

## Thermal Vibrations and a Lattice Mode in Calcite and Sodium Nitrate

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The observed direction of thermal motion of the oxygen atoms in calcite can be explained if the environment of the calcium atom is taken into consideration as well as the  $\text{CO}_3$  group. Rotation of Ca octahedra accompanied by an alternate steepening and flattening which retains the  $\bar{3}$  point-symmetry and the Ca–O bond-length unchanged is associated with a screw-like movement of  $\text{CO}_3$  in which rotation in its own plane is geared to translation perpendicular to its plane. Concerted movements of all atoms in the structure satisfying these requirements can be described in terms of a single oscillating parameter; they represent a single lattice mode. They are predictable using the assumption that small departures, in the 'static' structure, of particular position parameters from ideal values indicate weaknesses of a kind that allow a large amplitude to vibrations in which the same parameters oscillate about their 'static' value. Comparison of  $\text{CaCO}_3$  and the isomorphous  $\text{NaNO}_3$  with  $\text{LaAlO}_3$  and  $\text{LiNbO}_3$ , which have very similar formal geometry but great differences in relative bond strength, helps to illustrate the principle involved.

### Introduction

Recent accurate work on the anisotropic thermal displacements of oxygen atoms in calcite (Chessin, Hamilton & Post, 1965) and the isomorphous sodium nitrate (Cherin, Hamilton & Post, 1967) gave results which are at first sight surprising, and which the authors do not attempt to explain. They observed that while the displacement ellipsoid had its shortest principal axis along the C–O or N–O bond, as expected, its longest axis was not in the plane of the  $\text{CO}_3$  or  $\text{NO}_3$  group, but inclined at about  $45^\circ$  to it.

Consideration of the problem on the lines to be described below showed, however, that not only was the direction of the large displacement amplitude capable of explanation, but it could actually have been predicted from a knowledge of the 'static' structure and certain rather general principles. Since the approach used may be a help towards analysing and interpreting thermal modes in other structures, the argument will be developed as if the thermal amplitudes in this case had not been known but had to be predicted.

### The (static) structure

Calcite and sodium nitrate are isomorphous, with space group  $R\bar{3}c$ . Using hexagonal axes of reference, there are 6 formula units per cell, with atoms in special positions as follows:

Ca or Na in	$6(b)$ ,	$0, 0, 0$
C or N in	$6(a)$ ,	$0, 0, \frac{1}{4}$
O in	$18(e)$ ,	$x, 0, \frac{1}{4}$ .

The lattice parameters and oxygen position parameters at room temperature are as follows:

	$\text{CaCO}_3$	$\text{NaNO}_3$
$a$ (Å)	4.990	5.071
$c$ (Å)	17.002	16.825
$x$	0.2571	0.2456

One usually thinks of the structure as built from planar  $\text{CO}_3$  or  $\text{NO}_3$  groups arranged at nodes of a rhombohedral lattice with their planes perpendicular to the triad, and Ca or Na ions midway between them. This description, however, fails to direct attention to the grouping of oxygen atoms round the Ca or Na, which is essential for our present discussion. We therefore take a different approach, beginning with the oxygen atoms and leaving out the carbon or nitrogen atoms until we have found suitable interstices in which to place them.

It is convenient to re-write the oxygen parameter  $x$  as  $\frac{1}{4} + \zeta$ , where  $\zeta = -0.0762$  for  $\text{CaCO}_3$ ,  $-0.0877$  for  $\text{NaNO}_3$ . This will allow geometrical comparison with the oxygen array in high-temperature  $\text{LiNbO}_3$  (Megaw, 1968*a*) for which  $\zeta = +0.0492$ , and with an ideal hexagonal close-packing, for which  $\zeta = 0$ .

Consider a hexagonally close-packed array of oxygen atoms. Let the origin be taken on a centre of symmetry midway between layers, so that layer heights (in arbitrary units) are 1, 3, 5, 7 . . . . There are octahedral interstices at the symmetry centres between the layers. Suppose cations are inserted in those at heights 0 and 6 along the same triad axis ( $A$  or  $A'$  in Fig. 1) and repeated by rhombohedral lattice translations so that they come at heights 4 and 10 along the triad axis through  $B$ , 8 and 14 along the triad axis through  $C$ . The other interstices are left empty, and cease to be symmetry centres. The height of the unit cell is 12 units, *i.e.* there are 6 layers of oxygen atoms per cell. The filled octahedra share corners, building up a three-dimensional corner-linked framework. This ideal structure is the actual structure of  $\text{RhF}_3$  and  $\text{PdF}_3$  (Hepworth, Jack, Peacock & Westland, 1957).

Changing the value of  $\zeta$  does not change the linkage pattern of the structure. It represents a rotation of the filled octahedra about their triad axes, alternate octahedra rotating in opposite senses. Figs. 2(*a*) and 3(*a*), 2(*c*) and 3(*b*), show this for positive and negative values of  $\zeta$  respectively; the positive value corresponds to an

opening out of the structure, in which the two cation–oxygen bonds become more nearly collinear, and the negative value to a contraction in which the inter-bond angle decreases and the octahedra overlap in projection. The parameter  $\xi$  is in fact a measure of the azimuthal tilt angle  $\omega$ ; it is easily shown by geometry that  $\omega = 3\xi \cos \pi/6$ .

Examples of frameworks of this kind with positive values of  $\xi$  are found in  $\text{VF}_3$  (Jack & Gutmann, 1951) and the  $\text{NbO}_3$  framework of high-temperature  $\text{LiNbO}_3$  (Megaw, 1968*a*). The azimuthal tilts are roughly  $10^\circ$  and  $7^\circ$  respectively. If they were  $30^\circ$  ( $\xi = +0.17$ ) the structure would be fully opened out, with the two cation–oxygen bonds collinear; this would be the ideal perovskite framework. In  $\text{CaCO}_3$  and  $\text{NaNO}_3$ , however,  $\xi$  has negative values corresponding to tilts of about  $-12^\circ$  and  $-14^\circ$  respectively. Thus one may think of the cation–oxygen framework in these structures as a perovskite framework which has contracted so far that it has actually overshoot the close-packed state.

During these rotations, we have assumed that the filled octahedra behave as rigid bodies. The same is not true of the empty octahedra, which change shape. The only feature we need consider is their shared face. In hexagonal close-packing it is equal in size to the faces of the filled octahedra. As  $\xi$  changes, it remains an equilateral triangle, but its corners (which belong to different filled octahedra) move apart for positive values of  $\xi$ , close in for negative values of  $\xi$  (Fig. 3). It is clear that the centre of this triangle must provide the site for C or N; and that therefore the azimuthal tilt, which determines the size of the triangle, will be controlled by the need to provide the correct C–O or N–O distance. In fact it is only the presence of C or N that makes possible the negative tilt, because the O–O edge lengths of the triangle would be too small for stability if the corners were not bonded to a central atom.

Geometrically, the structure is fully determined by its symmetry and the three parameters  $a$ ,  $c$  and  $\xi$ . It is useful to relate these to three structure-building parameters, of which two are obviously the C–O and Ca–O (or N–O and Na–O) bond lengths; we take the third to be the angle between Ca–O (or Na–O) and the triad axis. Let these new parameters be  $l_1$ ,  $l_2$ ,  $\varphi$ . Then, by simple geometry,

$$l_1 = \frac{1}{3} a(1 + 3\xi),$$

$$l_2 = \frac{1}{3} a \left[ (1 - 3\xi + 9\xi^2) + \frac{c^2}{16a^2} \right]^{1/2},$$

$$\tan \varphi = 4 \frac{a}{c} (1 - 3\xi + 9\xi^2)^{1/2}.$$

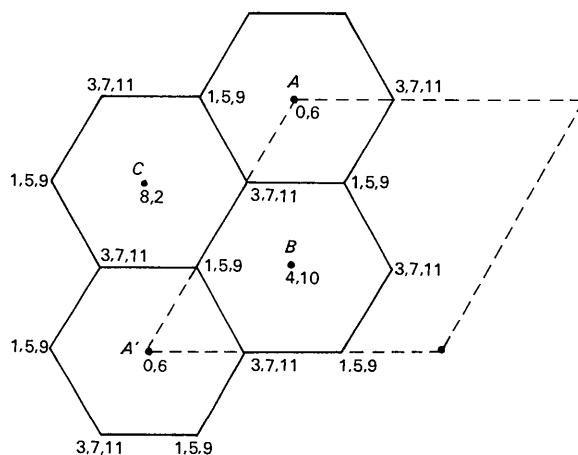


Fig. 1. Projection on (0001) of hexagonally close-packed array of oxygen atoms, with octahedra outlined. Unit cell shown by dashed line; origin is at A. Heights are in units of  $c/12$ . Heights of centres of filled octahedra projecting at A, B and C are marked.

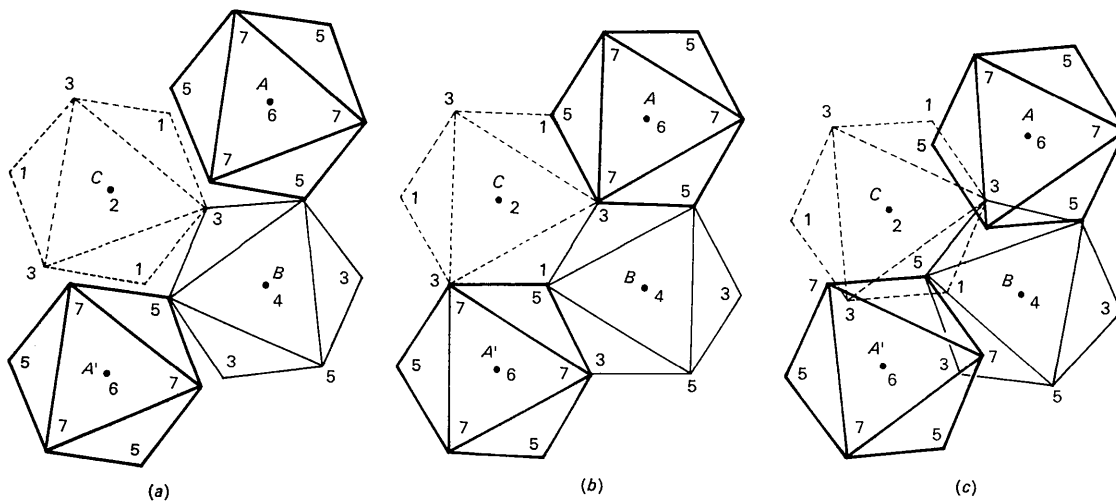


Fig. 2. Projection on (0001) of four octahedra of corner-linked structure, (a) with  $\xi$  positive, (b) with  $\xi$  zero (ideal close packing), (c) with  $\xi$  negative. Conventions as in Fig. 1, except that thick, thin, and dashed lines are used for octahedra centered at three different heights, and upper faces of octahedra are indicated.

These equations allow us to make any needed calculations about the shapes and sizes of parts of the structure (see Appendix). In particular, if the lengths  $l_1$ ,  $l_2$ , and the angle  $\varphi$  are known beforehand, we can predict the lattice constants  $a$  and  $c$  and the azimuthal tilt. The lengths are (in principle) known from other structures in which the same bonds appear; the angle  $\varphi$  needs further discussion.

At this stage, we invoke a general principle which may be stated as follows.

In a structure with a given linkage pattern, the group of neighbours immediately surrounding each cation tends to have the highest local symmetry possible without reconstruction of the linkage pattern, except in so far as it is distorted by other near-neighbour forces.

(The term 'second-nearest neighbour' is deliberately avoided, because it cannot be defined in a way that meets the point, and without definition is misleading. 'Near-neighbour forces' in the above context may for example be cation-cation repulsions through a 'window' formed by anions, or anion-anion repulsions in polyhedron edges or between polyhedra; they do *not* include interactions between atoms heavily shielded from each other by intervening parts of the structure.)

In the present case we therefore assume, as a first approximation, that the octahedron surrounding Ca will be regular, though this is not a space-group requirement. This gives us  $\varphi = 54.7^\circ$ . We need also estimates of the C-O and Ca-O bond lengths from other structures; for the former, Sass, Vidale & Donohue (1957) suggest 1.26 Å as a reasonable value, and for the latter the sum of the Goldschmidt radii gives

2.38 Å. Substitution in the above equations gives  $a = 5.07$ ,  $c = 16.4$  Å,  $\xi = -0.085$ , in very reasonable agreement with the observed values.

If we want to improve on this approximation, it cannot be done merely by putting in a better value of the C-O length (supposing we had better *a priori* means of knowing it). It is easily seen that a fault still lies in the assumed value of  $\varphi$ , for which the experimental value turns out to be  $53.1^\circ$ , *i.e.* the octahedron is somewhat elongated along the triad axis. By the principle enunciated above, we must look for another near-neighbour interaction tending to produce elongation. This is easily found: it is the Ca-C repulsion along the triad axis. (Though the carbon atom is certainly not to be taken as ionic, it carries some residual positive charge.) Ca and C are separated by about 4.2 Å, and 'see' one another through the face of the Ca octahedron; hence a small but non-negligible repulsion is to be expected. Opposing it are the forces responsible for maintaining the shape of the regular octahedron, which may include oxygen-oxygen repulsions in the octahedron edges as well as forces favouring  $90^\circ$  bond angles at Ca. The observation that distortion occurs, but remains small, is evidence that the Ca-C repulsive forces and the shape-maintaining forces are of the same order of magnitude. Since the former forces are small, it follows that the octahedron is rather 'soft' with respect to compression or elongation along the triad axis.

The attribution of the elongation to cation-'cation' repulsion is supported by the fact that it is much smaller for sodium nitrate ( $\varphi = 54.4^\circ$ ) where the electrostatic charges are smaller. Moreover, in calcite the octahedron becomes slightly more regular at lower tem-

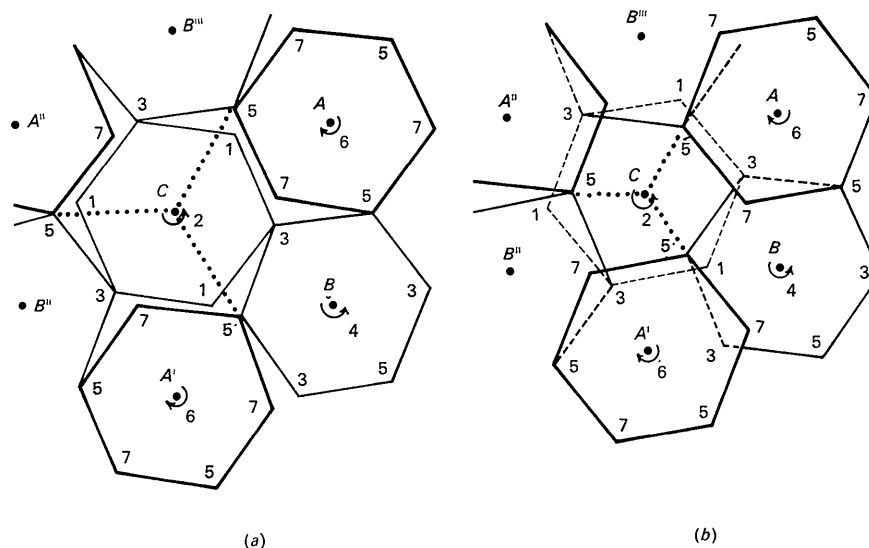


Fig. 3. Part of the same projection as Fig. 2, showing complete environment of one calcium atom and one carbon atom projecting at C, (a) with  $\xi$  positive, (b) with  $\xi$  negative. Arrows show direction of rotation of octahedra centred at A.6, B.4, C.2. Heavy dotted lines show bonds from carbon at C.5 to three oxygen atoms. Dashed lines in (b) indicate outlines of octahedra overlapped by others at higher level.

peratures ( $\Delta\varphi=0.15^\circ$  for  $\Delta T=-170^\circ\text{C}$ ) where we should expect the shape-maintaining forces to be relatively greater.

So far, we have shown

(i) that the shape and size of the calcite unit cell, and its atomic position parameter (determining the azimuthal tilt angle) can be predicted to a good approximation merely from a knowledge of the usual Ca-O and C-O bond lengths and an assumption of regularity in the octahedron;

(ii) that the small differences between this approximation and the observed structure can be explained qualitatively by assuming 'softness' in the octahedron against forces (originating in cation-cation repulsion) which tend to stretch or compress it along its triad axis.

The ideas of structure-building that have given an understanding of the 'static' structure can now be carried over to help to explain the character of the vibrations it can undergo.

### Rules for the vibrating structure

The character of the static structure suggests the general rules likely to be satisfied by the structure when undergoing any thermal vibration of reasonably large amplitude. They are as follows.

- (1) The C-O bond length will remain constant.
- (2) The Ca-O bond length will remain constant.
- (3) The Ca octahedron will not lose any symmetry, and can therefore change its shape, if at all, only by changes in its  $\varphi$  angle, *i.e.* by stretching or compression along its triad axis.
- (4) The  $\text{CO}_3$  group will retain its trigonal symmetry.

These conditions should preferably be satisfied throughout the whole vibration, but at any rate they should hold good at either extreme. We assume that modes which do not satisfy them will have much smaller amplitudes, so small that we can here neglect them altogether.

To find the character of the mode, we consider the crystal as instantaneously frozen in one extreme position. The problem then is, by arguments of symmetry and by trial and error, to find a set of displacements which give an instantaneous structure satisfying the above rules.

### Deduction of the most important mode

We begin by assuming that the  $\text{CO}_3$  group behaves as a rigid body with a large amplitude corresponding to rotation in its own plane about the triad axis. This satisfies rules (1) and (4). The lines of displacement of the oxygen atoms are shown in Fig. 4 as short heavy lines (though the amplitudes are not to scale).

Consider the extremity of the oscillation at which the  $\text{CO}_3$  group centred vertically above *A* at height  $\frac{3}{12}$  (which we shall call *A.3*) has moved clockwise, as shown by the arrows in Fig. 4. So will all other groups

related to it by lattice translations, *e.g.* *B.7*, *C.11*. We have to ask: will the other group, that at *A.9* (and its translation repeats at *B.1*, *C.5*), have moved clockwise (towards the black circles) or anticlockwise (towards the open circles)? The possibilities are shown in Fig. 5. The octahedron round calcium at *A.6* is formed by oxygen atoms belonging to  $\text{CO}_3$  groups at *B.7* and *C.5*. If the two different  $\text{CO}_3$  groups have rotated in different directions, the octahedron will be distorted in projection [(Fig. 5(*b*)] which breaks rule (3). If they have rotated in the same direction [Fig. 5(*a*)], the projection of the octahedron retains its regular hexagonal shape.

It can be seen, however, that if we retain our original assumption according to which the line *PQ* lies in the plane of projection, both arrangements break rule (2). Though in Fig. 5(*a*) the octahedra round *A.6* and *B.4* are both regular, they are of different sizes, with different Ca-O lengths. Hence a vibration in which the oxygen atoms move entirely in the plane of projection does not satisfy our empirical rules.

The remedy is fairly obvious. We must allow the oxygen atoms vertical movements of such a kind that

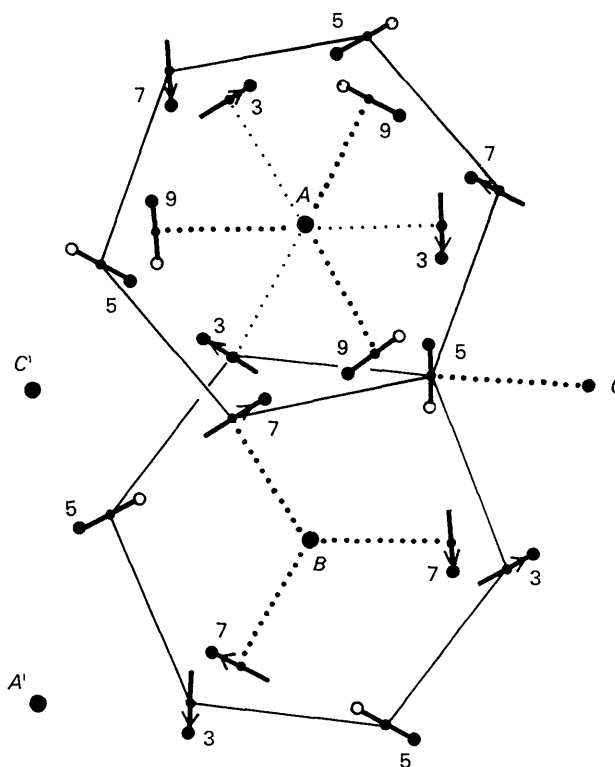


Fig. 4. Projection on (0001), showing effects due to rigid-body movements of  $\text{CO}_3$  group about triad axis. Conventions as in Fig. 1. Short heavy lines represent directions of thermal displacement; those carrying arrows show clockwise rotation of groups centred at *A.3* and *B.7*, while the others, belonging to groups centred at *A.9* and *C.5*, have solid dots for clockwise rotation and open circles for anti-clockwise. Octahedra of 'static' structure centred at *A.6* and *B.4* are outlined.

decreased horizontal components of Ca-O are associated with increased vertical components and *vice versa*. This means a change in the angle  $\varphi$ . Since the angle is non-ideal in the static structure, changes in it are permitted by rule (3).

Consider the atom at height 5, whose movement is represented in Fig. 5(a) by the line  $PQ$ . Its Ca neighbours are at  $A.6$  and  $B.4$ . To keep these distances equal whether the atom is at  $P$  or  $Q$ ,  $PQ$  must lie at right angles to the line joining  $A.6$  to  $B.4$ . The angle made by this with the plane of projection is  $\tan^{-1} \frac{c/6}{a/\sqrt{3}}$  which, for calcite, is about  $44^\circ$ , with  $A.6$  at the upper end. Hence the predicted angle between  $PQ$  and the triad axis is  $44^\circ$ , with the end  $Q$  uppermost. Similar arguments applied to the atom at height 3 with displacement  $RS$ , attached to calcium atoms at  $B.4$  and  $C.2$ , show that it should have the same slope, with  $R$  uppermost, *i.e.* the line lies between directions  $+c$  and  $-b$ , as observed. The observed angle (Chessin, Hamilton & Post, 1965) is quoted as  $48^\circ \pm 2^\circ$ .

The two  $\text{CO}_3$  groups thus have rotational movements of the same sense but vertical movements of opposite senses. If we are right in assuming rigid-body movement, the carbon atoms will move vertically along the triad axis in phase with their oxygen atoms. There is no experimental evidence available about the thermal

movements of the carbon atoms. It has been suggested (Cherin, Hamilton & Post, 1967) that the oxygen atoms will ride on the carbon atoms. As far as this mode is concerned, it should rather be pictured as the carbon atom riding on the oxygen atoms.

We have thus found a mode in which concerted movements of all the oxygen atoms, fixed in direction and in relative phase, can give an instantaneous structure at either extremity of the oscillation which satisfies the empirical rules, and have shown that the direction of displacement in this mode coincides with the experimentally observed direction of the longest principal axis of the thermal ellipsoid.

### Description of the mode

All atoms in the structure are involved in concerted movements. Alternate corner-linked octahedra are elongated or compressed along their triad axes, without change of Ca-O bond length;\* thus their projections on (0001) alternately shrink and swell (Fig. 6)

\* Actually the Ca-O bond length in the 'static' position must be very slightly shorter than at either extremity of the oscillation, but the difference is small compared with the other effects we are considering. The same is true even if we make  $QR$  an arc centred on the carbon atom, as strictly we should.

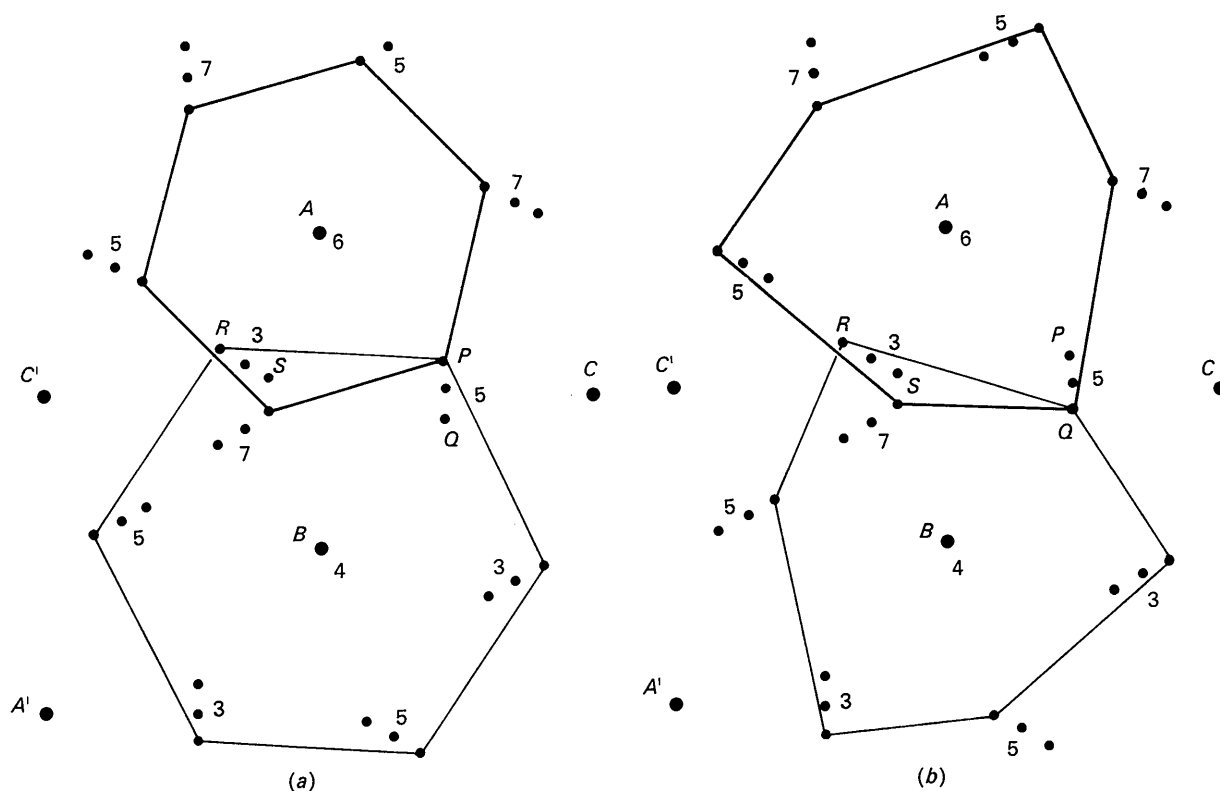


Fig. 5. Same octahedra as in Fig. 4, showing distortions due to (a) clockwise, (b) anti-clockwise rotation of  $\text{CO}_3$  group centred at  $C.5$ .

while remaining regular hexagons. In consequence, octahedra are rotated about their triad axes by an angle  $\psi$ , proportional to  $\Delta\phi$  (see Appendix), all with the same sense of rotation at the same extremity of the oscillation.

Three-dimensionally, the oxygen atoms move in a line inclined at about  $45^\circ$  to the (0001) plane, and perpendicular to the C–O bond.

By this movement, the triangle of oxygen atoms surrounding any particular carbon atom retains its shape and size, but suffers a screw-like displacement – rotation about the triad axis geared to translation along the axis. The simplest assumption about the carbon atom is that it remains rigidly at the centre of its oxygen triangle.

It is important to distinguish between the rotation  $\psi$  involved in the oscillation and the azimuthal tilt  $\omega$  of the static structure. Though both are about the same axis,  $\psi$  is a consequence of distortion of the octahedron, while  $\omega$  represents a rigid-body movement;  $\psi$  has the same sense for all octahedra, while  $\omega$  has opposite senses for alternate octahedra;  $\psi$  results in rotation of the  $\text{CO}_3$  group without change of size, while  $\omega$  results in shrinkage of the triangle without rotation. This is illustrated in Fig. 6. The horizontal component of the thermal displacement,  $PQ$ , is at right angles to the displacement of the static oxygen position (midpoint of  $PQ$ ) from the ideal close-packed position  $O$ , and the two are independent in magnitude. The angle  $\omega$ , and the parameter  $\xi$  to which it is proportional, have fixed values and a fixed sign for a given structure at a given temperature. On the other hand, the angle corresponding to thermal motion oscillates between positive and negative values, through zero, and we take  $\psi$  as its extreme magnitude in either sense.

It is implicit in our assumptions that the mode is an optic and not an acoustic one, because all lattice repeats are taken to be identical in phase. Again, in applying rule (3) we have necessarily retained point-symmetry  $\bar{3}$ . On the other hand, the glide-plane symmetry of the space group  $R\bar{3}c$  has been lost. The space group of the instantaneous structure at either extremity of the oscillation is thus  $R\bar{3}$ .

### Discussion

It is clear from the above derivation that the reason for the existence of this mode lies in the relative softness of the Ca octahedron against deformations along its triad axis which do not change the Ca–O bond length. The movement comprising cooperative flattening and steepening of alternate octahedra leaves unaltered the overall lattice parameters  $a$  and  $c$  and the azimuthal tilt parameter  $\xi$  (except for second-order small changes ignored in this discussion). It requires no internal distortions of the  $\text{CO}_3$  group, which can thus remain rigid, provided its rotation is geared to translation.

A comparable example of screw-like motion of a tightly bound group has been found in sodium alum (Cromer, Kay & Larson, 1967) for three oxygen atoms of the  $\text{SO}_4$  group. Here the major axes of the thermal ellipsoid of oxygen atoms not lying on the triad axis, while lying (as one would expect) nearly normal to the S–O bond, are also inclined at about  $65^\circ$  to the triad axis. Cromer, Kay & Larson showed that rotation without translation would bring about too large a change in the length of the other bonds to the oxygen atom (in this case hydrogen bonds for which the oxygen is acceptor), while if rotation is geared to translation the bond lengths can be kept nearly constant. Arguments as to the effect on the structure as a whole of such rigid-body movements of the  $\text{O}_3$  triangle are harder to develop: there are more independently-variable structural requirements than in calcite, there is the possibility of distortion of the  $\text{SO}_4$  group by compression along the triad axis, and it would be hard to assess the effect of changes in the O–H  $\cdots$  O angle, which is likely to be very ‘soft’.

For calcite, the evidence is incomplete, since the published data do not include information about the carbon atom. If its mean square displacements along and perpendicular to the triad axis were approximately

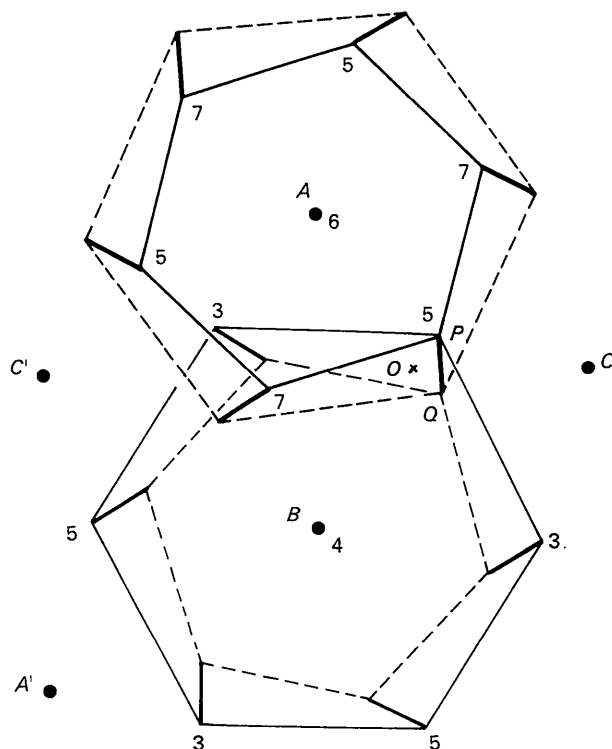


Fig. 6. Same part of structure as in Fig. 5(a). Octahedra at one extremity of oscillation shown by full thin lines, at other by dashed lines. Heavy short lines are projections of oxygen movements. Point  $O$  marks ideal close-packed position corresponding to  $PQ$ .

equal to those of the components of the oxygen atom in the same directions, it would confirm the view that the mode described here is the most important. There is some evidence in support of it from the isomorphous sodium nitrate. Cherin, Hamilton & Post (1967), assuming that the oxygen is 'riding' on the nitrogen but that the latter is moving isotropically with a mean-square displacement equal to that of oxygen in the direction along the H–O bond, have calculated corrections to the bond length, and obtain corrected lengths ranging from 1.259 to 1.266 Å between room temperature and 150°C, 1.311 Å at 200°C. With our model, the corrected lengths range from 1.247 to 1.254 Å up to 150°C, and the value at 200°C is 1.263 Å. This seems a more plausible result. The mean square displacement at 200°C is however so large that one cannot put too much weight on conclusions drawn from it by arguments involving the kind of approximations we have been making.

Nothing in these arguments precludes the possibility that other modes exist – including, perhaps, one in which the CO<sub>3</sub> group is a flat trigonal pyramid with its apex alternately above and below its base. What they *do* indicate is that this particular mode can by itself explain the most important observed features of the thermal vibration.

It is interesting to compare the mode that we have found in calcite with what we should expect for the related structures LaAlO<sub>3</sub> (de Rango, Tsoucaris & Zelwer, 1966) and LiNbO<sub>3</sub> (high-temperature form) (Abrahams, Levinstein & Reddy, 1966; *cf.* Megaw, 1968*a*). These have the same space group  $R\bar{3}c$  and are both based on a corner-linked octahedral framework, but are distinguished geometrically from CaCO<sub>3</sub> by their positive value of  $\xi$  [see Fig. 3(*a*)] and physically by the different character of their cations. In LaAlO<sub>3</sub> and LiNbO<sub>3</sub> the octahedra contain small highly-charged cations, and the oxygen atoms forming the edges are in such close contact that covalent repulsive forces are large. Such octahedra are likely to exhibit hardness against any change of shape, and experimentally it is found that in most structures they depart little from regularity (see Megaw, 1968*b*). This is in contrast to the very considerable variety of shapes found for Ca octahedra [for example in  $\gamma$ -Ca<sub>2</sub>SiO<sub>4</sub> (Smith, Majumdar & Ordway, 1965)] where the central atom is so large that, for a regular shape, the corner oxygen atoms are not in contact with each other, and distortion is therefore very easy. On the other hand, in LaAlO<sub>3</sub> and LiNbO<sub>3</sub> the bond to the non-octahedral cation is weak, both in its length and its angular relationship – in contrast to the C–O bond in calcite. It is this bond which effectively controls the azimuthal tilt angle. (Some part may be played by the stiffness of the bond angle Al–O–Al or Nb–O–Nb, but it is small enough to ignore for our present purposes.) Hence in these structures we expect a mode in which the octahedra behave as rigid units but the oscillations involve changes of the azimuthal tilt angle.

### Thermal expansion

Qualitatively, one can see the effect of the predicted mode in calcite on the thermal expansion. Large thermal expansions are not to be associated directly with directions of large thermal amplitudes, but with directions of forces in respect of which, locally, the structure is weak. In calcite, the weakness is that of the Ca–O octahedron along its triad axis, all other movements being, in a sense, driven by this one. The force tending to produce distortion is, as we saw, electrostatic, and independent of temperature; the shape-maintaining forces decrease as the thermal amplitudes increase. Hence we expect decrease of  $\varphi$  with increasing temperature; the octahedron, already steeper than the ideal, becomes more so.

With our usual assumptions about constant bond lengths, we find the following geometrical relations:

$$\Delta a/a = 0.5\Delta\varphi, \quad \Delta c/c = -1.4\Delta\varphi.$$

The corresponding contributions to the thermal expansion are

$$e_a = 0.5d\varphi/dt, \quad e_c = -1.4d\varphi/dt; \quad e_c/e_a = -2.8.$$

But we expect  $d\varphi/dt$  to be negative. Hence, if this effect were the whole source of thermal expansion, we should have a negative expansion in the (0001) plane and a positive expansion nearly 3 times as large at right angles to it.

Experimental values found by Chessin, Hamilton & Post (1965) are  $\alpha_a = -3 \times 10^{-6} \text{ deg}^{-1}$ ,  $\alpha_c = 25 \times 10^{-6} \text{ deg}^{-1}$ . The signs agree with expectation, but the ratio  $\alpha_c/\alpha_a$  is larger than expected if the change of octahedron shape is the only effect. It is, however reasonable to suppose that there will also be a small increase of bond length, which we may take as making an isotropic contribution. Suppose its magnitude is  $x \times 10^{-6}$ . Then the ratio  $e_c/e_a$ , derived from experimental data, will be  $\frac{25-x}{-3-x}$ ; equating this to the geometrical value,  $-2.8$ , we find  $x=4$ . An expansion coefficient of  $4 \times 10^{-6}$  is smaller than that of CaO, larger than that of diamond, and may be regarded as very reasonable for bond-length effects in calcite. The corresponding value of  $d\varphi/dt$  is  $-14 \times 10^{-6} \text{ rad deg}^{-1}$ , which implies a decrease of  $5'$  in  $\varphi$  for a temperature increase of 100°C.

It is interesting to compare the expansion coefficients for sodium nitrate with those for calcite. They are very much larger,  $9 \times 10^{-6}$  and  $114 \times 10^{-6} \text{ deg}^{-1}$  respectively (Cherin, Hamilton & Post, 1967), giving  $x=35$  and  $d\varphi/dt = -52 \times 10^{-6} \text{ rad deg}^{-1}$ . These values are so large that it is not safe to assume the validity of the approximations which were acceptable for calcite; nevertheless it seems fairly clear that other modes than the one we have been examining are becoming of comparable importance.

Turning to the perovskite structures, we see that in LaAlO<sub>3</sub> the weakness is in the Al–O–Al angle (or in

the La-O bonds which serve as struts to maintain the angle). Here the effect of increasing importance of electrostatic cation-cation repulsions relative to nearest-neighbour forces is a tendency to straighten out the Al-O-Al line. This implies an increase of  $\zeta$  with increasing temperature, until it reaches its ideal value of  $\frac{1}{3}$  (the straight-line value). But straightening contributes only to the coefficient  $\alpha_a$ , not to  $\alpha_c$ . The observed values (calculated from data of Geller & Bala, 1956) are about  $13 \times 10^{-6}$  and  $7 \times 10^{-6} \text{ deg}^{-1}$  respectively (between room temperature and  $250^\circ\text{C}$ ). We may attribute  $7 \times 10^{-6} \text{ deg}^{-1}$  to a bond-length expansion, leaving  $6 \times 10^{-6} \text{ deg}^{-1}$  to be accounted for by change of azimuthal tilt angle.

### Conclusion

Both types of structure considered above thus illustrate the importance of recognizing the occurrence of 'soft' bond angles in the static structure. This is a preliminary to the identification of important lattice modes. It also allows an analysis of the thermal expansion, associating part of it with such modes, accounting for the anisotropy and leaving only a smaller roughly isotropic part to be attributed to bond-length expansion.

### APPENDIX

#### Geometrical relations

In Fig. 7, let  $A$  be the projection of Ca,  $C$  that of carbon,  $O$  the position of the oxygen atom for ideal close packing,  $M$  its position in the static structure,  $P$  the projection of the extreme position during an oscillation. Three-dimensionally, the positions corresponding to  $C$ ,  $M$ , and  $O$  lie in the same plane,  $A$  at a height  $c/12$  above it, and  $P$  at a height  $u_v$  below it. We have also

$$AO = \frac{1}{3}a$$

$$OM = -\zeta a \text{ (definition of } \zeta)$$

$$MP = u_h \text{ (definition of } u_h).$$

Let  $\angle OAM = \omega$ ,  $\angle MAP = \psi$ .

Let the C-O and Ca-O bond lengths be  $l_1$  and  $l_2$  respectively; let the angle between Ca-O and the triad axis be  $\varphi$  (with subscripts, where necessary, specifying the projected position of the oxygen atom).

Since  $\varphi$  is close to its ideal value,  $\cos^{-1} 1/\sqrt{3}$ , for numerical evaluation of coefficients of first-order small quantities (such as terms in  $\zeta a$ ,  $u_h$ , or  $u_v$ ) we may write

$$\sin \varphi = \sqrt{\frac{2}{3}}, \quad \cos \varphi = \sqrt{\frac{1}{3}}, \quad \tan \varphi = \sqrt{2}.$$

(i) For the static structure,

$$\begin{aligned} AM &= l_2 \sin \varphi_M = (AO^2 + 2AO \cdot OM \cos 60^\circ + OM^2)^{1/2} \\ &= \frac{a}{3} (1 - 3\zeta + 9\zeta^2)^{1/2}, \end{aligned} \quad (1)$$

$$l_2 \cos \varphi_M = \frac{c}{12}. \quad (2)$$

Hence

$$\tan \varphi_M = \frac{4a}{c} (1 - 3\zeta + 9\zeta^2)^{1/2} \quad (3)$$

and

$$l_2 = \left[ \left( \frac{a}{3} \right)^2 (1 - 3\zeta + 9\zeta^2) + \left( \frac{c}{12} \right)^2 \right]^{1/2}. \quad (4)$$

Moreover,

$$l_1 = a(\frac{1}{3} + \zeta). \quad (5)$$

Equations (3), (4), (5), give the 'physical' parameters  $l_1$ ,  $l_2$ ,  $\varphi$  in terms of the geometrical parameters  $a$ ,  $c$ ,  $\zeta$ .

(ii) From (1) and (5),

$$(l_2 \sin \varphi_M)^2 - l_1^2 = -\zeta a^2.$$

Substituting, from (5),

$$-\zeta a = \frac{1}{3}a - l_1,$$

we get

$$(l_2 \sin \varphi_M)^2 - l_1^2 = \frac{1}{3}a^2 - a l_1. \quad (6)$$

This is a quadratic in  $a$ , giving

$$a = \frac{3}{2}l_1 \left[ 1 + \left\{ \frac{(2l_2 \sin \varphi_M / l_1)^2 - 1}{3} \right\}^{1/2} \right]. \quad (7)$$

(Here the + sign for the square root has been chosen because  $a$  must be positive.) Writing

$$\frac{(2l_2 \sin \varphi_M / l_1)^2 - 1}{3} = g^2 \quad (8)$$

we have

$$a = \frac{3}{2}l_1(1 + g). \quad (9)$$

Substitution in (5) gives

$$-\zeta = \frac{1}{3} \frac{g-1}{g+1}. \quad (10)$$

Moreover

$$c = 12l_2 \cos \varphi_M. \quad (11)$$

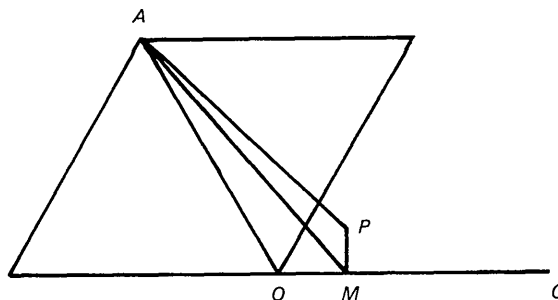


Fig. 7. Projection on (0001), to show relation between interatomic distances, displacement of oxygen from ideal position, and thermal amplitude.



Equations (8), (9), (10), (11) give the geometrical (directly observable) parameters  $a$ ,  $c$ ,  $\xi$ , in terms of the 'physical' parameters  $l_1$ ,  $l_2$ ,  $\varphi$ .

(iii) Further,

$$\omega = \angle OAM = \frac{OM \sin 60^\circ}{AO} = -\frac{3\sqrt{3}}{2} \xi = -2.6\xi \quad (12)$$

This relates the azimuthal tilt angle to the atomic position parameter.

(iv) To find the variation of  $\varphi$  with  $\xi$  or  $\omega$ , we eliminate  $a$  by using (1) and (5), and obtain

$$\left(\frac{l_2}{l_1}\right)^2 \sin^2 \varphi = 1 - \frac{9\xi}{(1+3\xi)^2}. \quad (13)$$

Differentiation with  $l_1/l_2$  constant gives

$$\frac{d\varphi_M}{d\xi} = -\frac{27}{2\sqrt{2}} \left(\frac{l_1}{l_2}\right)^2 \left(1 - \frac{6\xi}{1+3\xi}\right) (1+3\xi)^{-2}.$$

Substitution of observed values of  $l_1$ ,  $l_2$ ,  $\xi$ , gives, to a rough approximation,

$$\frac{d\varphi_M}{d\xi} = -8 \quad (14)$$

or, using (12),

$$\frac{d\varphi_M}{d\omega} = 3. \quad (15)$$

(v) To find the variation of  $a$  and  $c$  with  $\varphi$ , assuming  $l_1$ ,  $l_2$  constant, we use (7) and (11):

$$\frac{da}{d\varphi} = \frac{4}{3} \left(\frac{l_2}{l_1}\right)^2 \frac{\sin \varphi_M \cos \varphi_M}{g(1+g)} d\varphi \quad (16)$$

and

$$g = 1.63.$$

Hence

$$\frac{da}{a} = 0.5d\varphi. \quad (17)$$

Also

$$\begin{aligned} \frac{dc}{c} &= -\frac{\sin \varphi_M}{\cos \varphi_M} d\varphi \\ &= -1.4d\varphi. \end{aligned} \quad (18)$$

Hence decrease of  $\varphi$ , *i.e.* a steepening of the octahedron, produces an increase in  $c$  and a decrease in  $a$  (comparable to a Poisson contraction, though with a different physical origin) in the ratio

$$\frac{dc}{c} / \frac{da}{a} = -2.8. \quad (19)$$

(vi) In the vibrating structure, we are interested in the inclination of the vibration direction to the horizontal plane, *i.e.* in  $\tan^{-1}u_v/u_h$ . At the centre of the oscillation we have

$$l_2^2 = AM^2 + \left(\frac{c}{12}\right)^2$$

and at the extremity

$$l_2^2 = AP^2 + \left(\frac{c}{12} + u_v\right)^2.$$

By our hypothesis, these two values must be equal. But

$$AP^2 = AM^2 - 2AM \cdot MP \sin\left(\frac{\pi}{6} - \omega\right) + MP^2 \quad (20)$$

where  $MP = u_h$ . Hence

$$2AM \sin\left(\frac{\pi}{6} - \omega\right) \cdot u_h - u_h^2 = 2 \frac{c}{12} u_v + u_v^2.$$

Neglecting terms in  $u_h^2$  and  $u_v^2$ , and using (11),

$$\sqrt{3}l_2 \sin \varphi_M \left(1 - \frac{\omega}{\sqrt{3}}\right) u_h = 2l_2 \cos \varphi_M u_v$$

or

$$\begin{aligned} \frac{u_v}{u_h} &= \frac{\sqrt{3}}{2} \tan \varphi_M \left(1 - \frac{\omega}{\sqrt{3}}\right) \\ &= \frac{\sqrt{3}}{2} \left(1 + \frac{3}{2} \xi\right) = 1.09 = \tan 47\frac{1}{2}^\circ \end{aligned} \quad (21)$$

(vii) Let the rotation of the carbonate group be  $\mu$ , *i.e.*

$$\mu = \angle MCP = u_h/l_1. \quad (22)$$

We can relate this to the rotation of the octahedron  $\psi$ , which is  $\angle MAP$ ,

$$\begin{aligned} \psi &= \frac{MP \cos\left(\frac{\pi}{6} - \omega\right)}{AM} = \frac{u_h \cos\left(\frac{\pi}{6} - \omega\right)}{l_2 \sin \varphi} \\ &= \sqrt{\frac{3}{8}} (1 + \sqrt{3}\omega) \frac{l_1}{l_2} \mu. \end{aligned}$$

Using (12) and evaluating,

$$\frac{\psi}{\mu} = \sqrt{\frac{3}{8}} (1 + 0.34) \frac{1}{1.83} = 0.45. \quad (23)$$

(viii) We can also relate to  $\mu$  the change in  $\varphi$  due to the vibration.

$$(l_2 \sin \varphi_P)^2 = AP^2 = (l_2 \sin \varphi_M)^2$$

$$-2u_h l_2 \sin \varphi_M \sin\left(\frac{\pi}{6} - \omega\right)$$

and

$$\begin{aligned} (l_2 \cos \varphi_P)^2 &= \left(\frac{c}{12} + u_v\right)^2 \\ &\simeq \left(\frac{c}{12} + u_h\right)^2 \quad \text{from (21)}. \end{aligned}$$

Hence

$$\begin{aligned} (\tan \varphi_P)^2 &= \left(\frac{12l_2}{c} \sin \varphi_M\right)^2 \left[1 - \frac{u_h}{l_2} \left(\frac{\sqrt{3}-\omega}{\sin \varphi_M} + \frac{2}{\cos \varphi_M}\right)\right]. \end{aligned} \quad (24)$$

Differentiating with respect to  $u_h$ , keeping everything else constant,

$$\begin{aligned} \Delta\varphi_P &= -\frac{\cos\varphi \sin\varphi}{2} \left( \frac{\sqrt{3-\omega}}{\sin\varphi} + \frac{2}{\cos\varphi} \right) \frac{u_h}{l_2} \\ &= -1.3 \frac{u_h}{l_2} = -0.7. \end{aligned} \quad (25)$$

Hence, from (23),

$$\psi = 0.65 |\Delta\varphi_P|. \quad (26)$$

This may be compared with the relation between the static azimuthal tilt  $\omega$  and  $\Delta\varphi_M$ , from (15)

$$\Delta\omega = 0.33 \Delta\varphi_M. \quad (27)$$

We thus find that the static deformation of  $\varphi$  produced by a given azimuthal tilt is about twice the instantaneous deformation produced by an oscillation amplitude of the same magnitude.

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## Désordre Linéaire dans les Cristaux (cas du Silicium, du Quartz, et des Pérovskites Ferroélectriques)

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Many crystals produce a diffuse scattering of X-rays which is localized in a series of replanes. It is shown that the corresponding linear disorder in the crystal may have various origins. In silicon, scattering is due to thermal vibrations and is well explained by the elastic properties of the crystal. In neutron irradiated quartz the radiation damage is responsible for the major part of the scattering. The case of BaTiO<sub>3</sub> and KNbO<sub>3</sub> is discussed in detail. A linear disorder is proposed which accounts better for the different distributions of the scattering in the 4 allotropic phases than the alternative explanation of the soft mode. In spite of some neutron inelastic scattering results it is not yet possible to distinguish between static and dynamic disorder.

### Le désordre linéaire

Quand un cristal produit une diffusion cohérente de rayons X en dehors des directions de diffraction, celle-ci est nécessairement due à un défaut de périodicité du cristal. Si le désordre est très irrégulier, le rayonnement diffusé est réparti assez uniformément dans toutes les directions de l'espace et, en conséquence, cette diffusion est faible partout, donc difficile à détecter et à caractériser: en fait, elle a grande chance de rester inaperçue à moins que l'expérimentateur ait eu une raison spéciale de la rechercher. Par contre, si la diffusion est concentrée en d'étroites régions du diagramme, elle devient observable. Il n'est donc pas étonnant que ce soient de

tels cas qui aient été signalés. C'est l'un de ces cas, qui a fait l'objet de nombreuses publications depuis plusieurs années et présente un intérêt assez général, que nous allons étudier ici.

Remarquons que le diagramme photographique est presque indispensable pour l'observation globale de la répartition de diffusions dont on ne connaît pas, *a priori*, la nature, Or, les générateurs de rayons X monochromatisés équipés de chambres photographiques sont rares, tandis que tout appareil de diffraction électronique permet d'observer de telles diffusions. Aussi est-il naturel que les phénomènes dont nous allons parler aient été mis en évidence avec les électrons plutôt qu'avec les rayons X. D'autre part les rayons X exigent un échantillon sous forme de cristal unique de dimensions bien plus considérables que les électrons,

### References

- ABRAHAM, S. C., LEVINSTEIN, H. J. & REDDY, J. M. (1966). *J. Phys. Chem. Solids*, **27**, 1019.  
 CHERIN, P., HAMILTON, W. C. & POST, B. (1967). *Acta Cryst.* **23**, 455.  
 CHESSIN, H., HAMILTON, W. C. & POST, B. (1965). *Acta Cryst.* **18**, 689.  
 CROMER, D. T., KAY, M. I. & LARSON, A. C. (1967). *Acta Cryst.* **22**, 182.  
 GELLER, S. & BALA, V. B. (1956). *Acta Cryst.* **9**, 1019.  
 HEPWORTH, M. A., JACK, K. H., PEACOCK, R. D. & WESTLAND, G. J. (1957). *Acta Cryst.* **10**, 63.  
 JACK, K. H. & GUTMAN, V. (1951). *Acta Cryst.* **4**, 246.  
 MEGAW, H. D. (1968a). *Acta Cryst.* A**24**, 583.  
 MEGAW, H. D. (1968b). *Acta Cryst.* A**24**, 589.  
 RANGO, C. DE, TSOUCARIS, G. & ZELWER, G. (1966). *Acta Cryst.* **20**, 590.  
 SASS, R. L., VIDALE, R. & DONOHUE, J. (1957). *Acta Cryst.* **10**, 567.  
 SMITH, D. K., MAJUMDAR, A. & ORDWAY, F. (1965). *Acta Cryst.* **18**, 787.

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