

On the Arrangements of Ions in Crystals

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It is shown that the observed structure of ionic crystals is close to that which maximizes the volume subject to the constraint of fixed cation-anion distance. The disposition of the centres of the cations and/or anions is often 'arranged as the centres of hard spheres in closest packing'. The term *eutactic* is proposed for the circumlocution between inverted commas.

'Close packing' in ionic crystals

The problem of predicting, *a priori*, the structure that a crystal will adopt is, even today, too difficult. Faced with this problem one looks for approximate but general principles that serve both as aids to rationalizing crystal structures and as guides to predicting the structures of new compounds. An example from the crystal chemistry of metals is the 'space principle' (Laves, 1939) which states that atoms of an element or alloy pack together to fill space as well as possible. The wide occurrence of hexagonal closest packing (h.c.p.) or cubic closest packing (c.c.p.) is rationalized on this basis.*

From the earliest days of crystallography it was apparent that arrangements of ions (more particularly of anions) corresponding to close packing occurred in many ionic crystal structures also. This led to the description by Bragg & West (1927) of many mineral structures as close packings of large anions with smaller cations in the tetrahedral and octahedral interstices of the packing. This view of the structure of ionic crystals remains in current texts (Pauling, 1960; Bragg & Claringbull, 1965; Wells, 1975). It is shown here that this description is misleading and obscures a fundamental difference between ionic crystal structures on the one hand and metal (alloy) structures on the other.

The conventional view of ionic crystal structures is based on several misconceptions that have persisted and reinforced each other. They are as follows.

(a) Anions are much larger than cations

Early sets of ionic radii such as those of Pauling (1960) certainly show that anions such as O^{2-} (1.40 Å), F^- (1.36 Å) are substantially larger than most cations, e.g. Al^{3+} (0.5 Å), Na^+ (0.95 Å). However, the basis underlying these radii was a consideration of the theoretical properties of *free* ions and not those of ions in

crystals. In crystals, anions are subject to a positive Madelung potential [typically $12z \text{ V}$ (O'Keeffe, 1967) where z is the charge of the anion in units of the electron charge] which has the effect of contracting the charge cloud. A good example of this effect is afforded by the stabilization of the O^{2-} ion in crystals; the free O^{2-} ion is unstable and hence has 'infinite' extent. Conversely cations are subject to a negative potential having the reverse effect. A quantitative discussion of these points has been given by Paschalis & Weiss (1969).

There are now firm grounds, both experimental and theoretical, for believing that ionic radii (to the extent that the concept has meaning) are quite different from the older values (Tosi, 1964). A set of ionic radii more consistent with recent theory and with experimental electron density maps in crystals is the 'crystal radii' (Shannon & Prewitt, 1969; Shannon, 1976). This set shows (for sixfold coordination): O^{2-} (1.26 Å), F^- (1.19 Å), Na^+ (1.16 Å), Al^{3+} (0.67 Å) and Ca^{2+} (1.14 Å). Thus in crystals such as NaF or CaO one has packings of ions of comparable size.

(b) In minerals the volume per O^{2-} ion is constant

This remarkably fruitful concept worked only because it was applied to a limited range of materials involving cations of comparable size. In practice one finds a virtually continuous range of volume per O^{2-} ion from, for example, 13.8 in BeO to 42.1 Å³ in BaO.

(c) Many anion packings approximate close packings of spheres

In the densest packings of equal-sized hard spheres in contact, the fraction of space occupied by the spheres (the packing density) is $\pi\sqrt{2}/6=0.740$. Although the anion packing in corundum, to take just one example, is generally described as h.c.p., in fact the corresponding packing density of equal-sized hard spheres with this arrangement is only 0.595.

(d) Cation coordination is determined by size (radius ratio)

Again just one counter example should suffice. In spinel, $MgAl_2O_4$, it is the larger ion (Mg^{2+}) that has tetrahedral coordination and the smaller (Al^{3+}) octahedral coordination. In a *regular* MgO_4 tetrahedron

* But note that in metallic elements that have both close-packed and body-centred cubic structures, the volume difference for the two polymorphs is usually less than 1% (Rudman, 1965) in contrast to the hard-sphere value of 9% increase in volume in going from closest-packed to body-centred cubic packing.

the O–O distance is 3.05 Å (compare the crystal radius of 1.26 Å given above).

The difficulty is that close-packing geometry can arise in several different contexts, only one of which is as the solution to the problem of the closest packings of equal-sized spheres. For this reason an alternative term is proposed to describe the arrangements of points in space corresponding to the centres of spheres in closest packing (*i.e.* those periodic arrangements of points in which each has 12 equidistant nearest neighbours). It is proposed to call such arrangements *eutactic* (Greek *ευτακτος*, well-arranged) with the corresponding noun *eutaxy*.*

Brunner (1971) has pointed out that eutaxy arises in the different context of arranging a fixed number of points in a fixed volume such that the distance apart of nearest neighbours is a maximum. Eutaxy arises therefore either in requiring maximum density for fixed distance apart or in requiring maximum distance apart for fixed density. It is shown in what follows that ion packings in crystals, although often approximately eutactic, conform to neither of these conditions but arise in a third, distinct, context.

Ionic crystals contain two fundamentally different kinds of ions (cations and anions), ions of each kind having as nearest neighbours only ions of the other kind. It is an empirical fact (*e.g.* Shannon & Prewitt, 1969) that for a given number of nearest neighbours (coordination number), interionic distances are essentially constant (constant 'bond length'). Subject to the constraint of fixed nearest-neighbour distance, it is anticipated that in crystals in which electrostatic (Madelung) forces determine the structure, the next nearest neighbours (ions of like charge) will tend to be as far apart as possible. Thus ionic crystal structures are expected to be ones of *maximum* volume subject to the constraint of fixed bond length. It is shown below that some common ionic crystal structures are close to conforming to this principle and that eutactic arrangements may arise in this third context also.

Maximum-volume structures

In this section the volume, V , per unit cell of a crystal is expressed in terms of one or more parameters, so that changing the parameters corresponds to a topological deformation of the structure. In every case we keep the cation–anion distance constant and equal to l , and then determine the values of the parameters which maximize the volume for constant l .

(i) The NaCl (*B1*) structure

Deformation of the NaCl (*B1*) structure to that of CsCl (*B2*) has been discussed earlier (Hyde & O'Keeffe, 1973). Two transformation paths involving either an orthorhombic or a rhombohedral intermediate were

considered. In either case the volume was given by†

$$V^2 = 8l^6(1 + 2x^3 - 3x^2)/(3 - 2x)^3, \quad (1)$$

where x is parameter such that $\frac{1}{2} - x$ measures the distortion from the *B1* structure ($x = 0$ is the *B2* structure). From (1) one obtains that V is a maximum for $x = \frac{1}{2}$ (*i.e.* no distortion). This is also the point of minimum electrostatic energy (*i.e.* maximum Madelung constant for constant l , Hyde & O'Keeffe, 1973). In the undistorted *B1* structure both anions and cations are of course disposed eutactically, so we have given an example in which eutactic arrangements are those both of constrained maximum volume and of minimum electrostatic energy.

(ii) The wurtzite (*B4*) structure

BeO is an example of a compound with this structure [compare (iii) below]. It is hexagonal, space group $P6_3mc$, Be in 2(a): 0, 0, u_1 ; $\frac{1}{3}, \frac{2}{3}, \frac{1}{2} + u_1$, O in 2(a): 0, 0, u_2 *etc.* Two parameters are needed to specify the structure: $\gamma = c/a$ and $u = u_1 - u_2$. The four shortest Be–O distances are equal when

$$\gamma^2 = 4/(12u - 3) \quad (2)$$

and then

$$V = \sqrt{27}l^3(u - \frac{1}{4})/2u^3. \quad (3)$$

V as given by (3) is a maximum for $u = \frac{3}{8}$, hence [from (2)] $\gamma = \sqrt{\frac{8}{3}} = 1.633$, and both ions are in (hexagonal) eutaxy. For BeO the observed parameters are $u = 0.378$, $\gamma = 1.602$.

(iii) β -BeO (Smith, Cline & Austerman, 1965)

This structure differs from the previous one in that, although Be is tetrahedrally coordinated by O, the topology of the structure is quite different. It is tetragonal, space group $P4_2/mnm$, Be in 4(g): $\pm(y, \bar{y}, 0; \frac{1}{2} + y, \frac{1}{2} + y, \frac{1}{2})$, O in 4(f): $x, x, 0$ *etc.* All four shortest Be–O distances are equal for

$$\gamma^2 = c^2/a^2 = 2 - 16xy \quad (4)$$

when

$$V^2 = l^6(2 - 16xy)/(1 - 2x + 2x^2 - 2y + 2y^2)^3 \quad (5)$$

with a maximum at $x = y = (\sqrt{13} - 1)/8 = 0.326$, $\gamma = [(\sqrt{13} - 3)/2]^{1/2} = 0.550$. The observed values for BeO are $x = 0.310$, $y = 0.336$, $\gamma = 0.577$, quite close to those for maximum volume. Here the anion packing is quite different from eutaxy.

(iv) The CaCl₂ (*C35*) and rutile (*C4*) structures

The CaCl₂ structure is orthorhombic, space group $Pn\bar{m}$, Ca in 2(a): 0, 0, 0; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, Cl in 4(g): $\pm(u, v, 0; u + \frac{1}{2}, \frac{1}{2} - v, \frac{1}{2})$. If $a = b$ and $u = v$ the structure is that of rutile (symmetry $P4_2/mnm$). In addition to u and v one

* The terms were suggested by Mrs. M. Hyde (private communication).

† Equation (1) corrects a typographical error in Hyde & O'Keeffe (1973).

has as parameters $\beta = b/a$ and $\gamma = c/a$. For all six shortest cation-anion distances to be equal

$$\gamma^2 = 4u + 4v\beta^2 - 1 - \beta^2. \quad (6)$$

With this condition

$$V^2 = l^2\beta^2(4u + 4v\beta^2 - 1 - \beta^2)/(u^2 + \beta^2v^2)^3. \quad (7)$$

It may readily be verified that V is a maximum for $u = v = \frac{3}{10}$, $\beta = 1$, $\gamma = \sqrt{\frac{2}{5}} = 0.632$.

Many oxides and fluorides have the rutile structure but none is known with the (lower-symmetry) CaCl_2 structure. Further, all these oxides and fluorides have parameters (Baur & Khan, 1971) close to the maximum volume ones (e.g. TiO_2 : $u = 0.305$, $\gamma = 0.634$). The parameters are also close to those ($u = 0.315$, $\gamma = 0.721$) for a maximum in Madelung constant for fixed l (Bollnow, 1925). Here again the parameters for maximum volume, for minimum electrostatic energy, and as observed are all very similar, but are different from those for an eutactic arrangement of anions (for hexagonal eutaxy, $\beta = \sqrt{\frac{2}{3}} = 0.816$, $\gamma = 0.5$, $u = 1/\sqrt{12} = 0.289$, $v = \frac{1}{4}$).

(v) *The bixbyite ($D5_3$) structure*

The bixbyite structure (also known as the type C rare-earth sesquioxide structure) is another example of one in which the anion arrangement is not eutactic. The structure is cubic, space group $Ia\bar{3}$, with Mn(1) in $8(a)$: $0, 0, 0$ etc.; Mn(2) in $24(d)$: $u, 0, \frac{1}{4}$ etc.; O in $48(e)$: x, y, z etc. For all metal ions to have six equidistant O neighbours the following equations must hold

$$y = \frac{-(128u^4 - 480u^3 + 648u^2 - 372u + 77)}{(256u^3 - 704u^2 + 1248u - 184)} \quad (8)$$

$$z = 2u^2 - 4u + \frac{9}{4} + 4uy - 3y \quad (9)$$

$$x = 2u^2 - 6u + \frac{19}{4} + 4uz - 5z. \quad (10)$$

The volume is given by

$$V^2 = l^6/(x^2 + y^2 + z^2 + u^2 - 2ux - u + x - z/2 + \frac{5}{16})^3. \quad (11)$$

Numerical solution of the problem of finding the maximum of V subject to constraints (8)–(10) gave the results in Table 1. Given for comparison in the table are the means of the parameters for ten compounds with this structure (and for which the parameters differ only slightly, one from another). Again it may be seen that the observed structure is close to that of constrained maximum volume, and again they are close to those for maximum Madelung constant (von Merrens & Zemmann, 1966).

Table 1. *Calculated and observed coordinates for compounds with the bixbyite structure*

	Calculated	Observed*
u	0.973	0.968
x	0.384	0.386
y	0.145	0.155
z	0.381	0.385

* Average of the parameters for Dy_2O_3 , Tm_2O_3 , Mn_2O_3 , In_2O_3 , (Hase, 1963) and for Mn_2O_3 , Y_2O_3 , Er_2O_3 and Yb_2O_3 (Fert, 1962).

Crystals with covalent (directional) bonding

It has been shown in some examples that observed ionic crystal structures are close to those for both a maximum in volume and a minimum in electrostatic energy subject to the constraint of fixed nearest-neighbour distance. Often the structure is also one which is favorable for directional bonding (so that e.g. O is tetrahedrally surrounded by cations) and could equally arise in this context also. It is instructive to consider examples where the requirements of maximum volume (Madelung constant) and covalency (bond angles) are in conflict. Not surprisingly the structure represents a compromise.

(vi) *The cooperite ($B17$) structure type*

The structure of PtS (PdO etc.) is tetragonal, space group $P4_2/mmc$, with Pt in $2(c)$: $0, \frac{1}{2}, 0$; $\frac{1}{2}, 0, \frac{1}{2}$, S in $2(e)$: $\pm(0, 0, \frac{1}{4})$. The four shortest Pt–S distances are equal and the volume is given by

$$V^2 = 4096\gamma^2l^6/(4 + \gamma^2)^3 \quad (12)$$

and thus is a maximum for $\gamma = 2$ at which the Pt atoms are in cubic eutaxy (i.e. c.c.p.) and S is surrounded by four Pt at the vertices of a regular tetrahedron. The configuration of the neighbours of Pt (or Pd in PdO) is significantly different from the square configuration characteristic for Pd^{II} or Pt^{II} – this would require $\gamma = \sqrt{2}$. The observed value ($\gamma \approx 1.75$) clearly represents a compromise.

(vii) *Cristobalites*

Elsewhere (O'Keeffe & Hyde, 1976) ways have been described in which the cubic C9 (idealized high cristobalite) structure can collapse (reduce volume) by concerted rotations of tetrahedra to produce the real structures of high- and low-cristobalite and of other compounds. The maximum volume (C9) structure, which is also the structure of maximum Madelung constant (Fischer & Zemmann, 1975) is not observed; clearly because the linear cation-anion-cation configuration which this would entail is unfavourable for covalent bonding (e.g. of O and Si in SiO_2). For a more detailed discussion of the observed bond angles in this structure family, reference may be made to the earlier publication (O'Keeffe & Hyde, 1976).

Conclusion

The main line of the argument may be summarized as follows:

(a) For a given coordination number, in ionic crystals the cation-anion distance is essentially constant.

(b) Subject to the constraint (a), the observed structure of crystals in which electrostatic (Madelung) energies predominate is close to that of maximum volume.

(c) Eutactic arrangements, when they occur in ionic crystals, are a consequence of (b).

The truth of (b) and (c), although they are counter to generally held views,* has been demonstrated for some examples.

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* In addition to the texts already cited, one might quote Bernal (1969) 'In all coherent structures there is a tendency to arrive at minimal volumes'.

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Structural Mechanism of Pyroelectricity in Tourmaline

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Pyroelectricity in tourmaline, known since antiquity, was ascribed by S. von Boguslawski to a charged, asymmetric, anharmonic oscillator based on the Einstein model of a crystal. His predicted values of the pyroelectric coefficient k were in good agreement with Ackermann's measurements in the range 200–400 K. We have tested Boguslawski's model by refining the structure, at 193 and 293 K, on a sphere of gem-quality elbaite. The pyroelectric effect is due primarily to the asymmetric anharmonic vibrations of O(1), the oxygen atom of point symmetry $3m$ which has a polar environment. Its centre of gravity moves 0.005 Å from 193 to 293 K. It is the only atom with a displacement well above experimental uncertainty. Its large thermal parameters, which are ten times their standard deviation at both temperatures, clearly invalidate the assumption of an ellipsoidal thermal movement. This probably holds for Na and O(2), which also have abnormally large temperature factors, but show no significant displacement.

Introduction

Pyroelectricity, the development of electric charges of opposite signs at the opposite ends of a crystal that undergoes a change in temperature, is one of the earliest recorded properties of crystals. Theophrastus (372–

287 BC) reported, probably of tourmaline, that 'it has the power of attraction, just as amber has, and some say that it not only attracts straws and bits of wood, but also copper and iron' (Lang, 1974).

Pyroelectricity was rediscovered in tourmaline, and first described in Europe in 1707 by Johann George Schmidt in a book entitled *Curiose Speculationen bey schlaflosen Nächten*. Schmidt mentions that the Dutch in 1703 brought, from Ceylon, a precious stone called tourmaline, which attracts ashes when a tip of its

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