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A Note on the Structure of Lithium Niobate, $LiNbO_3$

By Helen D. Megaw

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

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The structure of $LiNbO_3$, determined by Abrahams and co-workers, is more easily understood if it is described in terms of displacement parameters from an idealized structure with hexagonally close-packed oxygen atoms. The relationship to perovskite, the significance of the thermal changes, and the atomic movements in the ferroelectric reversal, all become more obvious and predictable in this way.

The structure of $LiNbO_3$ is known from the very detailed room-temperature work of Abrahams, Reddy & Bernstein (1966) and Abrahams, Hamilton & Reddy (1966), and from a less accurate survey up to 1200 °C, using powder methods, by Abrahams, Levinstein & Reddy (1966). Their work confirmed the more plausible of the two alternatives put forward by Bailey (1952) (*cf.* Megaw, 1954) and improved greatly on its accuracy. Differences in the choice of axes of reference, and of origin, somewhat hid the resemblance. The structure is pseudosymmetric, with small systematic displacements of atoms from an ideal higher-symmetry form. It is more easily understood if, keeping the axial directions chosen by Abrahams and co-workers, we move the origin slightly (permissible since the choice is arbitrary), and write all the atomic parameters in terms of small quantities expressing the displacements from the ideal.

The space group is $R3c$. Like previous authors, we use hexagonal axes of reference; then

$$a = 5{\cdot}148\ \text{Å}$$
$$c = 13{\cdot}863\ \text{Å}\,.$$

The atomic parameters found by X-rays (not significantly different from those found by neutrons) are, with Abrahams's origin,

Nb	0,0,0
O	$0{\cdot}0492 \pm 4,\ 0{\cdot}3446 \pm 5,\ 0{\cdot}0647 \pm 4$
Li	$0,0,0{\cdot}2829 \pm 23$.

The oxygen atoms are in general positions, forming a centrosymmetric array of six equidistant plane layers per unit cell, parallel to (0001). Since their separation is thus exactly $c/6$, it is preferable to take the origin at the centre of symmetry midway between layers, which means increasing the z parameters by $w = \frac{1}{12} - 0{\cdot}0647 = 0{\cdot}0186$. Any advantage in taking the origin at Nb is only for simplicity in calculating diffraction by the structure, not for understanding the structure when determined. The new Nb parameter, w, expresses directly the Nb displacement from the geometrical centre of the octahedron. The Li atom has a parameter close to $\frac{1}{3}$; let its difference from $\frac{1}{3}$ be w'.

We take the idealized structure as one having a close-packed array of oxygen atoms. There are six octahedral interstices lying on each triad axis, *i.e.* one between each pair of oxygen layers; the first and fourth contain Nb, the second and fifth are empty, the third and sixth contain Li. For such a structure the axial ratio c/a is $2\sqrt{2}$, and the coordinates of an oxygen atom are $0,\frac{1}{3},\frac{1}{12}$. We may write the actual parameters as:

Nb	$0,0,w$
O	$u,\frac{1}{3}+v,\frac{1}{12}$
Li	$0,0,\frac{1}{3}+w'$

with $u = 0{\cdot}0492$, $v = 0{\cdot}0113$, $w = 0{\cdot}0186$, $w' = -0{\cdot}0318$. Moreover, the value of the axial ratio c/a is $2\sqrt{2}\,(1+\frac{1}{2}\eta)$, with $\eta = -0{\cdot}0936$. Since the parameters expressing the departure of the structure from the ideal are all so small, the actual structure approximates closely to the ideal, and can usefully be discussed in terms of successive approximations, starting from the ideal.*

Consider first the Nb–O framework only – this is physically significant, because the Li–O bonds are so much weaker than the Nb–O. It consists of octahedra sharing corners, each O having two Nb neighbours only. There are Nb atoms at $0,0,0$; $\frac{1}{3},\frac{2}{3},\frac{1}{6}$; $\frac{2}{3},\frac{1}{3},\frac{1}{3}$; $0,0,\frac{1}{2}$; $\frac{1}{3},\frac{2}{3},\frac{2}{3}$; $\frac{2}{3},\frac{1}{3},\frac{5}{6}$; alternate atoms in this list are related to each other by the rhombohedral lattice operator $(\frac{2}{3},\frac{1}{3},\frac{1}{3})+$, and the others by the c-glide plane. In the ideal structure all octahedra are identical and regular; three, related by the lattice operator, are in parallel orientation, and the other three are rotated, relative to the first, by 180° about the triad axis. Each octahedron shares each corner of its upper face with a corner of the lower face of an octahedron of the next layer. This is shown in projection in Fig. 1(*a*) (the lower and upper halves of the unit cell being drawn separately for clarity). The antiparallel orientation of octahedra separated by $\frac{1}{2}c$ can be seen.

If this idealized model is regarded as a zero-order approximation to the actual Nb–O framework in $LiNbO_3$, the first-order approximation is that in which u is non-zero while v and w remain zero. This is shown in Fig. 1(*b*). It is still centrosymmetric, like the zero-

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* For the isomorphous $LiTaO_3$ (Abrahams, personal communication) the parameters expressed in the same form are $u = 0{\cdot}0501$, $v = 0{\cdot}0103$, $w = 0{\cdot}0146$, $w' = -0{\cdot}0397$.

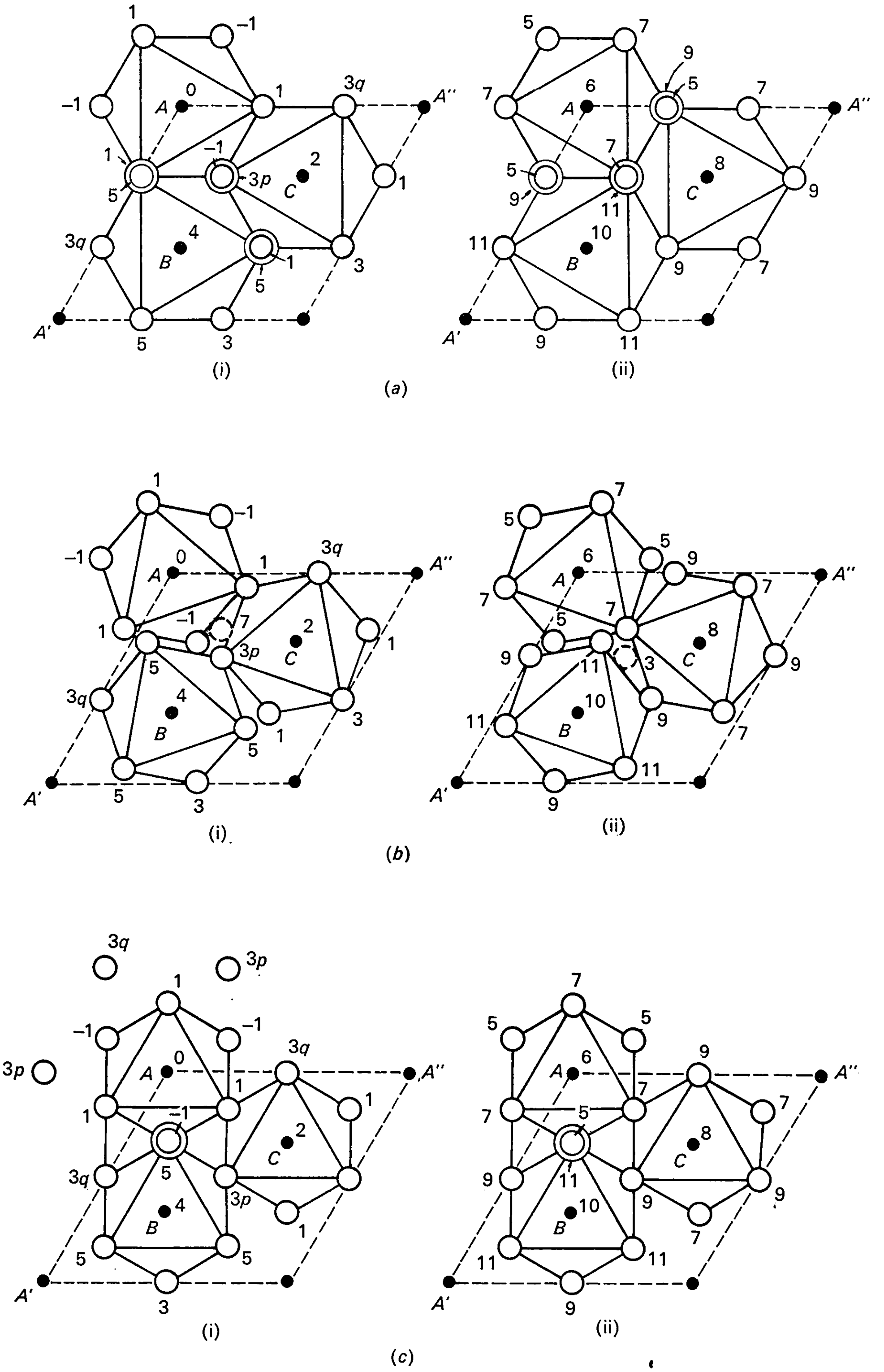

Fig. 1. Projection on (0001) of Nb–O framework; left-hand diagram gives lower half of unit cell, right-hand diagram upper half. Origin at upper left-hand corner. Heights of atoms marked in units of $c/12$. Small black circles, Nb; open circles, O; double circles, O's coinciding in projection. For each octahedron, edges of upper face are drawn in, those of lower face omitted. For labels p and q, see text. (*a*) Ideal hexagonal packing ($u=0$). (*b*) Intermediate value of u. (*c*) Perovskite structure ($u=\frac{1}{6}$). (These diagrams have been drawn with constant a, instead of constant octahedron size. In all, $v=0$.)

order approximation, with space group $R\bar{3}c$. The difference is that displacement of oxygen atoms in their own plane has caused rotation of the octahedra about their triad axes, and this rotation is in opposite directions for octahedra separated by $\frac{1}{2}c$. If the octahedra remain regular and unchanged in size (and there is no obvious reason why they should not) the lattice parameter a will increase while c remains constant, and c/a will therefore decrease from its ideal value.

The observed value of u corresponds to a rotation of 6·5° from the ideal hexagonal orientation. It is of interest to consider what would happen if u increased further. The opposed rotations of the octahedra would increase continuously up to a value of 30°, corresponding to $u=\frac{1}{6}$. Since their initial azimuthal difference was 180°, equivalent by symmetry to 60°, it would now be zero, *i.e.* all octahedra would be parallel. This is shown in Fig. 1(*c*). Lines joining octahedron centres pass through octahedron corners, showing that the framework is now fully extended. Further increase in u merely causes a renewed crumpling and collapse, structures with $u=\frac{1}{6}+u'$ being mirror images of those with $u=\frac{1}{6}-u'$.

The fully-extended framework is in fact the ideal perovskite framework. Topologically, the continuous change in u describes a smooth transition from the hexagonally-close-packed octahedral framework to the perovskite framework. The octahedra behave as rigid units, unchanging in size or shape, but hinged freely at their corners. In opening out from the close-packed configuration, the lattice parameter a increases by a factor $2/\sqrt{3}$, and the volume therefore by 4/3. This corresponds to the fact that the anion array in ideal perovskite is a cubic close packing with one anion in four missing.

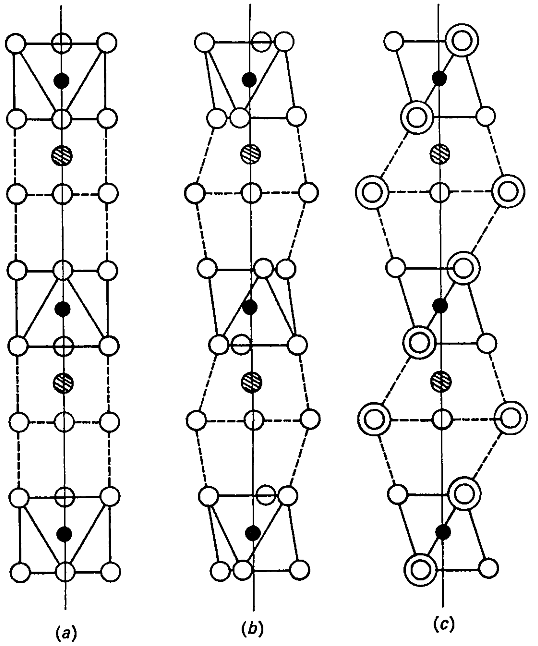

Fig. 2. Projection on $(11\bar{2}0)$ (whose trace is parallel to $A'A''$ in Fig. 1) of octahedra whose centres lie on triad axis through origin. Small black circles, and hatched circles, represent geometrical centres of octahedra occupied by Nb and Li respectively; open circles, O; double circles, O's coinciding in projection. Full lines, edges of Nb octahedra (nearer side only shown); dashed lines, outlines of Li octahedra and empty octahedra. (*a*) Ideal hexagonal packing ($u=0$). (*b*) Intermediate value of u. (*c*) Perovskite structure ($u=\frac{1}{6}$). Diagrams drawn with constant a; $v=0$).

What happens, in such a transformation, to the other octahedral interstices of hexagonal close-packing – those to be filled by Li and those to be left empty? In the zero-order approximation, they are of equal size and shape to those occupied by Nb. We can either consider the set lying on the same triad axis, as in Fig. 2(*a*), their octahedra sharing faces perpendicular to the axis, or we can consider the symmetry-related set at A,B,C in Fig. 3(*a*), all at height 0, their octahedra sharing edges to form a continuous sheet parallel to (0001). In the first-order approximation, as the Nb octahedron rotates as a rigid unit, the other two octahedra become distorted and enlarged, though remaining identical in shape with each other [Figs. 2(*b*), 3(*b*)]. The three oxygen atoms of the face common to these two octahedra in Fig. 2 move apart, opening up the 'window' between the cavities, while three other oxygen atoms at the same level close in, until at the perovskite limit [Fig. 2(*c*)] the original triangle has become part of a hexagon such that a point at its centre is equally distant from its corners and from the oxygen atoms in the layers above and below. The two octahedral cavities of ideal $LiNbO_3$ have in fact merged into the single 12-coordinated cavity of ideal perovskite. The cavity centred at $0,0,\frac{3}{12}$ can be picked out in Fig. 1(*c*); the six atoms of the hexagon at height 3 are shown, together with three of the lower layer at height 1 and one of the upper layer at height 5. The opening out of the window from triangle to hexagon can be seen in Fig. 1(*a*), (*b*) and (*c*) by following the displacement of atoms at height 3; those marked p move away from the axis, while those marked q move in towards it.

Hitherto we have considered the framework only, not distinguishing between Li octahedra and empty octahedra; both, at this approximation, are identical in shape. Choice of one as a site for Li destroys the centrosymmetry and reduces the space group to $R3c$, even when all position parameters remain zero. The only way to retain the higher symmetry would be to insert the Li in the middle of the face common to both octahedra, *i.e.* at $0,0,\frac{1}{4}$. Here, in the ideal close-packed structure, it would have three very near oxygen neighbours, three others much more distant in the same plane, and six at intermediate but fairly long distances, three above and three below. As u changes from zero to $\frac{1}{6}$, there is no further decrease in symmetry, but the Li–O distances gradually become more alike, until at the perovskite limit they are exactly equal.

It is not suggested that a change of framework configuration from one extreme to the other can take place in any actual material. It will, however, be of interest to compare $LiNbO_3$ with other structures having different values of u, including examples near the perovskite limit. This will be considered below.

The reduction of symmetry caused by putting Li into octahedral interstices allows the parameters v, w, w', to become non-zero, and hence brings us to the second-order approximation – the actual $LiNbO_3$ structure. Both w and w' represent displacements of the cations along the triad axes, away from the geometrical centres of their octahedra; for both, the direction is – as we should expect – away from the face common to their two octahedra. The effect of v is less easily visualized. It acts differently on the three different types of octahedra, as shown in Fig. 4. The Nb octahedron centred at the origin has oxygen atoms with the following coordinates:

$$u, \tfrac{1}{3}+v, \tfrac{1}{12};\ \tfrac{1}{3}-u+v, -u, \tfrac{1}{12};\ -\tfrac{1}{3}-v, -\tfrac{1}{3}+u-v, \tfrac{1}{12};$$
$$-u+v, -\tfrac{1}{3}+v, -\tfrac{1}{12};$$
$$-\tfrac{1}{3}+u, u-v, -\tfrac{1}{12};\ \tfrac{1}{3}-v, \tfrac{1}{3}-u, -\tfrac{1}{12}\,.$$

The octahedron is irregular. The edges of its upper face, adjacent to the empty octahedron, are longer than those of its lower face, adjacent to the Li octahedron; since, however, when repeated by a lattice translation, the long and short edges are nearly collinear in the (0001) plane, their mean is very little altered. We note that displacement of Nb is towards the *longer* edge, in contrast to what happens in $KNbO_3$ (Katz & Megaw, 1967). The Li octahedron is a little smaller than when v was zero; it is rotated slightly, but not additionally distorted. Correspondingly, the empty octahedron is rather larger.

Thermal changes

On general grounds, one would expect increasing temperature to decrease the deviations from an idealized structure, and also to increase the specific volume. This poses a problem concerning u. Decreasing u would result in a decrease of volume, which would be hard to compensate by any reasonable value of the expansion of the octahedron itself. We conclude that the zero-order model is *not* that towards which the actual structure will tend with increasing temperature, but rather that it will approach the first-order model with increasing u; the displacement parameters v and w will approach zero.

The experimental evidence supports this, so far as it goes. Standard deviations are unfortunately large, but the trends of increasing u and decreasing w appear to be significant, though it is not possible to say whether the changes occur steadily over the temperature range 0–1200 °C or are chiefly concentrated in the latter part of it, say from 1000–1200 °C. Information about v is less reliable, because while the room temperature value from single-crystal work is positive, the powder-diffraction values both at room temperature and other temperatures (except at 1200 °C) are all negative, with standard deviations greater than their difference from zero.

Above 1200 °C the predicted structure is the first-order approximation described above, for which the symmetry is $R\bar{3}c$, v and w are zero, w' is $\frac{1}{12}$, but u is not necessarily zero. This is like that proposed by Abrahams, Levinstein & Reddy, but they first put forward the space group $R\bar{3}$ (while admitting $R\bar{3}c$ as a possible alternative). There was no direct experimental evidence* to rule out $R\bar{3}$, but the loss of symmetry involved would be very unusual, and there is nothing to suggest it occurs. (That $R\bar{3}$ is the space group of ilmenite is irrelevant, since the cation sequence and octahedral distortions are quite different.)

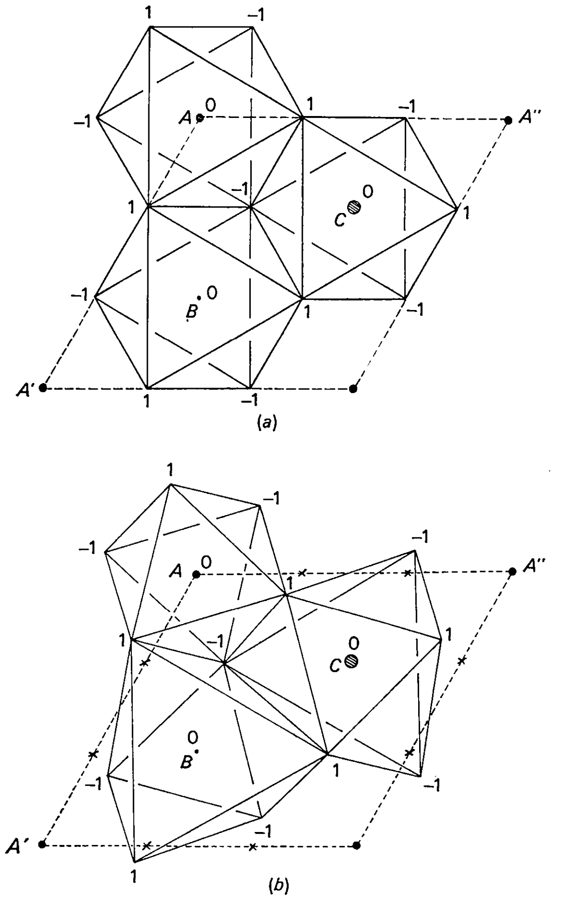

Fig. 3. Projection on (0001) of layer of octahedra with centres at height 0. Heights of atoms marked in units of $c/12$. Small black circles, Nb; hatched circle, Li; dot, centre of empty octahedron. (*a*) Ideal hexagonal packing ($u=0$, $v=0$). (*b*) Intermediate value of u ($u=0{\cdot}083$, $v=0$). Crosses mark reference points at $\frac{1}{3}, 0$; $\frac{2}{3}, 0$; $0, \frac{1}{3}$; $0, \frac{2}{3}$.

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* More recently, Niizeki, Yamada & Toyoda (1967), from a study of growth ridges and etched hillocks on $LiNbO_3$ crystals, have confirmed that the high-temperature space-group is $R\bar{3}c$. They call attention also to the importance of the size of Li in allowing occupation of the 3-coordinated site, and to the character of the octahedral tilt.

Any great change in u at the transition is unlikely, and a decrease particularly unlikely, because it would imply either a decrease in the specific volume, which is experimentally not found, or a very large increase in the size of the octahedra to compensate for it.

For symmetry $R\bar{3}c$, Li lies at the centre of a triangle of oxygen atoms for which Li–O is $\frac{a}{3}(1+3u)$; next nearest neighbours above and below are at a distance

$$\frac{a}{\sqrt{3}}\left[1-\frac{1}{2}u+\frac{3}{2}u^2+\frac{2}{3}\left(\frac{c}{2\sqrt{2}a}-1\right)\right].$$

The triangular coordination is somewhat unexpected, but if parameters just above the transition are equal to those just below, the distances are not unreasonable: three neighbours at 2·06 Å and six at 2·74 Å, as compared with three at 2·07 Å and three at 2·24 Å in the room temperature structure. An alternative possibility is that of statistical disorder of Li between sites equidistant from the triangle above and below it.

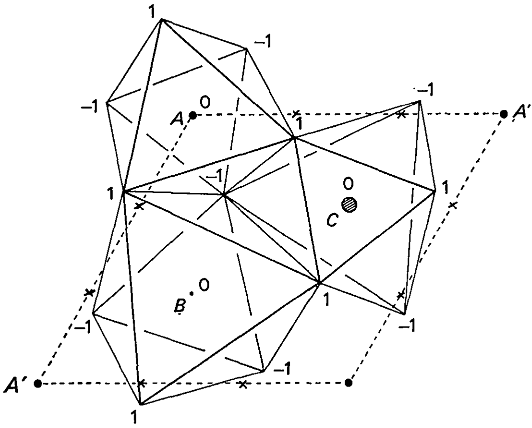

Fig. 4. Same as 3(*b*) except that v is 0·033.

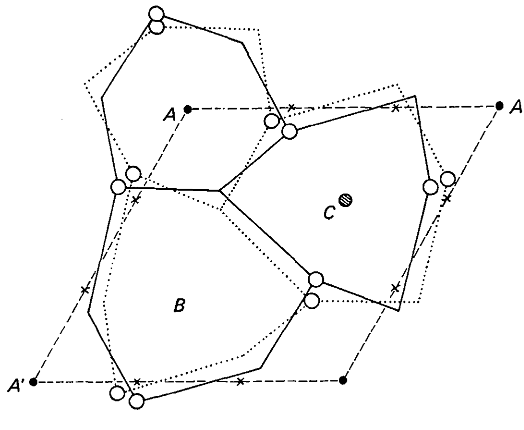

Fig. 5. Outline of octahedra shown in Fig. 4 (full lines) and same after ferroelectric reversal (dotted lines). Oxygen atoms of the upper layer are marked by circles. After reversal octahedron at *C* is empty because its Li has moved out of it into the layer below, while that at *B* is filled by Li which has moved down from the layer above.

Ferroelectric reversal

The ferroelectric reversal mechanism envisaged by Abrahams and his co-workers just below the transition temperature follows naturally. The measured parameters suggest that there is no steric difficulty, in this temperature range, to prevent the Li atom from slipping through the triangular face of its octahedron into the adjacent empty octahedron. The existence of a big enough opening is perhaps a more important matter for its feasibility than the actual distance to be moved by Li. The movement of Nb within its own octahedron parallel to the triad axis is easy. The movement of O is entirely in the (0001) plane; the prototype atom moves towards the origin, from $u,\frac{1}{3}+v,\frac{1}{12}$, to $u-v,\frac{1}{3}-v,\frac{1}{12}$, with corresponding movements of other atoms, causing an interchange of size between the upper and lower faces of the Nb octahedron, and an interchange of shape between the original Li octahedron and the empty octahedron (Fig. 5). Using room temperature parameters, the atomic displacements required for ferroelectric reversal are $2cw=0{\cdot}52$ Å for Nb, $2c(\frac{1}{12}-w')=1{\cdot}4$ Å for Li, $2a(\sqrt{3}/2)v=0{\cdot}10$ Å for O;* and allowing for some change in parameters below the temperature where reversal is known to become possible, the actual displacements may be considerably less. Even as they stand, these values are not unreasonably large. It is not their magnitude that matters, however, so much as the height of the potential energy barrier to be crossed en route – the stress energy in the triangular window through which Li must pass, and in other O–O edges of the octahedra as they change shape. These, of course, must be accompanied by changes in the electron distributions round the oxygen atoms, which, in association with their displacements perpendicular to the axis, provide the link between the Li and Nb displacements parallel to the axis.

The ferroelectric reversal model of Abrahams and his co-workers differs from that proposed earlier by Megaw (1954, 1957) in not requiring any change of u. The postulated movements of Nb and Li are the same in both (now not merely postulated but measured); but Megaw had implicitly assumed that a large change in u was needed to provide an opening for the to-and-fro passage of Li between octahedra, and therefore that, during the actual reversal process, u must mo-

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* Abrahams, Levinstein & Reddy quote displacements of O relative to a fixed Nb. It is much easier to follow the process if the centre of symmetry of the oxygen array is kept fixed, as we have done. Physically one might expect the centre of gravity of the whole to remain at rest, in which case the displacement of Nb would be about half the displacement of the oxygen array along **c**, and in the opposite direction. Displacements of oxygen atoms in the (0001) plane, described by the parameter v, are of course independent of this.

mentarily increase to its ideal-perovskite value of $\frac{1}{6}$. This is now seen to be wrong. The fact that, in the temperature range where ferroelectric reversal occurs, the experimental value of u gives an opening of about the right size for the passage of Li, without the need for any momentary increase, is a very satisfactory feature of the new model.

More detailed discussion of the thermal expansion of $LiNbO_3$, in comparison with that of other niobates, will be left to another paper (Megaw, 1968).

Related materials

Though topologically it is possible to transform an octahedral framework continuously from the hexagonal close-packed configuration to the ideal perovskite configuration (and a model can be made to illustrate this), physically it does not follow that all intermediate configurations must be stable. Actual examples can be located in the sequence by an index f, defined as the ratio of their u parameter to that of perovskite, which expresses their relative departure from the hexagonal extreme.

Towards the hexagonal end we have high-temperature $LiNbO_3$, with f roughly 0·35 (assuming its u to be about the same as for the low-temperature form). Towards the perovskite end we have $LaAlO_3$ (de Rango, Tsoucaris & Zelwer, 1966) with $u=\frac{1}{6}-0{\cdot}025$, and f therefore about 0·85. The two structures are strictly isomorphous if we may assume that Li is ordered in its special position in the former, even though its coordination number is then 3 (with 6 much more distant neighbours) as compared with 9 for La in the latter. $PrAlO_3$ and $NdAlO_3$ (Geller & Bala, 1956) are isomorphous with $LaAlO_3$, but depart further from the perovskite extreme, as judged from their axial ratio, which we expect to be correlated with u.

A corresponding series is known for trifluorides of transition metals (Jack & Gutmann, 1951; Gutmann & Jack, 1951; Hepworth, Jack, Peacock & Westland, 1957; Hepworth & Jack, 1957). The trifluorides of Mo, Ta, Nb have the ideal perovskite framework, those of Rh, Pd, Ir the ideal hexagonal framework, while RuF_3, VF_3, CoF_3, FeF_3, TiF_3 lie in the intermediate range, with RuF_3 near the hexagonal end at $f\simeq0{\cdot}1$ and the others between $f\simeq0{\cdot}35$ for VF_3 and $f\simeq0{\cdot}6$ for TiF_3.

The most interesting properties of $LiNbO_3$ stem from its departure from the high-temperature form – the reduction of the space group to $R3c$, and the introduction of parameters, v, w, w'. In attempting to explain them, however, the high-temperature form characterized by a particular value of u must be taken as a starting point. Other members of the series based on trigonal tilting of perovskites with or without A cations may provide useful comparisons for this purpose.

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