may note one fundamental point: that if electron density is concentrated into certain directions to strengthen some bonds, other directions must be impoverished. Put crudely, this might be called a law of conservation of bond strength, obviously analogous to Pauling's law of electrostatic valence; it will however not only affect the cation-oxygen bonds but also the non-bonding O-O contacts. Contact distances as well as bond strengths

must depend on the electron distribution. Illustrations of the consequences of this effect are as follows.

(i) No O atom can form more than one strong (short) Nb-O bond, and if it does so its second Nb-O bond is weak (and long). Hence there are lines of alternating short and long Nb-O bonds, and the direction of one Nb displacement determines that of its neighbour along the line.

(ii) Where an O atom forms two intermediate bonds, there will be a tendency to make the bond angle less than  $180^\circ$ . This effect is not important for the purposes of the present paper.

(iii) Where external forces act on an O-O edge to shorten (or lengthen) it, another edge sharing an O atom with it will be lengthened (or shortened) so that the mean remains nearly constant.

(iv) Where there is a more irregular distribution of external forces, changes in polarization tend to neutralize the irregularity, allowing edge lengths to remain more nearly equal.

Hence the recognition of polarization supplements the treatment in terms of central forces in two important aspects. It shows how the Nb displacement in one octahedron helps to determine that in the next; and it provides a justification for the assumption in § 1.2 that differences in the *mean* lengths of relaxed and unrelaxed edges are physically significant even when there is considerable scatter of individual lengths within each group, whether random or due to symmetry-clamping.

### 1.4. *Application to thermal expansion*

Though the exact form of the relationship between  $e$  and the Nb displacement is not given by the theory, it is a reasonable empirical hypothesis to assume proportionality between them. We go further and suggest that, *to a working approximation, the constant of proportionality will be the same for all structures at all temperatures.*

The theory does not attempt, at this stage, to explain the absolute magnitude of the Nb displacement or the nature of its variation with temperature. Discussion of these points will be left to a later paper. On general grounds, we expect that within a given phase the displacement will decrease with increasing temperature, and experimental evidence for this in one case will be given in § 5.1.

Using our two general postulates – (a) that increase of temperature causes decrease of Nb displacement, (b) that, independently, it also causes increase of specific volume – we can now proceed to predict or explain the thermal expansion of all phases whose structure is known.

We can also foresee the possibility of displacive transitions as resulting from a discontinuous change in the system of bond stresses at the end of a long continuous change, but we cannot make predictions except in terms of the detailed geometry of particular cases, and none will be attempted in this paper.

### 1.5. Empirical treatment

The distortion parameters  $e$  and  $s$ , like the mean edge length and the tilts, are defined geometrically in terms of the observed structure, and are therefore in one sense independent of the theory – though without the theory we might not have recognized them as being of any interest. We wish to relate them to the macroscopic lattice parameters.

Geometrical relationships in pseudosymmetric structures are all more simply described if structural parameters are expressed in terms of small deviations from the ideal. For the macroscopic parameters we choose one axial length and the difference from unity of not more than two axial ratios. For the octahedron we accept the choice made above, using  $l_m$ ,  $e/l_m$ , and  $s/l_m$ . The tilt angles, which are fairly small, are represented by the difference of their cosines from unity.

All parameters but the axial length and  $l_m$  are first-order small quantities. Equations connecting the macroscopic and the structural parameters can then be rearranged in any convenient way by neglecting second-order small quantities. Since few\* of the first-order quantities are greater than  $10^{-2}$ , the resulting relative errors will not generally be greater than  $10^{-4}$ , which is better than the accuracy of most of the experimentally-measured differences. This mathematical approximation is assumed throughout, whatever the stage of our physical approximations.

The geometrical formulae derived in what follows are thus independent of any theoretical assumption, but rely on the empirical assumption that differences between individual bond lengths are not so large as to upset any conclusions we have drawn about their means.

## 2. Geometrical relations

We proceed to set up equations for the lattice parameters in terms of the distortion parameters and tilts of the octahedron and the mean edge length. This must be done separately for each structure of different symmetry.

### 2.1. Sodium niobate (phase P)

The structure is orthorhombic, with space group  $Pbma$  and 8 formula-units per cell. Thus the octahedron is the asymmetric unit. The Nb displacement is two-corner, of magnitude 0.16 Å; it lies nearly but not exactly along [100] and its relaxed square is nearly in (010). [Fig. 2(a)].

We express the macroscopic parameters in terms of  $a$ ,  $\varepsilon$ , and  $\eta$ , defined as follows in terms of the pseudocubic subcell parameters  $a_p$ ,  $b_p$ ,  $\beta$ , and the orthorhombic parameters  $a_0$ ,  $b_0$ ,  $c_0$

$$\left. \begin{aligned} a &= a_p \\ \eta &= b_p/a_p - 1 \\ \varepsilon &= \beta - \pi/2 \end{aligned} \right\} \quad (1)$$

$$\left. \begin{aligned} a_0 &= \sqrt{2}a(1 + \frac{1}{2}\varepsilon) \\ c_0 &= \sqrt{2}a(1 - \frac{1}{2}\varepsilon) \\ b_0 &= 4a(1 + \eta) \end{aligned} \right\} \quad (2)$$

$$a_0/c_0 = \tan \beta/2 = 1 + \varepsilon \quad (3)$$

$$\text{Volume} = a^3(1 + \eta) \quad (4)$$

The tilt of the octahedron is most conveniently described by using orthogonal axes  $X'Y'Z'$  parallel and perpendicular to the edges of the square of oxygen atoms in which the Nb displacement occurs; these make small angles  $\omega$ ,  $\varphi$ ,  $\psi$ , as shown in Fig. 3, with the principal planes defined by symmetry axes  $XYZ$  of the structure. Different octahedra have tilt angles of the same magnitudes but different signs. Neglecting high-order small quantities, we can write

$$\left. \begin{aligned} \cos XX' &= \cos \omega \cos \psi \\ \cos YY' &= \cos \varphi \cos \psi \\ \cos ZZ' &= \cos \omega \cos \varphi \end{aligned} \right\} \quad (5)$$

Since, however, the  $a$ -glide plane requires the  $X'$  edge of the square to lie in the (010) plane,  $\psi$  is zero.

We expect the octahedron to be a tetragonal bipyramid with four relaxed edges  $l_r$  in (010) and eight unrelaxed edges  $l_u$  inclined to it. Its height  $h$  is given by

$$h^2 = 4l_u^2 - 2l_r^2 \quad (6)$$

Using (5), we have

$$\left. \begin{aligned} a_0 &= 2l_r \cos \omega \\ b_0 &= 4h \cos \varphi \\ c_0 &= 2l_p \cos \omega \cos \varphi \end{aligned} \right\} \quad (7)$$

Hence

$$a_0/c_0 = \sec \varphi,$$

whence, from (3)

$$\varphi^2 = 2\varepsilon \quad (9)$$

Then from (2) and (7)

$$a = \sqrt{2}l_r(1 - \frac{1}{2}\varepsilon - \frac{1}{2}\omega^2) \quad (10)$$

and from (7) and (8), and (1)

$$a(1 + \eta) = h \cos \varphi = h(1 - \varepsilon) \quad (11)$$

We rearrange the equations to give the edge lengths explicitly. From (9) and (10)

$$l_r = \frac{a}{\sqrt{2}}(1 + \frac{1}{2}\varepsilon + \frac{1}{2}\omega^2) = \frac{a}{\sqrt{2}}(1 + \frac{1}{4}\varphi^2 + \frac{1}{2}\omega^2) \quad (12)$$

From (6), (11) and (12),

$$\begin{aligned} l_u &= \frac{a}{\sqrt{2}}(1 + \frac{1}{2}\eta + \frac{3}{4}\varepsilon + \frac{1}{4}\omega^2) \\ &= \frac{a}{\sqrt{2}}(1 + \frac{1}{2}\eta + \frac{3}{8}\varphi^2 + \frac{1}{4}\omega^2) \end{aligned} \quad (13)$$

\* In  $\text{LiNbO}_3$ , some of the distortion parameters are of the order of magnitude of  $10^{-1}$ ; but as their changes over the whole temperature range are about a tenth of this the argument still holds good.

Hence

$$l_m = \frac{1}{3}(l_r + 2l_u) = \frac{a}{\sqrt{2}} \left(1 + \frac{1}{3}\eta + \frac{2}{3}\varepsilon + \frac{1}{3}\omega^2\right) \\ = \frac{a}{\sqrt{2}} \left(1 + \frac{1}{3}\eta + \frac{1}{3}\varphi^2 + \frac{1}{3}\omega^2\right) \quad (14)$$

and

$$e = l_r - l_u = \frac{a}{\sqrt{2}} \left(-\frac{1}{2}\eta - \frac{1}{4}\varepsilon + \frac{1}{4}\omega^2\right) \\ = \frac{a}{\sqrt{2}} \left(-\frac{1}{2}\eta - \frac{1}{8}\varphi^2 + \frac{1}{4}\omega^2\right). \quad (15)$$

The volume is

$$2\sqrt{2}l_m^3(1 - \varphi^2 - \omega^2). \quad (16)$$

Of the quantities on the right-hand side,  $a$  and  $\eta$  are determined macroscopically, and  $\varphi$  is directly related to the macroscopic parameter  $\varepsilon$ . Only  $\omega$  is unknown from macroscopic work, and needs either to be found from structure analysis or estimated by indirect means.

Equations (9) and (11) allow us to calculate  $\varphi$  and  $h$  from the macroscopic parameters in Table 1(a) and to compare them with the values found by structure analysis (Table 2). For  $\varphi$  we have  $8.6^\circ$  and  $9^\circ$  respectively, for  $h$   $3.923 \text{ \AA}$  and  $3.928 \text{ \AA}$ . The agreement merely confirms that the approximations used are satisfactory. We cannot find  $l_r$  and  $\omega$  independently, but accepting  $l_r$  as  $2.814 \text{ \AA}$  from Table 2, we find  $\omega$  from (12) to be  $8.9^\circ$ , as compared with  $8\frac{1}{2}^\circ$  from direct structure analysis.

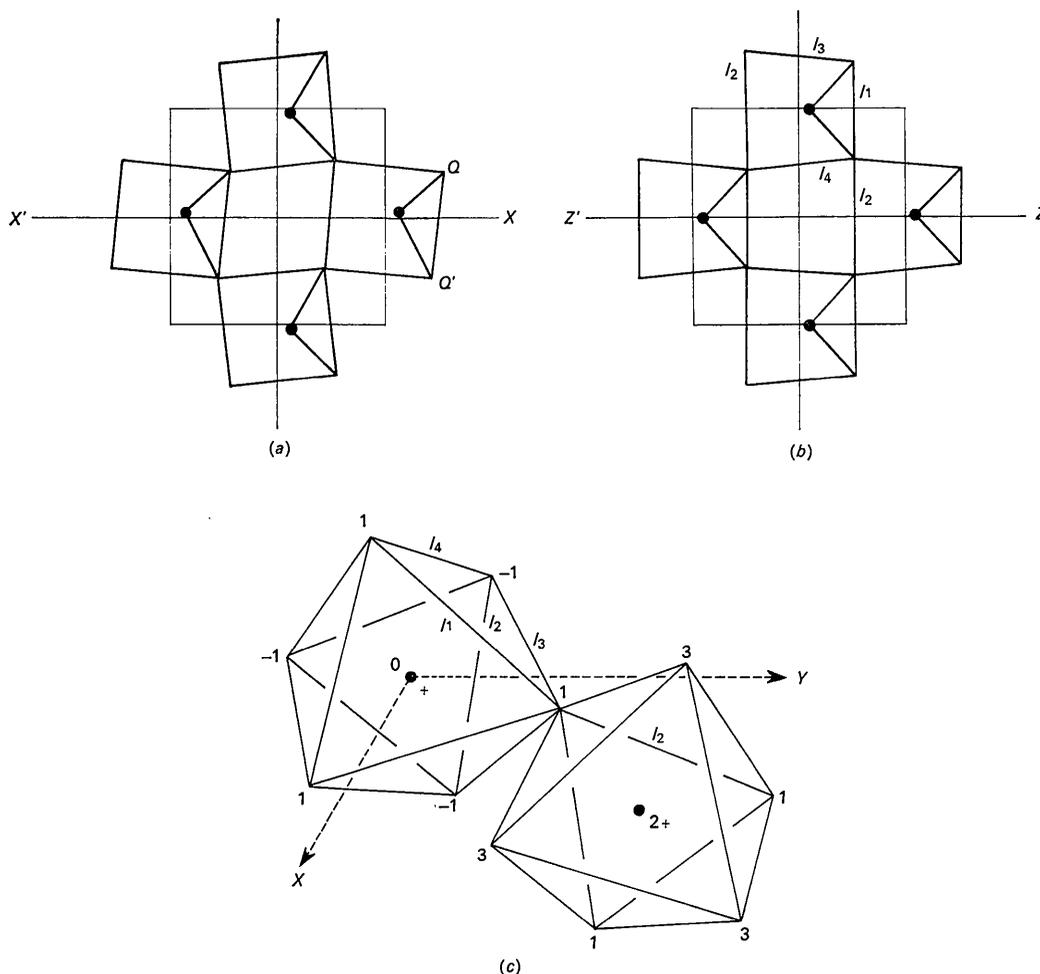


Fig. 2. (a)  $\text{NaNbO}_3$ . Projection on (010) of oxygen atoms forming equatorial squares and the enclosed Nb atoms. Nb displacements from centres of squares and relative tilts of squares about axes perpendicular to the paper (tilt angle  $\omega$ ) can be seen. The tilt  $\varphi$  takes place about  $XX'$ , the orthorhombic  $x$  axis, and shortens edges such as  $QQ'$  (nearly perpendicular to the axis) relative to the others. (b)  $\text{KNbO}_3$ . Section parallel to (010) through oxygen atoms of equatorial squares and the enclosed Nb atoms. Nb displacements from centres of squares can be seen. Edge lengths are marked.  $ZZ'$  is the orthorhombic  $z$  axis. (c)  $\text{LiNbO}_3$ . Projection on (0001) of two Nb octahedra sharing a corner. Heights are in arbitrary units; Nb atoms are both above the centres of their octahedra. Edge lengths are marked. (All distortions – tilts and displacements – slightly exaggerated to show their effect).

## 2.2. Potassium niobate, orthorhombic phase

The space group is  $Bmm2$ , and there is one formula-unit per cell; the octahedron is fixed in orientation. The Nb displacement, of magnitude  $0.20 \text{ \AA}$ , is two-corner; its direction\* is  $[001]$ , coinciding with a diad symmetry axis, and its relaxed square is in the  $(010)$  plane.

We use pseudocubic axes of reference, and define  $a$ ,  $\eta$ , and  $\varepsilon$  as in (1). Octahedron edges are then as follows [Fig. 2(b)]:

$$l_{12} = \frac{1}{2}(l_1 + l_2) = \frac{1}{2}a_0 = \frac{a}{\sqrt{2}}(1 - \frac{1}{2}\varepsilon) \quad (17)$$

$$l_{34} = l_3 = l_4 = \frac{1}{2}c_0 = \frac{a}{\sqrt{2}}(1 + \frac{1}{2}\varepsilon)$$

$$l_r = \frac{1}{2}(l_{12} + l_{34}) = \frac{a}{\sqrt{2}} \quad (18)$$

$$l_u = \frac{a}{\sqrt{2}}(1 + \frac{1}{2}\eta) \quad (19)$$

\* It is unfortunate that the axis most nearly coinciding with the direction of the Nb displacement has been differently named in orthorhombic  $\text{KNbO}_3$  and  $\text{NaNbO}_3$ ; but it is less confusing to keep the original names than to attempt to change them, as has been done by some authors. In both cases the direction of Nb displacement is the *longer* of the two orthorhombic axes  $a_0$ ,  $c_0$ .

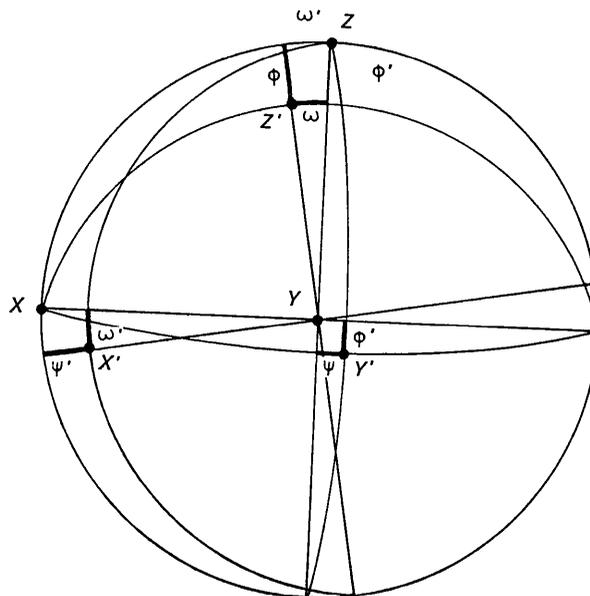


Fig. 3. Stereographic projection showing effect of octahedron tilts (angles of tilt somewhat exaggerated).  $XYZ$  are symmetry directions of structure,  $X'Y'Z'$  tetrad axes of octahedron (assumed regular). Tilt angles  $\omega$  and  $\phi$  are between  $Z'$  and the principal planes  $YZ$   $XZ$  respectively;  $\psi$  is between  $Y'$  and the principal plane  $YZ$ ; angles marked  $\omega'$ ,  $\phi'$ ,  $\psi'$  are very nearly equal to  $\omega$ ,  $\phi$ ,  $\psi$ .

Table 1(a). Lattice parameters of perovskite-type phases

Material	Phase	Temperature (°C)	$a_p$ (Å)	$\varepsilon$	$\eta$	$\text{Vol}^{1/3}$ (Å)
$\text{NaNbO}_3$	P	20	3.9148	0.0114	-0.00900	3.903
		360	3.9210	0.0064	-0.00071	3.920
	Q	20	3.922	(~0.01)	-0.0107	3.908
		260	3.925	?	-0.0060	3.917
		360	3.9156	0.0024	~0	3.919
	Cubic	440	3.9228	0.0008	~0	3.923
		640	3.9420	-	-	3.942
800	3.9494	-	-	3.949		
$\text{Na}_{0.975}\text{K}_{0.025}\text{NbO}_3$	'Phase II'	20	3.928	0.0096	-0.0095	3.912
$\text{KNbO}_3$	Orthorhombic	25	4.0375	0.0044	-0.0167	4.015
		205	4.0369	0.0041	-0.0133	4.019
	Tetragonal	220	3.9972	-	0.0166	4.019
		410	4.0080	-	0.0122	4.024
	Cubic	425	4.0214	-	-	4.021
510	4.0252	-	-	4.025		

Table 1(b). Lattice parameters and atomic parameters of  $\text{LiNbO}_3$

Temperature (°C)	$a$ (Å)	$c$ (Å)	$\eta$	$u$	(i)	$v$ (ii)	(iii)
24	5.1483	13.8631	-0.0936	0.0492	0.0113	0.0113	0.0113
200	5.1611	13.8700	-0.0972	0.0495	0.0113	0.0095	0.0076
400	5.1770	13.8811	-0.1013	0.0500	0.0113	0.0076	0.0038
600	5.1955	13.8881	-0.1068	0.0510	0.0113	0.0057	0
800	5.2152	13.8881	-0.1136	0.0535	0.0113	0.0038	0
1000	5.2414	13.8700	-0.1252	0.0580	0.0113	0.0019	0
1100	5.2626	13.8451	-0.1348	0.0615	0.0113	0.0010	0

Lattice parameters are from the work of Abrahams, Levinstein & Reddy, as shown in their Fig. 1, but using curves redrawn through their original numerical values, which were kindly supplied by Dr S. C. Abrahams. Atomic parameters  $u$  and  $v$  are based on the same paper, using the smoothed curve of Fig. 5 for  $u$  and the models described in the text for  $v$ .

Table 2. Nb displacements and O—O edge lengths of octahedra in alkali niobates

Material	Phase and temperature	Relation of octahedron to symmetry of structures	Type of Nb displacement	Magnitude of Nb displacement (Å)	Relaxed edge lengths (Å)	Unrelaxed edge lengths (Å)	Difference $e$ (Å)	Overall mean, $l_m$ (Å)
NaNbO <sub>3</sub>	Phase P, orthorhombic, 20°C	Asymmetric	Two-corner approx.   [100]	0.15	[001] 2.807 } [001] 2.825 } 2.816 [100] 2.810 } [100] 2.812 } 2.811 $s = -0.005$	2.756 2.799 2.770 2.817 2.786 2.831 2.798 2.825	0.018	2.802
NaNbO <sub>3</sub>	*Cubic, 640°C	Coincident	Central	0		2.796	0.018	2.802
Na <sub>0.975</sub> K <sub>0.025</sub> NbO <sub>3</sub>	Orthorhombic, 20°C (isostructural with phase Q)	Asymmetric	Two-corner approx.   [100]	0.21 ± 0.07	(Mean of 4)	(Mean of 8)	0.015 ± 0.005	2.807 ± 0.010
KNbO <sub>3</sub>	Orthorhombic, 20°C	One tetrad and two diads fixed	Two-corner   [001]	0.20	[100] 2.802 } [100] 2.894 } 2.848 [001] (2) 2.860 $s = 0.012$	(4) 2.780 (4) 2.884	0.022	2.840
KNbO <sub>3</sub>	*Tetragonal, 225°C	Three tetrads fixed	One-corner   [001]	?	(8)	2.826	0.023	2.841
KNbO <sub>3</sub>	*Cubic, 425°C	Coincident	Central	0		2.810	—	2.810
LiNbO <sub>3</sub>	Rhombohedral 24°C	One triad and three diads fixed	Three-corner   [0001]	0.26	Top (3) 2.879 } Bottom (3) 2.719 } 2.799 Inclined (3) 2.801 } Inclined (3) 2.840 } 2.820 $s = 0.021$	None	—	2.810

Bond lengths are accurate to about ±1 in the last figure quoted, except where otherwise stated. Edge lengths for phases marked \* have been calculated from the lattice parameters.

$$l_m = \frac{1}{3}(l_r + 2l_u) = \frac{a}{\sqrt{2}}(1 + \frac{1}{3}\eta) \quad (20)$$

$$e = l_r - l_u = -\frac{a}{\sqrt{2}} \cdot \frac{1}{2}\eta \quad (21)$$

$$s = l_{34} - l_{12} = \frac{a}{\sqrt{2}\varepsilon} \quad (22)$$

$$\text{Volume} = a^3(1 + \eta) = 2\sqrt{2}l_m^3. \quad (23)$$

It is worth noticing the different structural origin of the obliquity parameter  $\varepsilon$  in  $\text{KNbO}_3$  and  $\text{NaNbO}_3$ . In  $\text{NaNbO}_3$  it was associated with a tilt of the octahedron about the direction of the Nb displacement; in  $\text{KNbO}_3$  it is a consequence of the symmetry-clamping effect.

### 2.3. Potassium niobate, tetragonal phase

The space group is  $P4mm$ , and there is one formula-unit per cell; hence the octahedron is fixed in orientation. The Nb displacement is one-corner; its magnitude is still unknown, but its direction is  $[001]$ .

We choose lattice parameters as follows:

$$\left. \begin{aligned} a &= a_{\text{tetr}} \\ \eta &= \frac{c_{\text{tetr}}}{a_{\text{tetr}}} - 1 \\ \varepsilon &= 0 \end{aligned} \right\} \quad (24)$$

Here  $\eta$  is positive.

The edges in  $(001)$  are  $l_u$ , the others  $l_r$ . Then

$$l_u = \frac{a}{\sqrt{2}} \quad (25)$$

$$l_r = \frac{a}{\sqrt{2}}(1 + \frac{1}{2}\eta) \quad (26)$$

$$l_m = \frac{1}{3}(2l_r + l_u) = \frac{a}{\sqrt{2}}(1 + \frac{1}{3}\eta) \quad (27)$$

$$e = l_r - l_u = \frac{a}{\sqrt{2}} \cdot \frac{1}{2}\eta. \quad (28)$$

Since all relaxed edges are alike by symmetry,  $s=0$ . The volume is given by the same relation, (23), as in the orthorhombic phase.

Comparison of the two phases, using (21) and (28), shows that if  $e$  is positive, as required by the theory,  $\eta$  is positive for the tetragonal phase, negative for the orthorhombic, i.e.  $c_t/a_t > 1$ ,  $b_0/a_0 < 1$ . The former condition might seem intuitively obvious on almost any theory, the latter is a more specific confirmation of the present theory.

### 2.4. Lithium niobate

The geometry of this structure, determined by Abrahams and co-workers, has been discussed by Megaw (1968b). The space group is  $R3c$ . Referred to hexagonal axes, there are 6 formula-units per cell. Octahedra are all alike, oriented with a pair of opposite faces perpendicular to the triad axis, about which they are rotated relative to the idealized structure by a tilt angle  $\omega$ . The

Nb displacement (of magnitude  $0.26 \text{ \AA}$ ) is three-corner, along the triad axis. Edge lengths are as shown in Fig. 2(c).

We choose lattice parameters as follows:

$$\left. \begin{aligned} a &= a_{\text{hex}} \\ \eta &= c^2/8a^2 - 1. \end{aligned} \right\} \quad (29)$$

The distortions and tilt of the octahedron are given by the atomic position parameters  $u$  and  $v$ , and the Nb off-centre displacement by  $w$ , where  $u, v, w$  are derived as follows from the position parameters of oxygen,  $x, y, z$ , found by Abrahams and co-workers:

$$\left. \begin{aligned} u &= x \\ v &= y - \frac{1}{3} \\ w &= \frac{1}{12} - z. \end{aligned} \right\} \quad (30)$$

For convenience, we write

$$u' = u - \frac{1}{2}v. \quad (31)$$

The tilt angle is

$$\omega = \frac{3\sqrt{3}}{2} u'. \quad (32)$$

According to theory, all the edges are relaxed, but we may expect a substantial symmetry-clamping effect. In addition the edges perpendicular to the axis,  $l_1$  and  $l_2$ , show a top-and-bottom difference like that in  $\text{KNbO}_3$  but much greater; we shall not be concerned with it at this stage, except to note its relation to the parameter  $v$  (which also controls the smaller difference between  $l_3$  and  $l_4$ ):

$$l_1 - l_2 = \frac{2}{3}v. \quad (33)$$

The edge-length means of interest are:

$$l_{12} = \frac{1}{2}(l_1 + l_2) = \frac{a}{\sqrt{3}}(1 - \frac{2}{3}u') \quad (34)$$

$$l_{34} = \frac{1}{2}(l_3 + l_4) = \frac{a}{\sqrt{3}}(1 - \frac{1}{2}u' + \frac{1}{3}\eta) \quad (35)$$

$$l_m = \frac{1}{2}(l_{12} + l_{34}) = \frac{a}{\sqrt{3}}(1 - u' + \frac{1}{6}\eta) \quad (36)$$

$$s = l_{34} - l_{12} = \frac{a}{\sqrt{3}}(u' + \frac{1}{3}\eta). \quad (37)$$

$$\begin{aligned} \text{Volume per formula-unit} &= \frac{a^3}{\sqrt{6}}(1 + \eta) \\ &= \frac{3}{\sqrt{2}} l_m^3 (1 + 3u' + \frac{1}{2}\eta). \end{aligned} \quad (38)$$

## 3. Experimental evidence: comparison of different phases

### 3.1. Edge lengths

Experimental values of the edge lengths and their differences are listed in Table 2. For the cubic phases of  $\text{NaNbO}_3$  and  $\text{KNbO}_3$  and the tetragonal phase of  $\text{KNbO}_3$ , they are directly calculable from the lattice

parameters; in all the other examples a detailed structure determination was needed.

It is rather striking that in each case where a positive value of  $e$  was predicted it is found, and that its magnitude is very roughly the same in all examples. More exactly, the smaller values of  $e$  are associated with smaller values of the Nb displacement. Though the differences are close to the limit of error, it suggests that we might, as a working approximation, take  $e$  to be proportional to the displacement.

Symmetry-clamping effects are shown by  $\text{KNbO}_3$  and  $\text{LiNbO}_3$ , with values of 0.012 and 0.021 Å respectively. The larger effect in the latter is associated with the larger Nb displacement, indicating larger external forces acting on the octahedron. By contrast, the value of  $-0.005$  Å in  $\text{NaNbO}_3$  shows that the external forces are either weaker or more isotropic, or both.

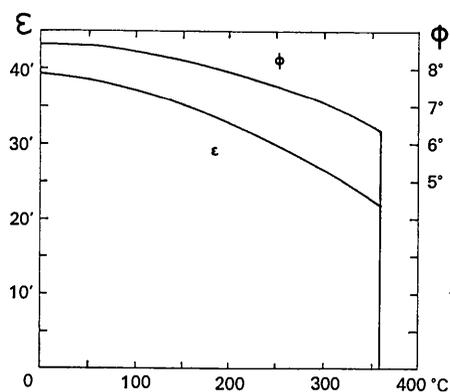


Fig. 4.  $\text{NaNbO}_3$ . Variation with temperature of lattice parameter  $\varepsilon$  and tilt  $\phi$  ( $=1/2\varepsilon$ ).

We notice also the top-and-bottom differences between  $l_1$  and  $l_2$  in  $\text{KNbO}_3$  and  $\text{LiNbO}_3$ , which are  $-0.092$  and  $+0.160$  Å respectively [cf. Fig. 2(b) and (c)]. The large magnitudes and the opposite signs are rather striking (the 'top' edge in each case being that towards which Nb is displaced). A justification for regarding the top-and-bottom mean as significant in spite of these large differences was given in § 1.3, but discussion of possible reasons for their occurrence will be left to another paper.

### 3.2. Octahedral tilts

Though these are not directly predictable, their values may be noted. For  $\text{NaNbO}_3$  at room temperature  $\phi = 8.6^\circ$ ,  $\omega = 8.9^\circ$ . For  $\text{LiNbO}_3$   $\omega = 6.5^\circ$ .

## 4. Thermal expansion

### 4.1. Macroscopic expansion

Expansion coefficients calculated from the lattice parameters are given in Table 3. It can be seen that they are much greater in phases where changes of octahedron tilt are possible (room temperature  $\text{NaNbO}_3$ ,  $\text{LiNbO}_3$ ) than for the others.

### 4.2. Changes of tilt

#### (a) $\text{NaNbO}_3$

The tilt about [100],  $\phi$ , is directly found from measured  $\varepsilon$ , using (9). Fig. 4 shows  $\varepsilon$  and  $\phi$ . The change in  $\varepsilon$  from 39' at room temperature to 22' at 360°C corresponds to a change of  $\phi$  from 8.6° to 6.5°.

The tilt about [010],  $\omega$ , is not directly deducible from lattice parameters alone. When  $l_r$  is known it can be calculated by using (12); at room temperature, it is thus found to be 8.5°. Data about edge lengths are

Table 3. *Linear expansion coefficients*

Substance	Temperature range	Linear expansion coefficients (in units of $10^{-6} \text{ deg}^{-1}$ )				Assumptions about tilts
		Macroscopic mean	$l_m$	$l_r$	$l_u$	
$\text{NaNbO}_3$	20–640 °C	16	–9	–16	–5	None
	20–360	13	{ (i) 4 (ii) –5	–1 –16	7 0	(i) $\Delta\omega^2 = 0$ (ii) $\Delta\omega^2 = \Delta\phi^2$
	360–640	20	—	—	—	
	640–800	12	12	—	—	None
$\text{KNbO}_3$	25–425	4	3	–10	10	None
	25–205	5	5	–1	8	None
	220–410	6	6	3	14	None
	425–510	11	11	—	—	None
$\text{LiNbO}_3$			(i)	(ii)	(iii)	
	20–1100	13	2	–2	–3	{ (i) $\Delta v = 0$ (ii) $v/(1200 - t) = \text{const.}$ (iii) $t \leq 600, v/(600 - t) = \text{const.}$ $t \geq 600, v = 0.$
	20–200	9	8	3	–2	
	200–400	12	9	4	0	
	400–600	12	8	3	–2	
	600–800	13	2	–4	0	
	800–1000	15	–9	–12	–8	
1000–1100	22	–13	–16	–13		

Rounding-off errors are  $\pm 1$ .

not available at other temperatures. As a working hypothesis we may assume that, since  $\omega$  is initially nearly equal to  $\varphi$ , its thermal changes will be of the same order of magnitude.\* In order to show how far uncertainty about  $\omega$  affects our other conclusions, we consider two models, one in which  $\omega$  remains constant and one in which it changes at the same rate as  $\varphi$ . Actual changes probably fall between the two extremes, as the later discussion will show.

### (b) LiNbO<sub>3</sub>

From equations (32) and (31), the tilt is known in terms of atomic position parameters which have been measured by Abrahams, Levinstein & Reddy (1966). Unfortunately the values obtained from powder diffraction work are subject to large standard deviations; there is nevertheless a trend towards increase in  $u$  with increasing temperature, but changes in  $v$  are indeterminate, because the standard deviation is of the same order of magnitude as  $v$ . We draw a smoothed curve through the experimental values of  $u$ , and consider three possible models for  $v$ , (i) that it is independent of temperature, (ii) that it drops linearly from its known room-temperature value to zero at 1200°C, (iii) that it drops linearly to zero at 600°C. The variation of  $\omega$  with temperature with these three assumptions is shown in Fig. 5.

One point to notice is the *increase* in tilt angle with increasing temperature for LiNbO<sub>3</sub> as compared with its decrease for NaNbO<sub>3</sub>. In both structures, however, the changes of tilt have the same physical effect – they increase the volume available between the octahedra for the second cation  $A$ . The difference arises from the fact that the LiNbO<sub>3</sub> structure represents a deviation from one whose framework has a close-packed array of oxygen atoms, and increased deviation must open it out, while the NaNbO<sub>3</sub> structure is a deviation from an ideal framework which is fully opened out, so that increased deviation must reduce its volume.

This implies that the effect of increasing temperature does not always result in an approach to the nearest structure of higher symmetry; each case must be examined on its merits. Here the over-riding requirement is that of increasing volume, whether for the  $A$  cation in particular or for the formula-unit as a whole. Possible reasons will be discussed in a later paper.

### 4.3. Changes of mean edge length of octahedron

This only differs from the macroscopic thermal expansion for structures in which there are changes of tilt.

\* The following rough argument suggests a reason for expecting that  $\Delta\omega^2 = \frac{1}{2}\Delta\varphi^2$ . If we defined our tilts with respect to the tetrad axes of ideal perovskite,  $\varphi$  would be replaced by two components,  $\varphi_1$  and  $\varphi_2$ , such that  $\varphi^2 \simeq \varphi_1^2 + \varphi_2^2$ . The strain energy of a small twist is proportional to the square of the angle. Since  $\omega$ ,  $\varphi_1$ ,  $\varphi_2$  refer to twists which are topologically similar, we may expect changes in them to involve equal changes of energy, and therefore  $\Delta\omega^2 \simeq \Delta\varphi_1^2 \simeq \Delta\varphi_2^2$ .

For NaNbO<sub>3</sub> from (14),

$$\frac{1}{l} \frac{dl_m}{dt} = \frac{1}{a} \frac{da}{dt} + \frac{1}{3} \frac{d\eta}{dt} + \frac{2}{3} \frac{d\varepsilon}{dt} + \frac{1}{3} \frac{d\omega^2}{dt} \quad (39)$$

For the two models put forward in § 4.2,  $\frac{d\omega^2}{dt}$  is 0 or  $\frac{2d\varepsilon}{dt}$  respectively.

For LiNbO<sub>3</sub>, from (36) and (32),

$$\frac{1}{l} \frac{dl_m}{dt} = \frac{1}{a} \frac{da}{dt} + \frac{1}{6} \frac{d\eta}{dt} - \frac{2}{3\sqrt{3}} \frac{d\omega}{dt} \quad (40)$$

or, since from (29)

$$\frac{d\eta}{dt} = 2 \left( \frac{1}{c} \frac{dc}{dt} - \frac{1}{a} \frac{da}{dt} \right), \quad (41)$$

$$\frac{1}{l} \frac{dl_m}{dt} = \frac{1}{3} \left( \frac{2}{a} \frac{da}{dt} + \frac{1}{c} \frac{dc}{dt} \right) - \frac{2}{3\sqrt{3}} \frac{d\omega}{dt} \quad (42)$$

The first term in (42) is of course the mean linear macroscopic coefficient. Increasing tilt thus implies that the mean edge-length expansion is less than the mean macroscopic expansion. The calculated value of  $dl_m/dt$  thus depends on our assumptions about  $dv/dt$ ; we continue to use the three models of § 4.2.

Values of  $\frac{1}{l} \frac{dl_m}{dt}$  calculated from these equations with the use of the lattice parameters of Table 1 are recorded in Table 3.

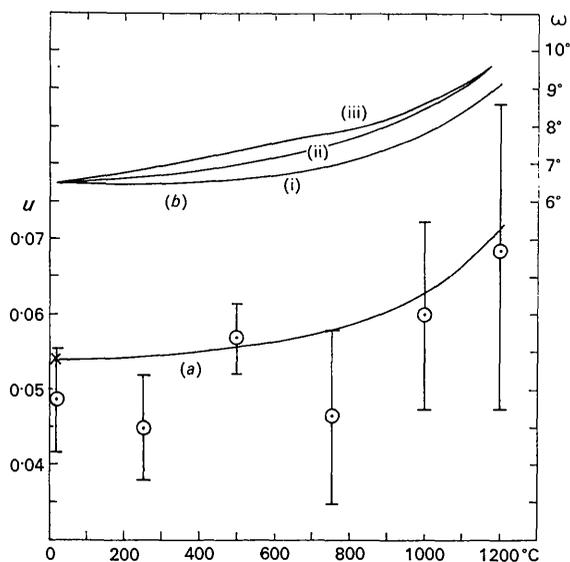


Fig. 5. LiNbO<sub>3</sub>. (a) Position parameter  $u$ . Points marked with circles and vertical lines show experimental values of Abrahams, Levinstein & Reddy, with their standard deviations. Point marked  $\times$  is from single-crystal work of Abrahams, Bernstein & Reddy. Smoothed curve drawn for present work. (b) Tilt parameter  $\omega$ , in degrees, deduced from curve (a), assuming (i)  $v$  constant, (ii)  $v$  decreasing linearly to zero at 1200°C, (iii)  $v$  decreasing linearly to zero at 600°C.

Where a cubic phase with known lattice parameters exists, and the edge lengths at room temperature have been directly measured, it is possible to calculate an overall thermal expansion which is independent of any assumptions about tilt as a function of temperature. This applies to  $\text{NaNbO}_3$  and  $\text{KNbO}_3$ . While it is not strictly applicable to  $\text{LiNbO}_3$ , the uncertainties about tilts are relatively much less important when the whole temperature range up to  $1100^\circ\text{C}$  is considered.

Looking at Table 3, a striking feature is the low value of the octahedron coefficients in phases where tilt is possible as compared with the macroscopic expansion coefficients of the same phases. The importance of distinguishing between the effects of tilt and of octahedron expansion is obvious. Since, however, changes in the mean octahedron edge length depend on independent changes in the relaxed and unrelaxed edges, more detailed discussion must be postponed till these have been considered.

It is interesting to note that the empirical electrostatic-valence relation noted by Megaw (1935) would have predicted an expansion coefficient of about  $2 \times 10^{-6} \text{ deg}^{-1}$ .

#### 4.4. Changes of relaxed and unrelaxed edges

(a) For  $\text{NaNbO}_3$  from  $20^\circ$ – $360^\circ\text{C}$  we have, from (12) and (13),

$$\frac{\Delta l_r}{l} = \frac{\Delta a}{a} + \frac{1}{2}\Delta\varepsilon + \frac{1}{2}\Delta\omega^2 \quad (43)$$

and

$$\frac{\Delta l_u}{l} = \frac{\Delta a}{a} + \frac{1}{2}\Delta\eta + \frac{3}{4}\Delta\varepsilon + \frac{1}{4}\Delta\omega^2, \quad (44)$$

where  $\Delta\omega^2$  is 0 or  $2\Delta\varepsilon$  for models (i) and (ii) respectively. These equations have been used to calculate the temperature coefficients in Table 3. From (15), the change in the relaxation extension is

$$\Delta e = l(-\frac{1}{2}\Delta\eta - \frac{1}{4}\Delta\varepsilon + \frac{1}{4}\Delta\omega^2), \quad (45)$$

giving  $-0.008 \text{ \AA}$  for (i) and  $-0.015 \text{ \AA}$  for (ii). Since the value of  $e$  at  $20^\circ\text{C}$  is  $0.018 \text{ \AA}$ , it is  $0.010 \text{ \AA}$  or  $0.003 \text{ \AA}$  at  $360^\circ\text{C}$ .

In spite of the uncertainty about the rate of change of  $\omega$ , we can conclude with certainty from the known values of  $\Delta\eta$  and  $\Delta\varepsilon$  that  $e$  decreases with increasing temperature, provided that (in accordance with our original postulate in § 1.3)  $\omega$  decreases. If the rate of decrease were much greater than in model (ii),  $e$  would become negative at  $360^\circ\text{C}$ , which is very improbable. Thus models (i) and (ii) represent extremes between which the actual rate of change of  $\omega$  is expected to lie.

For  $\text{KNbO}_3$  between  $25^\circ\text{C}$  and  $205^\circ\text{C}$ , equations (18), (19) and (20) give

$$\frac{\Delta l_r}{l} = \frac{\Delta a}{a} = -0.0002,$$

$$\frac{\Delta l_u}{l} = \frac{\Delta a}{a} + \frac{1}{2}\Delta\eta = 0.0015,$$

and

$$\Delta e = -\frac{1}{2}\Delta\eta = -0.0048 \text{ \AA}.$$

Between  $220^\circ\text{C}$  and  $410^\circ\text{C}$ , the corresponding values are  $0.0005$ ,  $0.0027$ ,  $-0.0062 \text{ \AA}$ . Temperature coefficients for  $l_r$  and  $l_u$  are listed in Table 3.

In both phases of  $\text{KNbO}_3$ ,  $e$  is directly associated with the axial ratio  $1 + \eta$  [cf. equations (20) and (28)]. Though  $\eta$  decreases with increasing temperature, in neither phase has it dropped to zero before the transition; the relative change before the transition is 20% in the orthorhombic phase, 26% in the tetragonal. The final equalization of edges occurs at the tetragonal-cubic transition, where it is associated with a volume contraction.

The symmetry-clamping effect  $s$  in orthorhombic  $\text{KNbO}_3$  is proportional to  $\varepsilon$  [cf. equation (22)]. From Table 1,  $\varepsilon$  is small – much smaller than in  $\text{NaNbO}_3$  – and changes in it are very small, close to the limit of experimental error.

In  $\text{LiNbO}_3$  all edges are relaxed; there is therefore no internal standard of comparison from which to find  $e$ . The change in the symmetry-clamping effect is, from (37) and (41),

$$\frac{1}{l} \frac{ds}{dt} = \frac{2}{3} \left( \frac{1}{c} \frac{dc}{dt} - \frac{1}{a} \frac{da}{dt} \right) + \frac{2}{3\sqrt{3}} \frac{d\omega}{dt}. \quad (46)$$

This is evaluated in Table 4 for the three models of § 4.2. We expect  $s$  to have a different temperature dependence from  $l_m$  but the three models vary too much between themselves to allow conclusions to be drawn as to its absolute value. However, all agree in suggesting that its temperature coefficient either stays constant or becomes more positive with increasing temperature. Now from (42) and (46),

$$\frac{1}{l} \frac{dl_m}{dt} + \frac{1}{l} \frac{ds}{dt} = \frac{1}{c} \frac{dc}{dt}, \quad (47)$$

and Table 4 shows that  $\frac{1}{c} \frac{dc}{dt}$  decreases with increasing temperature above  $500^\circ\text{C}$ . Hence  $\frac{1}{l} \frac{dl_m}{dt}$  must decrease as much or more with increasing temperature.

The expansion of  $l_m$  in  $\text{LiNbO}_3$  is therefore certainly anomalous. All three models suggest negative values, though it remains uncertain whether the abnormality is present at room temperature or only sets in above about  $600^\circ\text{C}$ .

The theory predicted that in any structure there would be an anomalous decrease in the length of relaxed edges with increasing temperature as a consequence of decreasing Nb displacement. (This, of course, only applies within a phase, as we cannot predict the sense of Nb displacement at a transition.) If, however, in a particular temperature range the Nb displacement changes little, the expansion coefficient of the relaxed edges will be the same as that of the unrelaxed. In

$\text{KNbO}_3$  and  $\text{NaNbO}_3$ , where there are unrelaxed edges for comparison, decrease in  $e$  is thus the obvious indicator of a decrease in Nb displacement. In  $\text{LiNbO}_3$ , where there are no unrelaxed edges, the negative values of the  $l_m$  expansion coefficient serve the same purpose.

We showed above that, for any of the three models of  $\text{LiNbO}_3$ , the experimental curve of  $c$  versus temperature followed roughly the same course as  $l_m$  versus temperature, which should also give Nb displacement versus temperature. The very flat shape of the  $c$  curve is thus an indication that Nb displacements are present but are decreasing with increasing temperature. The same flat curve is seen in  $\text{NaNbO}_3$  below  $360^\circ\text{C}$  and in orthorhombic  $\text{KNbO}_3$ ; in tetragonal  $\text{KNbO}_3$  there is a negative slope. Similar flat curves in less fully-known structures therefore give a strong suggestion that they too contain Nb displacements decreasing with increase of temperature.

### 5. Experimental evidence and conclusions concerning Nb displacement

#### 5.1. Sodium niobate, phase P

There is direct experimental evidence concerning the Nb displacements at different temperatures. Both the large [100] component and the small [001] component have been found from visually estimated intensities of high-angle X-ray reflexions, by the method described by Megaw & Wells (1958). The photographs used were taken by Dr K. Łukaszewicz, to whom the author wishes to express her gratitude.

Both components decrease with increasing temperature (the smaller component being almost negligible). The resultant displacement is plotted against temperature in Fig. 6. It can be seen that between  $0^\circ$  and  $360^\circ\text{C}$  it drops nearly linearly to about half its initial value. (Points above  $360^\circ\text{C}$  refer to phase R, which will be discussed later in § 6.3.)

We now plot the Nb displacement  $\mu$  against values of  $e$  calculated from (45) using the lattice parameters appropriate to the temperature, with  $\omega$  as in models (i) and (ii) (Fig. 7). In each case the points lie nearly on a straight line, on either side of the straight line through the origin to the point at  $20^\circ\text{C}$ , whose slope is  $0.018/0.147 = 1/8.2$ . This line corresponds to a model with

$$\Delta\omega^2 = 0.3\Delta\varphi^2. \quad (48)$$

From the evidence of this graph we make the simple empirical assumption that the Nb displacement is directly proportional to the relaxation extension:

$$\mu = 8.2e. \quad (49)$$

We proceed to test it for other materials.

#### 5.2. Potassium niobate

Here the Nb displacement is only known at room temperature (Katz & Megaw, 1967). We can however predict it at all temperatures if we assume that (49) holds good, not only within the orthorhombic and tetragonal phases individually but also for any discontinuous changes at the phase transitions. With  $\Delta e$  given by  $\pm \frac{1}{2}\Delta l\eta$ ,  $\Delta\mu$  is  $\pm 4.1 \times 2.8\Delta\eta$ ; using values of  $\eta$  from Table 1, the values of  $\Delta\mu$  in the two phases and at the two transitions are  $-0.04$ ,  $-0.05$ ,  $+0.04$ ,  $-0.14 \text{ \AA}$ , totalling  $0.19 \text{ \AA}$ . Hence we predict a room temperature Nb displacement of  $0.19 \text{ \AA}$ . The experimental value is  $0.20 \text{ \AA}$ . The good agreement is a confirmation of the hypothesis expressed in equation (49).

The graph of predicted Nb displacement against temperature is plotted in Fig. 8. We note the discontinuities at the two transitions, and in particular the increased displacement at the orthorhombic-tetragonal transition.

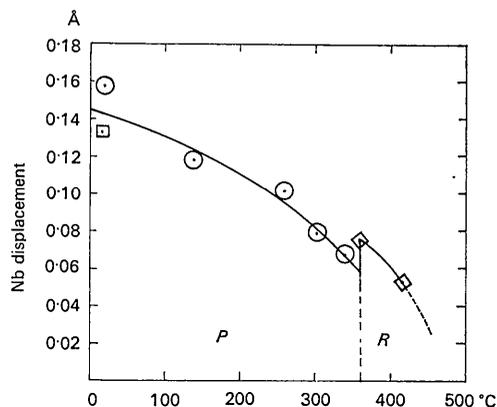


Fig. 6.  $\text{NaNbO}_3$ . Observed variation of Nb displacement  $\mu$  with temperature (experimental values).  $\square$  Value from structure determination.  $\circ$  Values from visually estimated intensities, phase P.  $\diamond$  Values from visually estimated intensities, phase R (A. Sakowski-Cowley, private communication).

Table 4. Temperature variations of parameters in  $\text{LiNbO}_3$

°C	$\frac{1}{a} \frac{da}{dt}$	$\frac{1}{c} \frac{dc}{dt}$	$\frac{ds}{dt}$			$\frac{1}{l} \frac{dl_m}{dt}$		
			(i)	(ii)	(iii)	(i)	(ii)	(iii)
0-200	12	3	-5	0	4	8	3	-2
200-400	15	4	-5	0	5	9	4	0
400-600	18	3	-6	-1	4	8	3	-2
600-800	19	0	-1	5	0	1	-5	0
800-1000	26	-6	3	6	2	-7	-12	-8
1000-1100	42	-9	4	9	4	-13	-17	-13

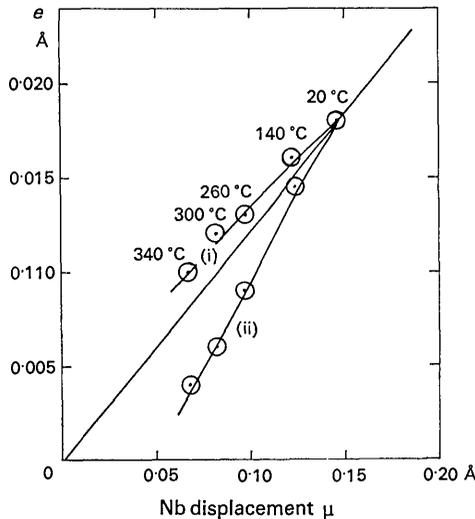


Fig. 7.  $\text{NaNbO}_3$ . Variation of Nb displacement  $\mu$  with edge-length difference  $e$ . (i) Model with  $\Delta\omega^2=0$ , (ii) Model with  $\Delta\omega^2=\Delta\phi^2$ .

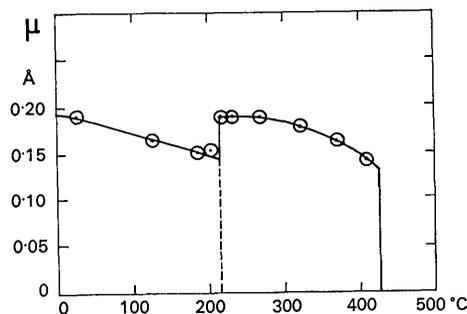


Fig. 8.  $\text{KNbO}_3$ . Predicted variation of Nb displacement  $\mu$  with temperature.

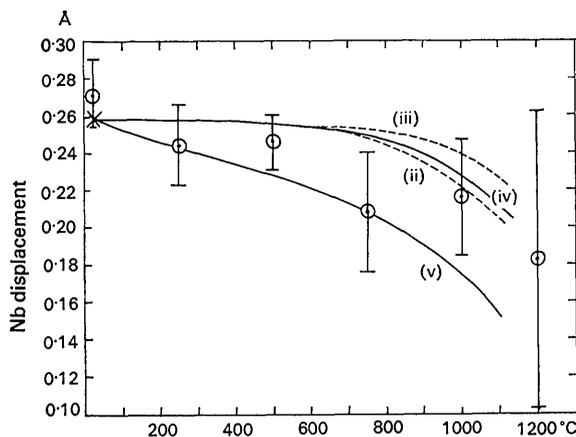


Fig. 9.  $\text{LiNbO}_3$ . Predicted and observed variation of Nb displacement  $\mu$  with temperature. Points marked with circles and vertical lines show experimental values of Abrahams, Levinstein & Reddy, with their standard deviations. Point marked  $\times$  is from single-crystal work of Abrahams, Bernstein & Reddy. Lines (ii), (iii), (iv), (v), are calculated for different models described in the text; of these, (iv) and (v) are derived directly from lattice parameters. [(i) nearly coincides with (ii).]

### 5.3. Lithium niobate

Here the Nb displacement is known from the  $z$  parameter of the oxygen atom as measured by Abrahams, Levinstein & Reddy (1966); writing  $z = \frac{1}{2} - w$ ,  $\mu = \omega c$ . These results are plotted in Fig. 9. We shall see how far they can be predicted from our hypothesis. Here, however, we cannot predict the room-temperature value, because there are no measurements of lattice parameters when the displacement is zero; we have to take the room-temperature value as the datum line from which to measure changes.

Since in this structure there are no relaxed edges, we cannot make a reliable direct estimate of the relaxation extension  $e'$ . Its temperature derivative is more informative. We have

$$\frac{1}{l} \frac{de'}{dt} = \frac{1}{l} \frac{dl_r}{dt} - \frac{1}{l} \frac{dl_u}{dt} = \frac{1}{l} \frac{dl_m}{dt} - \frac{1}{l} \frac{dl_u}{dt}, \quad (50)$$

and since  $\frac{1}{l} \frac{dl_u}{dt}$  is a normal expansion coefficient, we expect it to be positive and to increase with temperature. Now  $de'/dt \leq 0$ , hence  $dl_m/dt \leq dl_u/dt$ ; therefore the maximum observed value of  $dl_m/dt$  should give a lower estimate for  $dl_u/dt$ . For all three models we find (see Table 4) that  $\frac{1}{l} \frac{dl_m}{dt}$  remains nearly constant from room temperature to about  $600^\circ\text{C}$ , with values about  $8 \times 10^{-6}$ ,  $4 \times 10^{-6}$ , and  $-1 \times 10^{-6} \text{ deg}^{-1}$  respectively, and decreases thereafter. Hence, taking differences from room temperature values, we can write

$$\frac{\Delta e'}{l} = \frac{\Delta l_m}{l} - \frac{1}{l} \left( \frac{dl_m}{dt} \right)_0 \Delta t. \quad (51)$$

In taking  $\frac{1}{l} \frac{dl_u}{dt}$  as the 'normal' expansion coefficient, we are referring to a hypothetical edge that is completely unrelaxed. The actual edges are triply relaxed, because this is a three-corner displacement. In the previous materials, we were either dealing with the difference between a singly relaxed edge and an unrelaxed one (tetragonal  $\text{KNbO}_3$ ) or between a doubly relaxed edge and a singly relaxed ('partly unrelaxed') edge (orthorhombic  $\text{KNbO}_3$  and  $\text{NaNbO}_3$ ). Empirically, we may write

$$e' = (n_1 - n_2)e, \quad (52)$$

where  $n$  is the number of dimensions in which relaxation affecting an edge has occurred; here  $e' = 3e$ . Then from (49),

$$\Delta\mu = \frac{8.2}{3} \Delta e' = 7.6 \frac{\Delta e'}{l}, \quad (53)$$

which, with (51), enables us to calculate  $\Delta\mu$  for models (i), (ii) and (iii).

This method of prediction of the Nb displacement is unsatisfactory because, in addition to the uncertainties of its assumptions, it requires a knowledge of the

atomic position parameter  $u$  which is at least as hard to determine as the Nb displacement itself. By making a simple empirical assumption, however, we can use a similar argument to predict  $\Delta\mu$  from lattice parameters only. Equation (47) allows this to be done if we know, or can assume,  $ds/dt$ . Now  $s$ , the symmetry-clamping parameter, depends on external forces, whose temperature variation is independent of  $d\mu/dt$ , and for  $\text{KNbO}_3$  we saw that  $ds/dt$  was much less than  $d\mu/dt$ . If, for  $\text{LiNbO}_3$ , we make the order-of-magnitude assumption that  $ds/dt=0$ , then from (47),

$$\frac{1}{l} \frac{dl_m}{dt} = \frac{1}{c} \frac{dc}{dt}, \quad (54)$$

and using (51) and (53),

$$\Delta\mu = 7.6 \left[ \frac{1}{c} \Delta c - \frac{1}{c} \left( \frac{dc}{dt} \right)_{\max} \Delta t \right]. \quad (55)$$

(Some discussion of possible reasons for expecting  $ds/dt$  to be small will be given in a later paper.)

It can be seen from Table 4 that the maximum value of  $\frac{1}{c} \frac{dc}{dt}$  occurs at about 200–400°C, and is  $4 \times 10^{-6} \text{ deg}^{-1}$ . We adopt this in equation (55) for model (iv).

It is the same as the value of  $\frac{1}{l} \frac{dl_u}{dt}$  used in model (ii), and as before it represents a lower estimate.

An alternative way of estimating  $\frac{1}{l} \frac{dl_u}{dt}$  is by comparison with the cubic phases of  $\text{NaNbO}_3$  and  $\text{KNbO}_3$ , in both of which it has the same value,  $11 \times 10^{-6} \text{ deg}^{-1}$ . This, replacing  $\frac{1}{c} \left( \frac{dc}{dt} \right)_{\max}$  in equation (55), gives model (v).

Values of the Nb displacement have been calculated for all five models, and are plotted in Fig. 9 (except that (i), which is very like (ii), has been omitted for clarity). Three results emerge.

(a) All models predict the order of magnitude of  $\mu$  and the general course of its temperature variation correctly.

(b) The exact behaviour of the atomic position parameter  $v$  makes rather little difference. Hence our predictions using only macroscopic parameters (full lines on the graph) are as good, to the present accuracy, as those relying on measurements of  $u$  and  $v$ . In particular, the qualitative conclusion of § 4.4 that the flat shape of the  $c$ -versus-temperature curve was associated with decreasing Nb displacement in the  $c$  direction has been shown to be justified.

(c) The course of the  $\mu$ -versus-temperature curve is fairly sensitive to the value assumed for  $\frac{1}{l} \frac{dl_u}{dt}$ , and can therefore only be predicted within rather broad limits. The difficulty is in finding a value based on experimental evidence for the 'normal expansion', *i.e.*

the octahedron edge-length expansion which  $\text{LiNbO}_3$  would possess if Nb remained undisplaced. Indeed, accepting the experimental values of  $\mu$  instead of trying to predict them, we could use this graph to find the normal expansion coefficient, and deduce that it lies somewhere in the range  $4$  to  $12 \times 10^{-6} \text{ deg}^{-1}$ .

The general picture of thermal changes in  $\text{LiNbO}_3$  is thus as follows. As the Nb displacement decreases, the average edge-length decreases with it. All edges decrease equally (the symmetry-clamping effect maintaining existing differences). This would be seen as a uniform macroscopic contraction were it not for the change of tilt, which, however, only produces changes in the plane perpendicular to the triad axis; thus decreases in the  $c$  parameter accompany decreases in Nb displacement, while increases in  $a$  indicate a change of tilt, in a direction to increase the volume available to Li. Changes in  $c$  parameter and changes in tilt do not necessarily proceed at the same rate, but both become more rapid as the transition point is approached.

We may use equation (53) to find the unrelaxed edge length at room temperature; it gives  $e' = 0.095 \text{ \AA}$ ,  $l_u = 2.715 \text{ \AA}$ . This of course is a hypothetical length not actually found in the structure. Completely unrelaxed edge lengths in  $\text{KNbO}_3$  and  $\text{NaNbO}_3$ , for comparison, are calculated to be  $2.832 - 0.022 = 2.810 \text{ \AA}$  and  $2.796 - 0.018 = 2.778 \text{ \AA}$  respectively. The hypothetical edge lengths of the three compound thus vary in the same direction as the ionic radii of the  $A$  cations.

#### 5.4. Conclusions

All the evidence is consistent with the hypothesis that off-centre Nb displacements  $\mu$  and relaxation extensions  $e'$  are proportional, with the same constant of proportionality for all the examples considered, both for continuous and discontinuous changes. The relation is

$$\mu = \frac{8.2}{n_1 - n_2} e', \quad (56)$$

where  $n_1, n_2$  are the numbers of dimensions in which relaxation affecting the edges has occurred.

This simple law of proportionality probably only represents a first-order approximation to a relation of more complicated form. For  $\text{NaNbO}_3$  and  $\text{KNbO}_3$ , however, it seems to fit the facts very well; for  $\text{LiNbO}_3$ , where many additional factors are involved, it is at least correct as regards the order of magnitude of the quantities concerned.

## 6. Less fully-known structures

### 6.1. Sodium niobate, phase $Q$

Phase  $Q$  is the ferroelectric phase. Geometrical relations are the same as for phase  $P$ , except that 4 is replaced by 2 in equations (2) and (7) for  $b_0$ .

Pseudocubic cell edges are known accurately as a function of temperature, but  $\varepsilon$  is only known approximately to have a value close to that in phase  $P$ .

Even with this limited information, we can show that  $e$  is positive. From (15),

$$\frac{e}{l} = -\frac{1}{2}\eta - \frac{1}{4}\varepsilon + \frac{1}{4}\omega^2.$$

Since  $-\frac{1}{2}\eta = 0.0054$ , and  $-\frac{1}{4}\varepsilon$  would be  $-0.0028$  if it were the same as in phase  $P$ , it is clear that no reasonable difference in  $\varepsilon$  could make  $(-\frac{1}{2}\eta - \frac{1}{4}\varepsilon)$  negative, and whatever the magnitude of  $\omega^2$ , its sign is positive; hence  $e$  is positive. It is likely (by analogy with phase  $P$ ) that  $\omega$  lies between 0 and  $\varphi$ ; then  $e$  lies between 0.007 Å and 0.022 Å. Since we have no reason to suppose that  $\omega$  is very different in phase  $Q$  from what it was in phase  $P$ ,  $e$  is probably nearer the upper of these limits.

### 6.2. Solid solution $\text{Na}_{0.975}\text{K}_{0.025}\text{NbO}_3$ (phase II)

More information is available about the potassium-containing solid solution, 'phase II', studied by Wells & Megaw, isostructural with phase  $Q$ . The accuracy of the refinement is not yet good enough to show significant differences in  $\mu$  and  $e$  from those of phase  $P$ , but the same general principles hold good for phase II (*cf.* Table 2). The tilt  $\omega$  is certainly less than in phase  $P$ ; its value is  $6.6 \pm 2^\circ$ . If the octahedron had the same shape as in phase  $P$ , its tilt would be  $7.4^\circ$ , which lies well within the limits of error quoted (which are estimated limits, not standard deviations).

It is expected that the tilts should be smaller in phase II than in phase  $P$ , because this provides a larger cavity to accommodate the proportion of larger K ions.

### 6.3. Sodium niobate, $\text{NaNbO}_3$ , phase $R$

This is orthorhombic, but the diad symmetry directions of the structure now all coincide with the tetrad axes of the octahedron. The displacement of Nb is one-corner, directed along the  $c$  axis. Its magnitude (A. Sakowski-Cowley, private communication) is slightly greater in phase  $R$  than in phase  $P$  just below the transition, but decreases very rapidly with increasing temperature (Fig. 6).

The relaxed edges are those with a component along  $c$ . We expect them to be longer than edges in the (001) plane, and to contract with increasing temperature as the Nb displacement decreases.

To make predictions about lattice parameters we should have to know the tilts. But, assuming they are not too large or too unequal about the three axes, we expect  $c$  to be the largest of the lattice parameters and to have the smallest thermal expansion. Preliminary results (A. Sakowski-Cowley, private communication) indicate that all three tilt angles are roughly equal (about  $5^\circ$ ). The flat shape of the graph of  $c$  versus temperature, and the fact that it lies above the  $a$  and  $b$

graphs, agrees with prediction. (In Table 1,  $\varepsilon = \frac{c}{a} - 1$ ,

$$\eta = \frac{b}{a} - 1.)$$

### 6.4. Other high temperature forms of $\text{NaNbO}_3$

Above phase  $R$  we have a complex succession of phases. From the evidence of certain difference reflexions persisting to about  $600^\circ\text{C}$ , it is known that octahedral tilts still remain, and the intensities of these particular reflexions can be associated with the tilt  $\varphi$ . It is clear from Table 3 that most of the macroscopic expansion is due to the gradual disappearance of tilts. Indeed, the change of mean octahedral edge-length is a rather large contraction. Without further information we cannot say how much of the contraction occurs continuously within phases, and how much discontinuously at phase transitions. Similarly, changes in Nb displacement may be discontinuous at transitions, and they need not always be decreases, even though there must be a net decrease over the whole range.

The temperature variation of the lattice parameters, in the light of our previous discussions, suggests that the Nb displacement has dropped to zero by about  $(470 \pm 30)^\circ\text{C}$ , and that thereafter, in phase  $S$ , there is a 'normal' octahedron expansion coefficient superimposed on the continuing change of tilt. We can predict the macroscopic expansion coefficient if we assume (i) (admittedly rather roughly) that the rate of change of tilt is constant from  $20^\circ$  to  $640^\circ\text{C}$ , being given by the difference of the macroscopic coefficient and the  $l_m$  coefficient, (ii) that the 'normal' coefficient is the same as in the cubic phase. From Table 3, the predicted value is then (in units of  $10^{-6} \text{ deg}^{-1}$ )  $16 - (-9) + 12 = 37$ , as compared with the experimental values (rather roughly determined) of about 26 to 41.

Above about  $500^\circ\text{C}$  the increased rate of expansion almost certainly implies increased rate of change of tilt, and at about  $530^\circ\text{C}$  there is certainly a discontinuous change in the system of tilts. Possibly at this transition there may be a renewed off-centre displacement of Nb. Unexpected though this may appear, there is no theoretical reason against it, and its occurrence would make it easier to account for the rather complex variation of lattice parameters from  $530^\circ\text{C}$  to  $640^\circ\text{C}$ . If the difference of the largest axial ratio from unity were entirely due to  $e$  and hence to  $\mu$ , the value of  $\mu$  would be about 0.07 Å up to about  $600^\circ\text{C}$ , after which it would drop very rapidly. If displacements occur, they may be parallel, as no reflexions with intensities suggesting antiparallel displacements have been noted. Direct measurements of dielectric constants or spontaneous polarization to test for ferroelectricity have not been made because the material becomes conducting. Thus there is no certain evidence, either structural or electrical, and the suggestion remains speculative.

## 7. Applicability to other octahedral structures

The advantage of niobates for testing the theoretical approach is that the intrinsic effect produces an off-centre displacement at room temperature which is measurable but not too large to allow linear approximations and averaging procedures to be valid. A

survey of other cations with off-centre octahedral environments has been given by Orgel (1958), and in principle the same approach should be applicable to them. There may, however, be difficulties where the effect is too small or too large.

Titanates are representative of the too-small effect. It seems clear now that the intrinsic effect is below the critical value at room temperature, and that forces due to the other cation (steric in BaTiO<sub>3</sub>, polarizing power in PbTiO<sub>3</sub>) are needed to produce off-centring. It is harder to allow correctly for such external effects.

Vanadates are representative of the too-large effect. Here the displacements are so large, and the consequent polarization changes so important, that some of our working approximations become dubious, and the lower local symmetries make the geometry harder to handle. Moreover, the large displacements represent such large energy differences that they are likely to be much less sensitive to temperature changes.

Nevertheless one would expect both titanates and vanadates and other octahedra with off-centre cations to show something of the same effects as the niobates, though the regularities may be harder to recognize because of the disturbing factors mentioned.

### 8. Summary

(1) To a first approximation, NbO<sub>6</sub> octahedra behave as homogeneous isotropic units, and the macroscopic expansion is the sum of parts due to the change of mean edge length of the octahedron and the change of octahedron tilt.

(2) When changes of tilt are allowed by symmetry, their contribution to the macroscopic expansion is considerably greater than that of changes of octahedron size.

(3) The mean edge-length coefficient of the octahedron is always very small, and may even be negative, as long as off-centre Nb displacements are present; but becomes much larger when Nb becomes central. This is in accordance with theory.

(4) The difference  $e$  between relaxed and unrelaxed edge lengths of the octahedron at room temperature is, for all the materials examined, whatever their geometry, of the sign predicted by theory from the character of the Nb displacement, and of about the same magnitude.

(5) As predicted by theory, the value of  $e$  varies with temperature in the same way as that of the Nb displacement,  $\mu$ . To a first approximation the two are proportional, with  $\mu = 8 \cdot 2e$  for one-corner and two-corner displacement, and  $\mu = 8 \cdot 2e'/3$  for three-corner displacement ( $e'$  not being found directly from the structure, as  $e$  is in the other cases).

(6) The constant of proportionality in this relation is the same for different materials, different phases of the same material, and continuous and discontinuous changes.

(7) The constant of proportionality found from experimental evidence for NaNbO<sub>3</sub> (phase  $P$ ) predicts correctly the room temperature displacement of Nb in KNbO<sub>3</sub>, using only the measured changes of axial ratio up to 425°C; it also gives an order-of-magnitude prediction of the temperature variation of the displacement of Nb in LiNbO<sub>3</sub>, using only measured lattice parameters up to 1100°C.

(8) Less fully known niobates appear to satisfy the same relations, so far as the evidence goes.

(9) Other octahedral framework structures with off-centre cations should show comparable effects, but the regularities may be harder to detect because of other complicating factors.

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