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Madelung Potentials and the Sizes of Ions in Oxides and Nitrides

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Abstract

It is shown that to a good approximation, the Madelung potential at anion sites in simple structures depends on the size of the cation but not on the cation charge or crystal structure. The effect of Madelung potential on ionic radii is illustrated by comparing the apparent radii of the oxygen and nitrogen ions.

Introduction

The ionic model of crystals succeeds in a spectacular way in calculating the cohesive energy of the highly symmetrical halides and, perhaps slightly less successfully, the oxides of the more electropositive elements (Tosi, 1964). It follows that a good first approximation to the charge distribution in such crystals is obtained by placing at atom sites non-overlapping ions of integral charge and of spherical symmetry. Particularly when one considers the rôle of interionic repulsion in determining crystal structure, it is natural to enquire into the appropriate radii to ascribe to such ions. A tacit assumption of all such attempts (see *e.g.* Tosi, 1964; Shannon & Prewitt, 1969) is that for a given coordination a *constant* radius can be ascribed to an ion. This is the case for instance in the set of radii most commonly used in discussion of oxides – that proposed by Shannon & Prewitt (1969). In this paper the 'crystal radii' of that set (as revised by Shannon, 1976) are used and are referred to as SP radii.

The SP radii are very successful in predicting bond lengths expected in oxide crystals. This is their purpose, and for this purpose the radius assigned to oxygen is irrelevant. However, in some instances ionic radii are taken as a literal measure of size – with the result that some erroneous ideas have developed concerning the rôle that anion packing plays in determining crystal structure and that radius ratios play in determining coordination numbers (O'Keeffe, 1977; O'Keeffe & Hyde, 1978).

A major problem that is the concern of this paper, is the observation that the size of an ion (to the extent that the concept has meaning), in particular an anion such as O^{2-}, is expected to be sensitive to its environment (Paschalis & Weiss, 1969; O'Keeffe, 1977). There are two effects: the first is the effect of coordination number, which is due largely to the repulsive term in the crystal energy, and is well understood within the framework of the ionic model. A more general discussion in terms of bond strengths that is applicable to irregular coordination has been given by Brown & Shannon (1973). The second effect, which has barely been discussed, arises from the varying Madelung potentials experienced by a given ion in different crystals.

The argument for expecting ionic radius to vary with Madelung potential may be simply sketched as follows. A free O^{2-} ion is unstable with respect to ionization (to $O^- + e^-$) by some 5–6 eV. In this sense a free O^{2-} ion may be said to have infinite radius. However, the ion in a crystal will experience a stabilizing potential of about 20 V (see below). Clearly the radial charge distribution of the ion will be sensitive to the magnitude of this potential. The effect will be for the charge distribution to contract as the (positive) potential due to the surrounding ions increases (Paschalis & Weiss, 1969).

In the light of the previous paragraph, it may be at first sight surprising that approximately constant ionic radii (for a given coordination number) can be used so successfully for oxides. However, it has been remarked (O'Keeffe, 1967) that to a first approximation the Madelung potential felt by a given ion is not very sensitive to the details of crystal structure. In simple binary oxides, for example, the Madelung potential, φ, depends only on the size (but not the charge) of the cation. In an oxide series such as that of MgO, CaO, SrO, BaO with the NaCl ($B1$) structure, the Madelung potential varies inversely as the interionic distance, l. Thus the potential at the anion site is given by

$$\varphi = 1{\cdot}7476 \times (2e)/4\pi\varepsilon_0 l, \qquad (1)$$

where e is the magnitude of the electron charge and ε_0 the permittivity of free space.

Madelung potentials in oxides

With standard methods (Tosi, 1964), the Madelung potential at oxygen sites has been calculated for a number of binary oxides. Structure types considered were $C8$ (SiO_2), $C1$ (Li_2O, Na_2O, K_2O, ThO_2), $C3$

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(Ag_2O), *C*4 (GeO_2, TiO_2, SnO_2), *B*1 (MgO, MnO, CaO, SrO, BaO), *B*4 (ZnO), $D5_1$ (Al_2O_3, Cr_2O_3), $D5_3$ (Sc_2O_3) and $D5_2$ (La_2O_3). Only the last of these has crystallographically distinct oxygen ions, but in this case the potentials at each site are almost equal (19·92 and 19·87 V). It is remarkable that for these diverse structure types, φ is given quite accurately by (1) when l is interpreted as the sum of *six-coordinated* SP radii for the appropriate cation and oxygen. This implies, of course, that if the SP radius for a cation in six coordination is taken as a measure of its size, then φ depends only on cation size and not on crystal structure. The point is made by Fig. 1 where φ is plotted as a function of cation radius. The line represents the prediction of (1). The data for the *B*1 structures do not fall exactly on this line as the SP radii [used to determine l in (1)] do not exactly reproduce the observed interatomic distances.

The result has a number of implications.

(*a*) If the results for oxygen are generalized to all ions, it follows that the electrostatic energy $\sum z_i e\varphi_i$ for a crystal can be expressed in terms of one Madelung constant and one set of radii. This is just what is done in the Kapustinskii (1956) approach to calculation of lattice energies.

It follows, too, that within the framework of the ionic model the lattice energy is not very structure sensitive in the sense that there may well be several structures of almost the same energy. And [compare (*b*) below] the energy difference between a solid ternary compound and its two solid components (*e.g.* between $MgAl_2O_4$ and MgO + Al_2O_3) will be close to zero, as is usually observed.

(*b*) For a given chemical compound, there will be no Madelung potential effect on ionic size (bond length). The effect of coordination number change will be present of course. This observation extends to ternary compounds such as $MgAl_2O_4$, where φ (25·8 V) is intermediate between those calculated for MgO and for Al_2O_3. Thus, to a first approximation, changes in the size of O^{2-} in going (say) from MgO to BaO can be assimilated in the radii assigned to the cations.

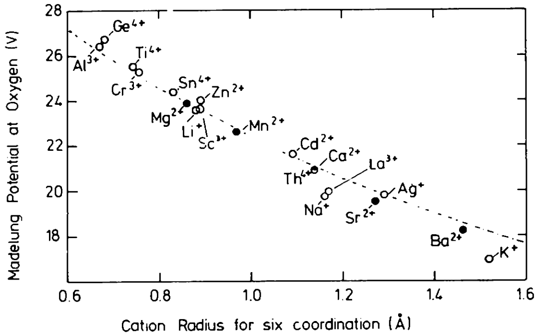

Fig. 1. Madelung potential at oxygen sites in binary oxides as a function of cation radius. Filled circles are for oxides with the *B*1 (NaCl) structure.

(*c*) A proposed new structure of an oxide (for example) can be verified by calculating φ at the oxygen site(s). This approach has been used successfully by Hoppe (1970) to identify probably wrong structures. This point is taken up in connection with the structures of lanthanum oxyfluorides below.

A case study – the lanthanum oxyfluorides

It has been remarked that in La_2O_3, φ at the two oxygen sites is 19·9 V. Similar values are expected at oxygen in other lanthanum–oxygen compounds. Zachariasen (1951) determined the structures of two forms of LaOF: β-LaOF which is rhombohedral and γ-LaOF which is tetragonal. In each structure there are two sets of anion sites and with data of limited accuracy it was not possible to decide which set of sites were occupied by fluorine and which by oxygen. A decision was made on the assumption that the La–F distances would be shorter than the La–O distances. Tanguy, Vlasse & Portier (1973) used similar arguments to determine the oxygen and fluorine positions in rhombohedral EuOF. On the other hand, Mann & Bevan (1970) carefully examined diffraction data for rhombohedral YOF and concluded that the oxygen and fluorine positions of the Zachariasen (1951) structure should be interchanged.

Both Templeton (1957) and Hoppe (1970) have shown that the Zachariasen distribution for β-LaOF was unlikely on electrostatic grounds. A consideration of Madelung potentials at oxygen is even more convincing as illustrated by Table 1. The values of φ at the oxygen site in the structures with O and F interchanged are very close to that found in La_2O_3.

It is very informative to enquire into the reason for the La–O bond being appreciably (~0·2 Å) shorter than the La–F bond. In both structures La is surrounded by four oxygen and four fluorine ions and each anion is surrounded by four lanthanum ions. The SP radii would predict bond lengths of 2·54 Å for La–O and 2·49 for La–F. However, these are examples of structures in which Pauling's (1929) electrostatic valence rule is not obeyed. In terms of the 'valence sum rule' (Brown, 1977) the La–O bond strength, *s*, is 0·5 (and the La–F bond strength 0·25). The empirical bond length–bond strength correlation of Brown & Wu (1976) then predicts the La–O bond length to be 2·41 Å. This should be compared with

Table 1. *Madelung potentials* (V) *at oxygen sites:* (1) *for the Zachariasen* (1951) *structures and* (2) *for the structures with* O *and* F *interchanged*

Compound	Structure (1)	Structure (2)
β-LaOF	13·4	19·95
γ-LaOF	13·9	19·05

2·61 Å and 2·59 Å calculated for the Zachariasen structures and 2·42 Å for both structures with the anions interchanged. Clearly then, Mann & Bevan are correct.

Evidence for the effect of φ on l

The stabilizing effect of the potential at an anion might reasonably be expected to increase as the instability of the anion increases. In particular it might be expected to increase in the order $F^- < O^{2-} < N^{3-}$ (for an estimate of the affinity of N for three electrons see Baughan, 1959).

Thus, we compare in Table 2 the interatomic distances in the isostructural series CdO, CaO, SrO, BaO with those in the series CdF_2, CaF_2, SrF_2, BaF_2. Note that the bond strength, s, is the same for every bond in each structure. Clearly oxygen is getting larger relative to fluorine as the bond length increases (φ decreases). This variation of anion radii with size of the cation has been noted by Johnson (1973).

More striking is the effect of Madelung potential on ionic polarizability. It is an effect that has long been recognized (for a discussion and references to early work see Wilson & Curtis, 1970), but is nevertheless often ignored by ascribing a constant polarizability to ions in crystals. Increasing Madelung potential at an anion site will result in decreased polarizability in the same way as it results in decreased size.

The Clausius–Mossotti equation relates the polarizability of a formula unit of volume $\bar{V}$ to the refractive index of the crystal n:

$$\alpha = 3\varepsilon_0 \bar{V}(n^2 - 1)/(n^2 + 2). \qquad (2)$$

For an insulating (large band gap) crystal the polarizability can be considered as a sum of ionic contributions, *i.e.* for MO

$$\alpha(MO) = \alpha(M^{2+}) + \alpha(O^{2-}),$$

and for MF_2,

$$\alpha(MF_2) = \alpha(M^{2+}) + 2\alpha(F^-),$$

so that

$$\Delta\alpha = \alpha(MO) - \alpha(MF_2) = \alpha(O^{2-}) - 2\alpha(F^-).$$

Table 2. *Differences* (*oxide minus fluoride*) *in bond lengths*, Δl (Å), *and in polarizabilities*, $\Delta\alpha/4\pi\varepsilon_0$ (Å^3), *for some isostructural oxides and fluorides*

Cation	Δl	$\Delta\alpha/4\pi\varepsilon_0$
Cd	0·014	
Ca	0·040	−0·40
Sr	0·069	0·63
Ba	0·077	0·93

In Table 2, $\Delta\alpha/4\pi\varepsilon_0$ (the quantity conventionally quoted as 'polarizability') is given for M = Ca, Sr and Ba. The values were calculated with the high-frequency refractive indices obtained from studies of infrared dispersion. Clearly, as the interatomic distance increases (φ decreases), the polarizability of the oxides increases more rapidly than that of the fluorides, and it is reasonable to ascribe the bulk of this effect to the change in radial extent of the anion electron distribution.

Apparent ionic radii in nitrides

If the ideas expressed above are correct, one would expect a greater variation in apparent radius with Madelung potential for the nitride ion than for the oxide ion. With the SP radii for cations (derived from bond lengths in oxides), the apparent radius of nitrogen in an isostructural series of nitrides can be determined. This has been done for the nitrides with the NaCl (B1) structure taking lattice parameters from Donnay & Ondik (1973). The results are shown in Fig. 2 where the apparent radius of N^{3-} is plotted as a function of interionic distance, l. It may be seen that the apparent radius varies by more than 10% and approximately linearly with l [and hence with φ – *cf.* (1)]. Even in the lanthanide series the nitride radius varies by 5%. CeN is clearly anomalous, suggesting an oxidation state of 4+ for the cation. CrN is the other large deviation from the line of Fig. 2. The lattice parameter has recently been confirmed (Eddine, Bertaut, Roubin & Pâris, 1977), but the bonding and electrical properties in this compound are unusual (Goodenough, 1963).

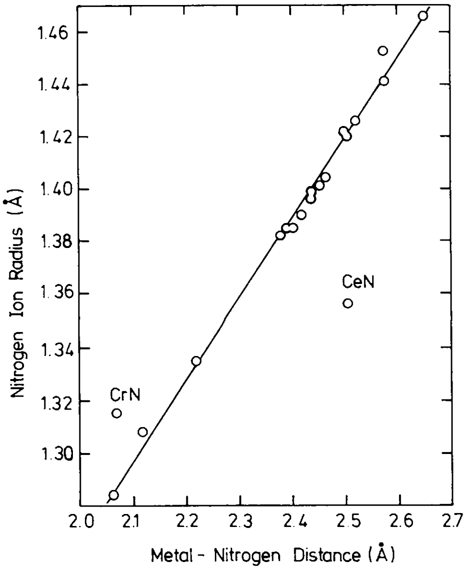

Fig. 2. Apparent radius of the nitride ion in nitrides with the B1 (NaCl) structure.

It does not appear useful to apply a similar analysis to other than first-row anions. The compounds are not so well described by the ionic model and complications arise from anion–anion bonding. For example, no simple pattern emerges from a comparable analysis of S^{2-} radii. It might be mentioned, however, that the behaviour of H^- closely parallels that of N^{3-}.

Conclusions

The main conclusions to be drawn from the results described in this paper are:

(1) it is not a satisfactory procedure to assume constant radii for anions, even in an isostructural series of compounds;

(2) variations of apparent anion radii can be correlated in an understandable way with Madelung potentials at anion sites;

(3) Madelung potentials at anion sites in simple crystal structures depend on the size (but not the charge) of the cations;

(4) to predict bond lengths in crystals, it is in general better to use empirical bond length–bond strength correlations (Brown, 1977) than to use tables of ionic radii.

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A Theoretical Comparison of the β, γ' and $2F_o - F_c$ Syntheses

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Abstract

A theoretical comparison of the β synthesis of Ramachandran & Raman [*Acta Cryst.* (1959), **12**, 957–964] with the weighted γ' and weighted $2F_o - F_c$ syntheses shows that, for partially known structures, the ratio of peak heights of the unknown atoms to those of the background is the same in all the syntheses. The β synthesis contains more background peaks than either the γ' or $2F_o - F_c$ syntheses. The $2F_o - F_c$ synthesis suppresses the peaks of wrongly positioned atoms most effectively and the γ' is the least effective. The syntheses which approach most closely the true electron density are the weighted $2F_o - F_c$ synthesis for non-centrosymmetric structures and the weighted γ' for centrosymmetric ones.

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