

a case will be defined as *partial enhancement*. The reflections displaying the higher symmetry are distributed in the pattern after a certain symmetry and are usually those in which one or more than one index is a multiple of an integer. For example, in the case of triclinic wollastonite, the *hkl* reflection, when *k* is even (a multiple of 2), is equal in intensity to, and located symmetrical against the *h0l* plane with, the  $(h+k)/2, \bar{k}, l$  reflection (Ito, 1950).

Introductory remarks on partial enhancement have been published (Sadanaga, 1959, 1963) and the detailed theory will be treated shortly elsewhere.

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## A Simple Theory of the Off-Centre Displacement of Cations in Octahedral Environments

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Off-centre displacement occurs when the effective size of a cation B is such that the unstressed B–O bond length is less than  $1/\sqrt{2}$  times the oxygen ‘diameter’. Assuming that all interatomic forces are central, there is then, for a symmetrically placed cation, a tension in the O–B–O diameters and a compression in the O–O edges of the octahedron. Elementary Born-theory treatment shows that for an isolated octahedron the tension will be relaxed by off-centre displacement of B. The relaxation will be shared with the O–O edges, which are therefore elongated. Relaxation can affect one, two, or three O–B–O diameters simultaneously, with different consequences for the edge lengths. The character and magnitude of the relaxation are independent of the symmetry and the structure, depending only on the B displacement. Predictions have been verified by experimental evidence from the structures and lattice parameters of KNbO<sub>3</sub> and NaNbO<sub>3</sub>. Quantitatively, the off-centring must be strongly influenced by polarization (involving non-central forces), which is also the means whereby effects within octahedra are communicated to their neighbours. Qualitatively, however, when the displacements are fairly small (as is true for Nb) the present description in terms of bond stresses is useful and allows predictions to be made. A further paper on thermal expansion is planned.

Interest in the off-centre displacements of ‘cations’ in octahedra has been stimulated by their important role in ferroelectrics of the perovskite type. That the cause of the displacement is not specific to ferroelectrics, but is more generally rooted in crystal chemistry, is now recognized. It has been discussed by Orgel (1958), who showed that it depended on the effective radius (not the conventional ionic radius) of the cation B relative to that of oxygen. The present note derives the same conclusion in a slightly different way, which allows predictions to be made about the character of the octahedral distortion in relation to the type and magnitude of the off-centre displacement.

The Born theory, in its simplest form, assumes that the equilibrium distance between two atoms depends only on the potential energies of their mutual attractive

and repulsive forces, and that the equilibrium distance is that for which the force on either atom is zero, *i.e.* the bond is unstressed. In crystal structures (as distinct from diatomic molecules) this cannot be true. Consider the octahedron as an isolated unit (a reasonable next approximation). There are repulsions in each of the O–O edges, and these produce tensions in each of the diametral O–B–O links (Fig. 1). Hence, even for a central B atom, the B–O bonds are elongated beyond their ‘unstressed’ length (a length which cannot be derived directly from measured interatomic distances, since all of these represent more or less stressed conditions, but which is a useful concept in discussion).

The O–O repulsions are partly electrostatic, partly of covalent origin. The ionic part varies slowly with O–O distance, but is always relatively weak. The co-

valent part increases very rapidly with decreasing distance over a narrow range of O-O values. At the lower end of this range, differences of length are so small as to be negligible for our purposes, and we may take the length as the effective oxygen diameter,  $\sigma$ . (Since the repulsion potential associated with an oxygen atom is dependent to some extent on its other neighbours – its electron cloud not remaining spherical – this ‘diameter’ may vary slightly from one compound to another; but we are concerned only with changes within a single compound, so that any changes in the form of the potential will be negligible in their effect). Edge lengths shorter than the oxygen diameter will not occur; edge lengths which are considerably greater correspond to very weak repulsive forces. It is edge lengths close to the value of the oxygen diameter which are of particular interest.

Thus, if the unstressed B-O length  $b$  is greater than  $\sigma/\sqrt{2}$ , repulsions in O-O and tensions in O-B-O are small. But if  $b$  is appreciably less than  $\sigma/\sqrt{2}$ , the O-O edge length is equal to  $\sigma$ , and B-O is greater than  $b$ ; hence large tensions are applied to O-B-O, which in turn cause large compressive stresses in O-O. If  $b$  is very much less than  $\sigma/\sqrt{2}$ , the octahedral configuration will be unstable and will not occur. We are concerned with the intermediate range where  $b$  is slightly less than  $\sigma/\sqrt{2}$ .

Consider first the variation of force with distance in an individual bond. Assuming the anion fixed, let  $F$  be the force which must be applied to the cation to increase the bond length by  $\Delta r$  from its unstressed value  $r_0$ . The Born potential between the atoms may be written

$$U = -Af_1(r) + Bf_2(r)$$

where  $f_1$  and  $f_2$  are functions of  $r$  whose exact form we do not need to know, provided that

- (i) both  $f_1$  and  $f_2$  decrease smoothly as  $r$  increases
- (ii)  $f_2$  depends on higher powers of  $r$  (over the range which interests us) than does  $f_1$ .

In the most familiar approximation,  $f_1$  and  $f_2$  are taken as  $r^{-m}$  and  $r^{-n}$  respectively, with  $n > m$ . We need make no assumption about the nature of the attractive force, whether it is ionic or partly covalent, except that it, like the repulsive force, is effectively central. This condition will need reconsideration below.

We are concerned with the force  $F = dU/dr$ , its slope  $dF/dr$ , and the rate of change of slope  $d^2F/dr^2$ . In the interesting range of  $r$ , the terms in  $A$  and  $B$  must be of comparable magnitude. For  $F$  at the point  $r = r_0$  the terms are equal, and  $U_0$  is a minimum because  $n > m$ . At each differentiation both terms change sign, and the  $B$  term increases relative to the  $A$  term by a factor of order of magnitude  $n/m$ . Thus for small values of  $r$  each of the quantities  $F$ ,  $dF/dr$ , and  $d^2F/dr^2$ , is of the same sign as its  $B$  term,  $-$ ,  $+$ ,  $-$ , respectively, and each changes sign at a successively greater value of  $r$ . For  $r > r_0$ ,  $F$  is positive, while  $dF/dr$  at first remains positive and  $d^2F/dr^2$  negative. This gives the shape of

curve shown in Fig. 2. As  $r$  increases, a maximum  $M$  is reached at which the slope  $dF/dr$  changes sign, but  $d^2F/dr^2$  is still negative. Hence the shape of the maximum is unsymmetrical and the negative slope at  $r = r_M + \delta r$  is less than the positive slope at  $r = r_M - \delta r$ . This general result holds good even if  $f_1(r)$  and  $f_2(r)$  are not simple inverse power functions. The detailed shape of the curve would then be different, but its qualitative features would be unchanged, and these are all that we shall need for our discussion.

The curve in Fig. 2 represents the value of an external force  $F$  needed to maintain an extension  $\Delta r$  against the tension in the bond. The equilibrium at any particular value of  $F$  is stable if changes in  $F$  produce displacements in the same direction, i.e. if  $dF/dr$  is positive.

We now consider an atom R (Fig. 3) acted on by two like bonds, PR and QR, in the same straight line, the atoms P and Q being fixed so that  $PQ = d > 2r_0$ .

Consider the two bonds separately. A force  $F_1$  acts on the atom R to produce an extension in the first bond, a force  $F_2$  to produce an extension in the second [Fig. 3(b)]. Plotting each against  $r$ , from origins at  $r_0$  and  $d - r_0$  respectively, we have the results shown in Fig. 4(a) and (b) for two different values of  $d - 2r_0$ . The net force acting on the atom is  $F_1 - F_2$ , and for equilibrium this must be zero. Thus the possible positions of the atom are at the symmetrical position A in either case illustrated, or at the off-centre positions B or C in Fig. 4(b).

Which of these positions is stable? The condition is that  $d(F_1 - F_2)/dr$  must be positive. Now in case (a),

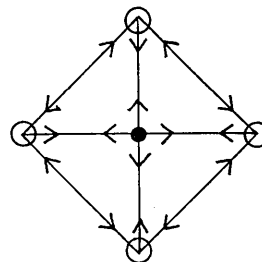


Fig. 1. Section of octahedron, with central B cation and oxygen atoms at corners. Arrows show directions of forces on atoms.

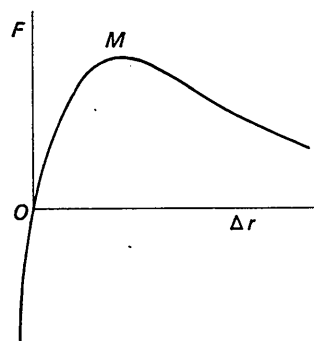


Fig. 2. Variation of force with distance for a pair of atoms, calculated for  $U = -A/r^2 + B/r^9$ ; origin is at  $r_0$ , the equilibrium distance for an unstressed bond.

at *A*,  $dF_1/dr$  is positive and  $dF_2/dr$  is negative; hence equilibrium is stable. In case (*b*), at *A*, the signs are reversed; equilibrium is unstable. But at *B*, where both  $dF_1/dr$  and  $dF_2/dr$  are positive, the former is greater; and at *C*, where both are negative, the magnitude of the latter is greater. Hence equilibrium is stable at both *B* and *C*.

It follows that the off-centring of the cation is a direct consequence of a Born-type interaction between cation and anion when the anion-anion repulsion has

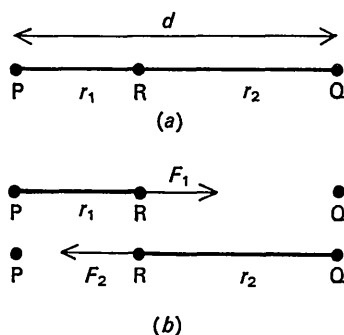


Fig. 3. Forces acting on atom R in a line between two atoms rigidly fixed at P and Q. (*a*) Off-centre position of R, showing long and short bonds. (*b*) External forces acting on bonds PR and QR, considered separately.

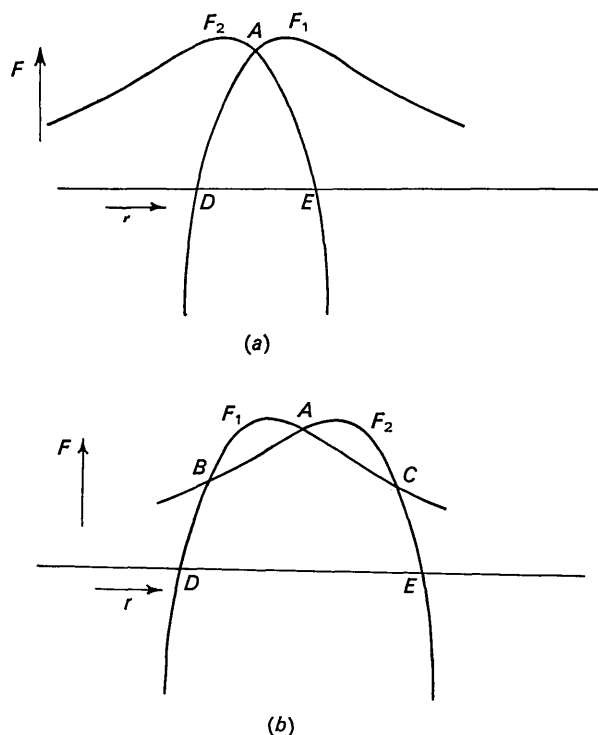


Fig. 4. Variation of forces acting on atom R with bond length. Distances  $r$  are measured from atom P. The curves for  $F_1$  and  $F_2$  are identical with each other and with that in Fig. 2, but that for  $F_2$  is drawn with  $r_2 = d - r_1$ , and the points *D* and *E*, corresponding to the origin in Fig. 2, are those for which  $r = r_0$ ,  $r = d - r_0$  respectively.

caused the cation-anion distance to be sufficiently extended beyond its unstressed value.

This, of course, is not the whole story. We have taken  $f_1$  and  $f_2$  as corresponding to central forces, and have also assumed that the tensions applied to the B-O bonds as a result of other interatomic forces are independent of changes in the individual B-O bond lengths. It can be seen qualitatively that neither of these assumptions is true. A closer approach of B to O will change the shape of the electron cloud of O, thus creating differences in  $f_1$  and  $f_2$  for the long and the short B-O bonds. Moreover, such a change in electron distribution could conceivably affect the repulsive forces in the O-O edges, and therefore change the effective applied tension in O-B-O. Quantitatively, both these effects would need to be considered. Qualitatively, it is clear that both must act to enhance the stability of the off-centring once it has set in. In particular, the change of polarization of O resulting from the displacement of B controls the relationship between the sense of the displacements in successive octahedra; but for effects concerning a single octahedron, the treatment in terms of stresses will be qualitatively correct.

The use of the word 'rattling' by Orgel in connexion with this off-centre displacement is unfortunate. As originally used to describe the situation of a too-small central cation in a coordination polyhedron, the metaphor clearly implied an indeterminacy of position which would correspond to a large apparent amplitude of vibration. What we have here is quite different: the cation is very exactly located, and held by rather strong forces. The Goldschmidt 'no-rattling' rule still holds, in the sense that a too-small cation cannot occupy a central or off-centre position at random, but instead finds a specific but unsymmetrical solution in which what happens inside the octahedron is communicated through changes of polarization of the oxygens to adjacent octahedra and other cations.

Orgel has considered displacements ranging from those of  $Ti^{4+}$ , which are intrinsically small (and perhaps only made possible by stresses acting on the octahedron from outside), to those of  $V^{5+}$ , which are characteristically so large that the octahedral environment is often hard to recognize. In this paper we shall consider only the moderately small displacements found for  $Nb^{5+}$ , where the effects of polarization are not so large as to make it unreasonable to treat the problem in terms of first-order deviations from an ideal structure with regular octahedra. (In writing  $Nb^{5+}$  we refer merely to the conventional valency, and do not imply that the atom is actually fully ionized).

We now accept that, qualitatively, a tension above a certain critical value in the O-Nb-O tie brings about an off-centre displacement of Nb, and thereby a relief of tension compared with what it would have been if the central position were kept. But the relief is not confined to O-Nb-O; it is shared with the O-O edges joining opposite ends of the relaxed O-Nb-O diameter in such a way that the stress energy as a whole is mini-

mized. These edges will therefore be *lengthened* compared with the unrelaxed edges.

The existence of such a *relaxation extension* – a difference between the average lengths of relaxed and unrelaxed edges – is a prediction of the theory. Its absolute magnitude cannot be predicted at present; what *can* be predicted is that its character and relative magnitude will be determined by the Nb displacement, and will (to a first approximation at least) be independent of the symmetry of the structure or the other cations present.

So far, we have considered displacement of Nb along one diameter of its octahedron, which leaves the tensions in the other two diameters practically unaltered. To relax the tensions in two diameters at once, the Nb displacement must approximately bisect the angle between them; to relax the tensions in all three at once, it must be approximately equally inclined to all three. Examples of all three types of displacement are known. We consider them in turn, to see what predictions can be made about the edge lengths for each type.

(i) *One corner-displacement.* The Nb atom is displaced towards one corner of the octahedron, say *C* in Fig. 5, relaxing the O–Nb–O tie along *CC'*. Consider the three square sections of the octahedron, *ABA'B'*, *ACA'C'*, *BCB'C'*. Only in the two with *CC'* as diagonal will the edges be relaxed; in the first-named, *ABA'B'*, they remain unrelaxed.

(ii) *Two-corner displacement.* The Nb atom is displaced in the plane of one of the squares, say *ABA'B'*, approximately towards the mid point of an edge *AB*. The ties *AA'*, *BB'*, are relaxed. The square *ABA'B'* in which both diagonals are relaxed will have a double relaxation effect in its edges, the others only a single effect. The four edges *AB*, *BA'*, *A'B'*, *B'A*, are therefore relaxed to the other eight edges. We may refer to them respectively as 'fully relaxed' and 'relatively unrelaxed' (abbreviated, where it cannot create confusion, to 'relaxed' and 'unrelaxed').

(iii) *Three-corner displacement.* The Nb atom is displaced in a general direction, typically, but not necessarily exactly, perpendicular to an octahedron face, say *ABC*. The three bonds Nb–*O<sub>A</sub>*, Nb–*O<sub>B</sub>*, Nb–*O<sub>C</sub>*, are shortened, and all three diametral ties are relaxed. Hence all edges are equally (and triply) relaxed.

It can be seen that the sequence three-corner, two-corner, one-corner, displacement corresponds to a decreasing sequence of O–Nb–O tensions.

If the only forces operative were those of the octahedron itself (the intrinsic effect) we should expect the Nb displacements, and therefore the relaxation extensions, to be independent of the structure in which the octahedron is incorporated (though perhaps dependent on the temperature); they should be constant for all structures at a given temperature. We know that other forces must generally exist; we assume that they (like the polarization) can enhance the magnitude of the effect without altering its character; but we cannot allow for them quantitatively. We can however say

that, wherever the Nb displacement falls in the sequence outlined above, its relation to the relaxation extension will be of the same kind, and as a first-order approximation we may predict proportionality between them. Since we do not yet know how to allow for differences in absolute O–O edge lengths between different compounds, we must at this stage draw our experimental evidence from examples showing one-corner or two-corner displacement, where comparisons can be made of relaxed and unrelaxed edges within the same octahedron.

Examples are found in KNbO<sub>3</sub> and NaNbO<sub>3</sub>, both of which have structures belonging to the perovskite family. In orthorhombic KNbO<sub>3</sub> (Katz & Megaw, 1967), the (010) symmetry plane of the structure is also a symmetry plane of the octahedron, and the plane of the two-corner Nb displacement; the four bonds in this plane, which we expect to be relaxed, have a mean length of 2.854 Å, while the eight bonds inclined to it have a mean length of 2.832 Å. The Nb displacement from the centre of its square is 0.20 Å. In tetragonal KNbO<sub>3</sub> the Nb displacement is parallel to the tetrad axis; its magnitude has not been measured experimentally, but the octahedron edges can be calculated directly from the lattice parameters measured by Shirane, Newnham & Pepinsky (1954). The eight relaxed edges, those with a component parallel to [001], have a length of 2.849 Å; the four unrelaxed edges, those in the (001) plane, have a length of 2.826 Å. Turning to NaNbO<sub>3</sub>, where the octahedron is the asymmetric unit of the structure, we find, as predicted, that the difference of symmetry makes no obvious difference to the relaxation effect. The Nb displacement is two-corner (though directed rather more towards one than the other) and its magnitude is 0.16 Å. The four edges in its plane are more nearly equal than in KNbO<sub>3</sub> (with a difference of 0.018 Å between extreme values) and have a mean length of 2.814 Å, as compared with the eight other edges which (with a fairly large scatter) have a mean length of 2.796 Å. (Data concerning this structure are from unpublished work by Łukaszewicz, Sakowski & Megaw, superseding the preliminary note by Wells & Megaw, 1961). The difference between the relaxation extensions in orthorhombic KNbO<sub>3</sub> and NaNbO<sub>3</sub>,

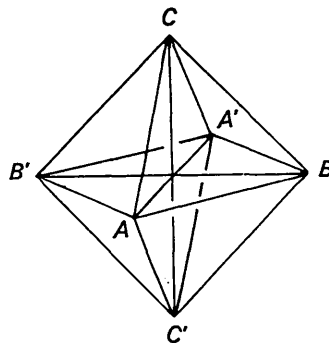


Fig. 5. Regular octahedron, to illustrate account in text of relaxation extension of edges.

which are 0.022 and 0.018 Å respectively, is of the same sign as the difference in Nb displacements, and is in agreement with the proposed linear relation between relaxation extension and Nb displacement.

Further work is in progress using these ideas. Points of particular interest are the application of the theory to thermal expansion, about which qualitatively correct predictions can be made, and the possibility, by considering forces acting on the octahedron from the other cations, of explaining differences of length within the group of relaxed edges without altering predictions about their mean length. Applications to other structures than those quoted here must also be considered,

though there are not many that are known in very full detail. The effect is not confined to octahedra; off-centring of the same kind can be observed also in tetrahedra. These developments will be taken up in a later paper.

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## The B–O Bond Lengths in Boron-Oxygen Compounds

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A simple molecular-orbital treatment of the  $\pi$ -electrons in a large variety of planar boron–oxygen compounds shows that variations in bond length are reasonably well explained in terms of a  $\pi$ -bond order. The  $\omega$ -technique method is of no advantage here as compared with the simple Hückel method.

In most boron–oxygen compounds, the boron atom is bonded to three or four oxygen atoms. In the latter case, the four B–O bonds are arranged tetrahedrally around the boron atom. When only three bonds are formed, the boron atom is surrounded symmetrically by three oxygen atoms, all four atoms lying approximately in the same plane. The bond length of the trigonal B–O bond varies over the range 1.28 to 1.43 Å.

Since the boron–oxygen framework is planar, it is reasonable to assume that, as a first approximation, the wave function can be divided into  $\sigma$ - and  $\pi$ -molecular orbitals. Then, in analogy to carbon  $\pi$ -electron systems, any differences in bond length might be attributed to differences in  $\pi$ -bond order. Therefore, it should be possible to apply a standard Hückel type analysis to molecules containing trigonally bonded boron atoms.

Applications of  $\pi$ -bond theory to B–O bonds are rare. Coulson (1964) has used simple  $\pi$ -bond theory to explain the differences in bond length between the interior and exterior B–O bonds in metaboric acid. Mateson (1960) has used it to correlate reaction rates of reactions involving substituted ethyleneboronic acids. Armstrong & Perkins (1967) have used the more sophisticated Pariser–Parr–Pople (PPP) method to investigate some substituted phenylboronic acids. All

these calculations predict a migration of charge from the oxygen to the boron atom leading to a  $\pi$ -bond order in the range 0.3 to 0.5. This agrees with the general shortening of the BO bond observed in going from a tetrahedral to a trigonal state.

Zachariasen (1963) has used Pauling's valence neutralization concept to correlate the variations in B–O and H–O bond lengths in crystalline borate molecules. Basically, the theory tries to take into account the effect of nearby atoms on the lengths of bonds formed with a given atom. A parameter, the bond strength,  $v_{ij}$ , is defined for each bond in such a way that  $\sum_j v_{ij} =$

valence of the  $i$ th atom. The bond length of a given type of bond is then correlated to its bond strength through an empirically determined bond-length–bond-strength curve. Using this method, Zachariasen is able to derive a bond-length–bond-strength curve which can predict bond lengths to within 0.04 Å.

The purpose of this paper is to report the application of simple  $\pi$ -electron theory to some boron–oxygen compounds in an attempt to correlate the observed differences in bond length with molecular structure. The  $\pi$ -bond orders of a number of boron–oxygen compounds were calculated by a standard Hückel-type analysis. Both the simple Hückel theory and  $\omega$ -techniques were employed. The calculations were carried out on a KDF 9 computer at the University of Oxford, using a Self-Consistent Hückel Molecular Orbital pro-

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