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Calculation of bond distances and heats of formation for BeO, MgO, SiO_2, TiO_2, FeO, and ZnO using the ionic model

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Abstract

The radius ratio model is criticized for its failure to accurately predict coordination number, its reliance upon an ambiguous entity (the ionic radius), and its inconsistency with modern quantum mechanical calculations. A purely theoretical version of the ionic model, without the assumption of fixed radii, was previously shown by Gordon and coworkers to accurately predict bond distances, heats of formation, and preferred structure type for the alkali halides. For BeO, MgO, and CaO the model also gives reasonable results, although it is somewhat less accurate due to ambiguity in the definition of the oxide ion wavefunction. For ZnO, SiO_2, and TiO_2, heats of formation calculated from this model are less negative than the experimental values by hundreds of kcal/mole which suggests substantial covalency, although bond distances are predicted with an average error of less than 0.1A for SiO_2 and TiO_2. For FeO, agreement with experiment is similar to that observed for MgO. Applications of the method to the prediction of Fe,Mg ordering in orthopyroxenes and in ludwigite are described. Schemes for adding covalency effects to the ionic model calculations are considered.

Introduction

Mineralogists have for some time used the ionic model to rationalize the structures observed for silicates and other minerals (Pauling, 1929). They have often assumed that radii could be assigned to ions in solids and preferred crystal structures could be predicted purely from the ratio of cation and anion radii. However, many workers have noted that the concept of ionic radius is quite ambiguous (Slater, 1964; Shannon and Prewitt, 1969), since quantum mechanics tells us that the tails of wavefunctions of atoms or ions extend to infinity. Experimentally, one could define the point of contact of rigid ions as that point along their line of centers at which the electron density is a minimum. Such experimentally-defined radii are not constant for a given ion, however; they vary substantially from one compound to another (Sanderson, 1967; Witte and Wolfel, 1958). They also differ substantially from the Shannon and Prewitt (1969) effective ionic radii; the experimentally-defined cation radii are larger and the anion radii correspondingly smaller than the traditional values.

It has also been often noted (*e.g.* Phillips, 1970) that the radius ratio predictions fail rather badly for the alkali halides, which considerable evidence suggests to be the most ionic class of materials. Since the alkali halides often show six coordination when the radius ratio model predicts either four or eight coordination, no change in the apportioning of bond distance into cation and anion radii can lead to significantly improved ionic radius ratio predictions. For other inorganic solids the radius ratio predictions are also commonly in error. This is illustrated in Figure 1 in which we plot r_+ *vs.* r_- for 44 different halides and oxides, divide the field into regions of predicted four, six, and eight coordination on the basis of r_+/r_-, and indicate the experimentally observed coordination number. The radius ratio predictions are incorrect for 18 of the 44 compounds. Although modified radii may give improved predictions for limited classes of materials (Whittaker and Muntus, 1970), no significant improvement in the predictive value of the radius ratio concept for broad classes of presumably ionic materials has ever been obtained.

Although the radius ratio model is thus quantum-mechanically unsound and has little predictive value, this is not the case for the ionic model in a more general formulation. Recently, both theory (Hohenberg and Kohn, 1964) and experiment (Coppens, 1977) have emphasized the importance of the electron density in determining the stabilities of materials. It thus

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seems reasonable to define an ionic compound in terms of its electron density. Following Gordon and Kim (1972) we define the ionic limit electron density at a given point in a solid as the sum of the electron densities from the component free ions placed at their lattice positions. Given the electron density distributions for the free ions, we can calculate the ionic limit total electron density and from this density various properties, such as the total energy. We know from the quantum-mechanical variation principle that a rearrangement of electron density leading to a final electron distribution incorporating covalent bonding effects will occur only if it lowers the total energy of the material. We can thus rigorously partition the observed total energy into an ionic limit energy, corresponding to the ionic limit electron density, and a covalency contribution or correction. In previous applications (Gaffney and Ahrens, 1970) of the ionic model, covalency effects on stability have been assessed as the difference between experimental heats of formation and those obtained from a semiempirical approach in which ion pair repulsions were fitted to experimental bulk moduli. However, as noted by Gaffney and Ahrens, the semiempirical repulsive parameters actually incorporate covalency effects, so that a clear separation of ionic and covalency contributions cannot be made.

The present work employs a theoretical version of the ionic model, based on the electron density definition described above. I first review previous work by Gordon and coworkers (Gordon and Kim, 1972; Kim and Gordon, 1974; Cohen and Gordon, 1975, 1976) employing this model and contrast their results with radius ratio predictions. New results are then presented for a number of oxide minerals, and covalency contributions to their stabilities are assessed. The reasonable accuracy obtained in the prediction of bond distance and heat of formation for these oxides suggests that the model may be useful in treating mineralogical problems, and applications to the question of Fe, Mg ordering in orthopyroxenes and in ludwigite are presented. Finally, I suggest some qualitative and quantitative approaches to the prediction of covalency corrections.

Computational method

The details of the modified electron gas (MEG) ionic model method have been fully described by Gordon and Kim (1972). The fundamental assumptions of the method are: (1) the total electron density at each point is simply the sum of the free ion densities, with no rearrangement or distortion taking place; (2) ion–ion interactions are calculated using Coulomb's law and the free electron gas approximation is employed to evaluate the electronic kinetic, exchange, and correlation energies; (3) the free ions are described by wavefunctions of Hartree–Fock accuracy, the highest quality presently attainable for heavy atoms.

The Coulombic part of the interaction energy between ions a and b is given by the expression:

$$V_{\mathrm{Coul}} = \frac{Z_a Z_b}{R} + \int\int \frac{\rho a(r_1)\rho b(r_2)}{r_{12}}\, dr_1 dr_2 - Z_b \int \frac{\rho a(r_1)}{r_{1b}}\, dr_1 - Z_a \int \frac{\rho b(r_2)}{r_{2a}}\, dr_2$$

where Z_a and Z_b are nuclear charges, R the internuclear distance, r_{12} the separation of electrons 1 and 2, r_{1b} the separation of electron 1 and nucleus b and $\rho a(r_1)$ the electron density arising from ion a evaluated at a distance of r_1 from the nucleus of a. The Hartree–Fock portion of the energy density of an electron gas is given by:

$$E_{\mathrm{HF}}(\rho) = \frac{3}{10}(3\pi^2)^{2/3}\rho^{2/3} - \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\rho^{1/3}$$

where the terms represent kinetic energy and exchange energy, respectively. The energy arising from the correlation of electron motions is then added, using a form described by Gordon and Kim (1972). If we then define the total energy density functional for an electron gas as:

$$E_G(\rho) = E_{\mathrm{HF}}(\rho) + E_{\mathrm{corr}}(\rho)$$

the contribution of this term to the interaction energy becomes:

$$V_G = \int dr\ \{[\rho a(r_a) + \rho b(r_b)]E_G(\rho a + \rho b) - \rho a(r_a)E_G(\rho a) - \rho b(r_b)E_G(\rho b)\}$$

The total interaction energy is just the sum of V_{Coul} and V_G. POTLSURF (Green and Gordon, 1974) was used to calculate interaction energies between closed shell atoms and ions using this method; it is available from the Quantum Chemistry Program Exchange (program number 251). All results presented here were obtained using this program.

Once the ion–ion interaction energy has been calculated, it can be partitioned into the sum of a long-range point-charge Coulombic term and a short-range ion-pair repulsion term. The sum of the point-charge Coulombic terms for an entire solid may be obtained simply from the nearest-neighbor distance and the Madelung constant. Madelung constants for simple structures have been tabulated (Johnson and Templeton, 1961); those for more complex structures can be evaluated by various general methods (Bertaut, 1952). Madelung constants used in this work were 1.633, 1.74756, 1.76268, 4.38 and 4.77, for the ZnS, NaCl, CsCl, quartz, and rutile structures, respectively. The total lattice energy is then given by this Madelung energy plus the sum of the short-range ion-pair repulsions. Generally, short-range repulsions between cation pairs are small enough to be neglected, and cation–anion and anion–anion repulsions need to be included only out to second-nearest neighbors (Cohen and Gordon, 1976). For example, the total lattice energy of MgO in the NaCl or Bl structure is given accurately by the sum of the Madelung energy, six times the Mg^{2+}–O^{2-} short-range pair repulsion energy, 6 times the O^{2-}–O^{2-} short-range repulsion, and 8 times the short-range repulsion of Mg^{2+} and O^{2-} second-nearest neighbors. Thus, the total lattice energy is constructed as a sum of pairwise interaction energies. Similar theoretical ionic models have been employed by others (Dienes *et al.,* 1975; Zhdanov and Pdyakov, 1977; Mackrodt and Stewart, 1979) and the results obtained are similar to those of Gordon and Kim (1972).

Note that no empirical parameterization is used in this method. The results may depend, however, upon the choice of free ion wavefunctions, as is discussed below for oxides. One can also incorporate correction factors which multiply the energy terms obtained from the free electron gas approximation so that they match experimental values of atom–atom interaction energies more closely (Cohen and Gordon, 1975). Such correction factors affect only slightly the results for the halides and oxides described here, and yield no significant general improvement.

In all the BeO, MgO, ZnO, and SiO_2 calculations, we used the Waldman–Gordon correction factors given in Table I of Cohen and Gordon (1975). For the Ti (III) halides, Clugston and Gordon (1977) obtained better distances and energies without the correction factors, so we did not use correction factors for the TiO_2 and FeO results reported here. Use of correction factors for the triatomic TiO_2 calculation was found to increase the calculated Ti–O distance by 0.05A and to raise ΔH_f° by about 67 kcal/mole, similar to the effect found by Clugston and Gordon (1977).

Once the total energy of the system with respect to the free gas phase ions has been evaluated, the heat of formation is obtained from the Born–Haber cycle by adding the ionization and sublimation energies of the cation obtained from National Standard Reference Data System tabulations (Moore, 1970; Stull and Prophet, 1970) and the O_2 dissociation energy and O^{2-} electron affinity used by Cohen and Gordon (1976), who estimated the enthalpy for the reaction $O + 2e^- \rightarrow O^{2-}$ to be 135(±7) kcal/mole. The total energy is evaluated at a number of different bond distances and the equilibrium geometry and heat of formation obtained by parabolic interpolation and compared with experimental values of distances (Sutton, 1958) and heats of formation (Stull and Prophet, 1970; Robie and Waldbaum, 1968).

Previous results

The MEG ionic model has been shown to yield highly accurate results for the alkali halides (Kim and Gordon, 1974; Cohen and Gordon, 1975). Calculated nearest-neighbor bond distances typically differ from experiment by 0.10A or less and calculated heats of formation are in error by less than 10 kcal/mole. This result holds both for alkali halide solids and for gaseous diatomics. Some typical results are shown in Table 1. In this and subsequent tables we have chosen to compare experimental and calculated heats of formation, rather than cohesive or lattice energies which correspond to formation of the solid from free gaseous ions. Such a comparison gives a more realistic estimate of the accuracy of the thermodynamic predictions, but also emphasizes the magnitude of our errors on a percentage basis, since the heat of formation is always considerably smaller than the lattice energy.

Although the Cs halides, which are most stable in the 8:8 coordinate CsCl crystal structure, have not yet been studied, the pressures for transformation of other alkali halides from the NaCl to CsCl poly-

Table 1. Calculated and experimental nearest-neighbor distances and heats of formation for gaseous and six coordinate solid chlorides using the MEG ionic model

	R(Å)		ΔH_f^o (kcal/mole)	
	calc.[a]	exp.[b]	calc.[a]	exp.[b]
NaCl (g)	2.34	2.36	-34	-43
KCl (g)	2.56	2.66	-51	-52
RbCl (g)	2.77	2.79	-49	-56
NaCl (s)	2.86	2.82	-96	-98
KCl (s)	3.07	3.15	-108	-104
RbCl (s)	3.19	3.29	-113	-103

a. Gordon and Kim (1972) Kim and Gordon (1974)
b. Experimental values from Gordon and Kim reference and from Tosi (1964).

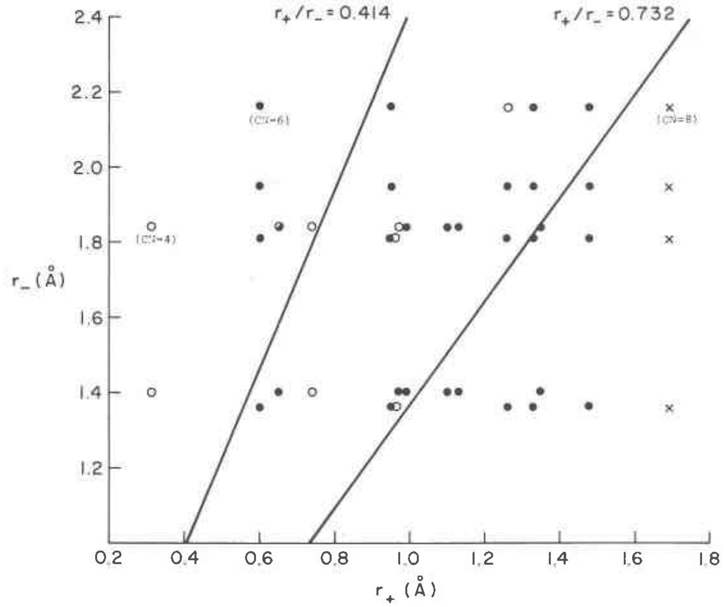

Fig. 1. Radius ratio *vs.* structure type for 44 halides and oxides. Radius ratios of 0.414 and 0.732 are shown by solid lines and observed coordination numbers shown as ×, ●, and ○ for 8, 6, and 4 coordination respectively. Radii are taken from Ahrens (1952).

morphs have been calculated (Kim and Gordon, 1974; Cohen and Gordon, 1975) and are in reasonably good agreement with experiment. Thus it appears that the relative stability of the 6 and 8 coordinate polymorphs of the alkali halides may be predicted accurately within the MEG model, without considering anion polarizability or other effects.

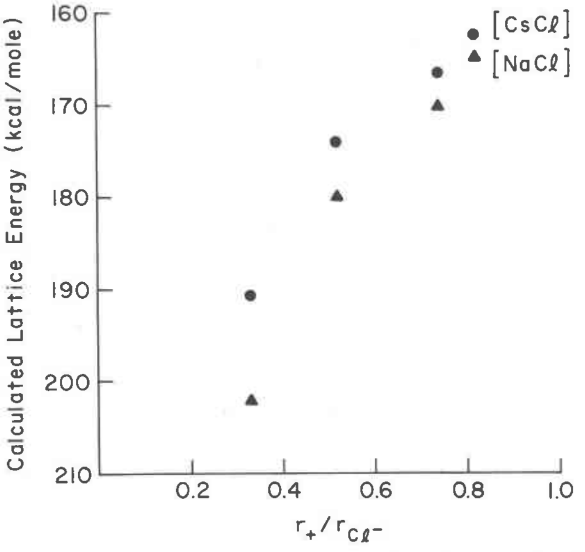

Fig. 2. Calculated lattice energies as a function of r_+/r_- for LiCl, NaCl, KCl, and RbCl in CsCl and NaCl structures (● for CsCl, ▲ for NaCl structures).

It is important to note that the variation in lattice energy with radius ratio obtained from MEG calculations for the NaCl and CsCl polymorphs of the alkali halides is much different from that suggested by many textbook diagrams. In traditional approaches the lattice energy of a given polymorph is assumed to become more negative as r_+/r_- decreases until the critical radius ratio for anion–anion contact is reached, at which point the energy remains constant as r_+/r_- decreases. Calculated MEG lattice energies for LiCl, NaCl, KCl, and RbCl, on the other hand, show a continuous lowering of the lattice energy of both NaCl and CsCl polymorphs as r_+ is reduced, as is shown in Figure 2. Although textbook diagrams of lattice energy *vs.* radius are of course expected to be only qualitatively correct, it is apparent that they are so seriously in error that they give a fundamentally incorrect idea of how lattice energy depends on distance and coordination number.

For the oxides MgO and CaO, the MEG model has also yielded reasonable results (Cohen and Gordon, 1976). Difficulty has arisen, however, in choosing the free oxide (O^{2-}) ion wave function to be used as input to the calculations. O^{2-} is not stable in the gas phase, but spontaneously dissociates to O^- plus an electron. The O^{2-} ion can, however, be stabilized by placing it in a potential well produced by an array of surrounding positive charges. A number of stabilized and unstabilized O^{2-} wavefunctions are available. Cohen and Gordon considered several and found the Yamashita and Asano (1970) wavefunction, obtained by stabilizing the O^{2-} inside a spherical shell of charge with magnitude +2, to give good bond distance predictions, heats of formation which were too negative, and bulk moduli which were much too small. The Watson (1958) O^{2-} wavefunction, with a stabilizing potential from a shell of +1 charge, gave bond distances rather well, heats of formation which were too positive, and good bulk moduli. For the calculations reported here, we have employed the Watson wavefunction and a wavefunction from Paschalis and Weiss (1969) using a +2 charge stabilizing sphere with a radius of 1.40A and employing a larger orbital basis set than did Yamashita and Asano (1970).

The difference in results for the different O^{2-} wavefunctions results from variations in their spatial diffuseness. The Watson +1 charge stabilized wavefunction has a larger probability at large distances from the nucleus than does the Paschalis and Weiss +2 stabilized wavefunction. In Figure 3 we plot the radial distribution function, $4\pi r^2|\Psi(r)|^2$, *vs.* r for the two wavefunctions to demonstrate this effect. Since the non-Coulombic part of the interaction between ion pairs arises primarily from the overlaps of the wavefunction "tails," the Watson wavefunction, with a higher tail, will give a larger short-range repulsion with a cation. Thus, the Watson wavefunction will lead to longer calculated equilibrium distances and less negative heats of formation. The +2 stabilized solution of Paschalis and Weiss has a lower tail than either the Watson or the Yamashita and Asano wavefunctions. Thus, calculations employing the Paschalis and Weiss +2 stabilized wavefunction give even shorter distances and more negative ΔH_f than those of Yamashita and Asano, although the difference is fairly small (.04A in R and 19 kcal/mole in ΔH_f for MgO). Note also that the stabilization produced by a shell of +2 charge at a radius of 1.40A is only about 80% as large as the Madelung potential at the O^{2-} site in MgO. Thus, the degree of stabilization giving the best results within the MEG model is actually fairly small.

The ΔH_f values calculated using the Yamashita and Asano or Paschalis and Weiss wavefunctions are sometimes found to be more negative than the experimentally-determined values. This suggests that our trial (ionic) wavefunction has a lower energy than the true wavefunction, which is inconsistent with the variation principle. This surprising result is simply a consequence of our neglect of the energy required to contract the O^{2-} wavefunction from its free ion form to its stabilized form. This energy has not yet been calculated. The neglect of this term will not affect the calculations of equilibrium bond distance, but it will systematically lower the ΔH_f° values.

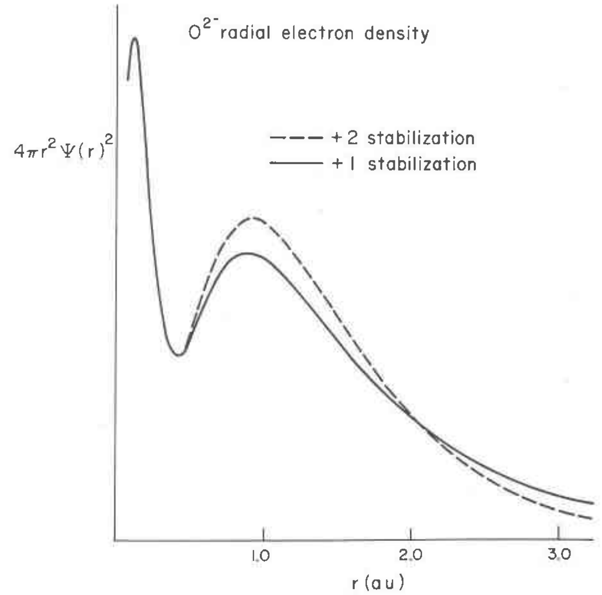

Fig. 3. Radial electron density ($4\pi r^2|\Psi(r)|^2$) for +2 stabilized Paschalis and Weiss (1969) and +1 stabilized Watson (1958) O^{2-} wavefunctions.

Our results correspond formally to the state of the system at 0 K with the zero-point vibrational energy neglected. Since distances and stabilities near 0 K are not generally known and since such temperature and zero-point effects are observed to be small, we will compare the theoretical results with experimental results obtained at standard temperature and pressure.

New results

Gaseous species

The equilibrium distances and energies for the gaseous species BeO, MgO, ZnO, and SiO_2 were calculated using a free unstabilized oxide ion wavefunction from Paschalis and Weiss (1969) and the +1 and +2 stabilized solutions described earlier. For later calculations on TiO_2 and FeO, only the Watson (1958) wavefunction was used, since it seemed to give the best results. These results are compared with the available experimental data in Table 2. Note that the characterization of these gas-phase species is often incomplete due to their instability with respect to the solid phase (and even with respect to the free elements). Although no experimental results are avail-

Table 2. Comparison of calculated and experimental equilibrium distances and heats of formation for gaseous metal oxides

	R(Å) calc.				ΔH_f^o (kcal/mole)			
	free[a]	+1[b]	+2[c]	exp.	free	+1	+2	exp.
BeO	1.40	1.30	1.19	1.33[d]	281	118	12	30 ± 3[g]
MgO	1.75	1.67	1.56	1.75[d]	215	106	39	1 ± 20[g]
ZnO	1.98	1.79	1.70	-	368	281	225	-
SiO_2[h]	1.64	1.48	1.38	(1.49)[e]	913	374	62	(-78)[e]
TiO_2[h]	-	1.59	-	-	-	263	-	-
FeO	-	1.83	-	1.63[f]	-	246	-	+60[g]

a. Paschalis and Weiss (1969), unstabilized
b. Watson (1953)
c. Paschalis and Weiss (1969), +2 stabilizing sphere
d. Herzberg (1950)
e. Pacansky and Herman (1978)
f. Engelking and Lineberger (1977)
g. Stull and Prophet (1970)
h. Linear ($D_{\infty h}$) geometry assumed

able for SiO_2, an accurate quantum-mechanical calculation (Pacansky and Hermann, 1978) using the *ab initio* Hartree–Fock method has recently predicted the properties given in Table 2.

From the data of Table 2 it is apparent that the best distance predictions are obtained from either the free or the +1 stabilized ion results. The use of a free ion wavefunction is inherently more reasonable for a diatomic or triatomic molecule than for a solid, since the stabilization by the cation array will be less in the small-molecule case. However, the calculated heats of formation are uniformly much too positive. Only the BeO +2 stabilized anion result lies within the experimental uncertainties. Comparison with the *ab initio* results indicates that the MEG method underestimates the stability of SiO_2(g) to a greater degree than it does that of BeO, MgO, or FeO. Although this result may be an artifact of the choice of O^{2-} ion wavefunctions in the calculations, it seems more probable that it arises from bond covalency, *i.e.* from a charge distribution in SiO_2(g) different from that obtained by the superposition of free ions.

Table 3. Calculated and experimental equilibrium M–O distances (in A) and heats of formation (in kcal/mole)

		BeO			MgO			ZnO		
Z		+2	+1	exp.	+2	+1[c]	exp.	+2	+1	exp.
4	R	1.70	1.84	1.64	1.94	2.12	~1.88[d]	2.14	2.33	1.95[a]
	ΔH_f^o	-212	-89*	-142*[b]	-229	-119	~133[e]	-39	+55	-83*[b]
6	R	1.79	1.99	-	2.06	2.29	2.10[a]	2.25	2.50	~2.09[d]
	ΔH_f^o	-232*	-73	-	-241*	-120*	-143*[b]	-68*	+53*	~71[e]
8	R				2.19	2.43	~2.28[d]	2.36	2.65	-
	ΔH_f^o				-215	-82	-	-44	+92	

a. Sutton (1958)
b. Stull and Prophet (1970)
c. 6 and 8 coordinate results from Cohen and Gordon (1976)
d. Changes in M-O estimated from Shannon and Prewitt (1969)
e. ΔH_f^o differences obtained from Navrotsky and Phillips

Solids

Calculated and experimental results are listed in Table 3 for the 4 (sphalerite), 6, and 8 coordinate polymorphs of BeO, MgO, and ZnO. Since ion–ion short-range interactions are included only through second-nearest neighbors, our method distinguishes between sphalerite and wurtzite structure only in using a 0.2% larger Madelung constant for the wurtzite structure (Waddington, 1959). This leads to an enthalpy difference of no more than 3 kcal/mole, and we can thus ignore this distinction and consider the sphalerite results as representative of four coordination. For BeO and MgO the experimental results lie between the +1 and +2 stabilized ion results. For all three oxide solids, calculations using the free unstabilized O^{2-} ion give bond distances which are much too long and heat of formation much too positive, which demonstrates their unsuitability for studies of solids. Results obtained using the unstabilized ion are consequently not shown. As expected, the calculated bond distances increase with coordination number, at a rate similar to that predicted from Shannon and Prewitt's (1969) radii. For each calculation and the experimental data, the most stable polymorph is indicated by an asterisk. Clearly the calculated heats of formation for the different polymorphs of BeO and MgO are quite similar. The +2 stabilized oxide wavefunction predicts the 6 coordinate polymorph to be most stable for both BeO and MgO because it gives an erroneously low value for the cation–anion repulsion, which is larger in the 6 coordinate form. The +1 stabilized wavefunction predicts correct coordination numbers for both BeO and MgO, although the calculated difference of ΔH_f for the four and six coordinate forms of MgO is essentially zero. For ZnO both oxide wavefunctions give too long a bond distance and too positive a ΔH_f by rather large amounts, and both predict ZnO to be most stable in six coordination, in disagreement with experiment.

Calculated bond distances and energies are given for the β-quartz and rutile forms of SiO_2 and TiO_2 and for sphalerite and NaCl forms of FeO in Table 4. The calculation of Madelung constants for quartz and rutile structures is reasonably difficult, since the constants depend upon the details of the crystal structure. We have therefore used only the Madelung constants corresponding to the observed structures (Hylleras, 1927; Baur, 1961) and have not considered the effect of variation of the *c/a* ratio or fractional coordinate of the anion within the unit cell. In addition, the short-range repulsions have been evaluated only for the average M–O distance in the structure rather than for the range of values actually observed and only using the +1 stabilized oxide wavefunction. Thus, the results for SiO_2 and TiO_2 must be considered preliminary. However, it is clear that for both SiO_2 and TiO_2 calculated and experimental heats of formation differ greatly, which suggests important covalency contributions to the stability of these compounds. On the other hand, the internuclear distances are predicted with reasonable accuracy, as was the case for gaseous SiO_2, and the preferred coordination numbers are correctly predicted. The results for TiO_2 are also similar to the results of Clugston and Gordon (1977) for $TiC1_3$; they obtained an accurate Ti–C1 distance prediction but a heat of formation about 280 kcal/mole more positive than experimental values.

For FeO the calculated bond distance and heat of formation show errors of magnitude intermediate between those for MgO and ZnO. Since Fe^{2+} in FeO has a nonspherical 3*d* shell it will experience a crystal field stabilization energy (CFSE) leading to a reduced bond distance and a lower heat of formation. Since the MEG method seems to seriously underestimate crystal field splittings (Clugston and Gordon, 1977), we have chosen to include this effect semiempirically, setting the CFSE to be 11.9 kcal/mole at 2.17A (Burns, 1970, Table 2.4) and scaling it as R^{-5}. Since the calculated minimum energy FeO distance in the absence of CFSE is quite long (2.38A), this CFSE correction is small and so has only the small effect on distance and energy shown in Table 4. A more accurate, shorter value for Fe–O distance in the absence of CFSE would have led to a larger, more realistic CFSE contribution.

In addition to calculating bond distances and heats of formation, we can also use the MEG results to evaluate elastic properties, such as bulk moduli. The general formula for the bulk modulus of an isotropic crystal is $B = V\,(d^2U)/(dV^2)$, where V is the volume and U the enthalpy. This reduces to $(1/18R)\,[d^2U(R)]/dR^2$ for the NaC1 structure and $1/(16\sqrt{3}R)\,[d^2U(R)]/dR^2$ for sphalerite. Thus, only the equilibrium distance and the dependence of total energy upon distance is required to obtain B. Calculated values using the Watson +1 stabilized O^{2-} wavefunction are listed in Table 5; they show significant departures from experimental values. For BeO, MgO, and CaO, which are most ionic, calculated B values are too large while for the more covalent ZnO the B value is too small. The largest error occurs for FeO. Since this approach underestimates the CFSE contribution in FeO, we have chosen to ignore it. Thus, this result is in much poorer agreement with experiment than that obtained by Ohnishi and Mizutani (1978), who evaluated semiempirically both crystal field and non-crystal field parts of the FeO bulk modulus.

Table 4. Equilibrium distances and heats of formation for SiO_2, TiO_2, and FeO

		SiO_2		TiO_2		FeO		
Z		calc.	exp.	calc.	exp.	calc.	calc. with CFSE	exp.
4	R	1.69	1.61[a]	1.82	~1.84[d]	2.24	2.23	2.03[s]
	ΔH	+88*	-218*[b]	-29	-	+15	+10	
6	R	1.93	1.78[c]	2.01	1.96[a]	2.38	2.36	2.17[f]
	ΔH	+139	-206[b]	-47*	-225*[e]	+5*	-2	-64*[e]

a. Sutton (1958)
b. Robie and Waldbaum (1968)
c. Sinclair and Ringwood (1978)
d. estimated from Shannon and Prewitt (1969) four vs. six coordination radii differences
e. Stull and Prophet (1970)
f. from Shannon and Prewitt (1969) radii

Discussion

Although none of the oxides considered here is described as accurately by the MEG model as were the alkali halides, it is clear that the model gives considerably more accurate heats of formation for BeO, MgO, and FeO than for ZnO, SiO_2, and TiO_2. With modest adjustment in the nature of the O^{2-} wavefunction, it will probably be possible to predict preferred coordination numbers and heats of formation of BeO and MgO with fair accuracy, while for ZnO, SiO_2, and TiO_2 calculated energies will be seriously in error no matter what O^{2-} wavefunction is used.

Table 5. Calculated and experimental bulk moduli (in megabars) using Watson (1958) +1 stabilized O^{2-} wavefunction

	calc.	exp.
BeO (z=4)	2.58	2.20[a]
MgO (z=6)	1.70	1.62[a]
ZnO (z=4)	1.18	1.39[a]
CaO (z=6)	1.34	1.06[a]
FeO (z=6)	1.23	1.74[b]

a. Anderson and Anderson (1970)
b. Mizutani et al. (1972)

Table 6. Comparison of MEG site energies with those of Ohashi and Burnham (1972) for Fe,Mg ordering in orthopyroxenes

	Colombic energy[a]		Repulsion energy		Total Site energy	
		kcal/mole	O & B	present	O & B	present
Orthoenstatite						
M1	-1252.3		220.2	269.6	-1032.1	-982.7
M2	-1129.3		187.6	226.6	-941.7	-902.7
				$U_{M_2} - U_{M_1}$	90.4	80.0
Orthoferrosilite						
M1	-1193.3		205.4	297.3	-987.9	-896.0
M2	-1097.3		187.7	273.7	-909.6	-823.6
				$U_{M_2} - U_{M_1}$	78.3	72.4

a. from Ohashi and Burnham (1972)

This difference might reasonably be ascribed to the greater covalency of the three latter oxides. The low coordination number of Zn in ZnO has often been attributed to covalency, and large covalency is also expected when the ions of the solid have high formal charges, as in SiO_2. Comparison of the MEG calculations with experimental values allows us to obtain a quantitative estimate of the effect of covalency upon the heat of formation.

Mineralogical applications

Although discrepancies between the MEG calculations and experiment are sizable, such calculations may nonetheless be of considerable value in explaining element partitioning between nonequivalent crystallographic sites in minerals. Ohashi and Burnham (1972) have calculated total site enthalpies in end-member orthopyroxenes, obtaining short-range Mg–O and Fe–O repulsions by fitting repulsive parameters to the experimental bulk moduli of MgO and FeO. They made the assumption that the enthalpy for ordering of Fe and Mg between the M1 and M2 sites of orthopyroxenes with intermediate compositions was equal to the difference between the M2–M1 site enthalpy difference for the Fe end member and that for the Mg end member. They obtained a value for this difference of 12 kcal/mole, which was later corrected to 5 kcal/mole based on an improved orthoenstatite crystal structure (Ohashi, private communication). Using the orthoenstatite structure of Morimoto and Koto (1969) and the orthoferrosilite structure of Sueno *et al.* (1976) and taking Ohashi and Burnham's (1972) values for electrostatic site energies, we obtain, using the MEG method, a difference of 8 kcal/mole, as shown in Table 6. The theoretical enthalpy differences are all somewhat larger than the observed free energy difference of 3.6 kcal/mole (Virgo and Hafner, 1969). Due to difficulty in obtaining equilibrium, ΔG has not been studied over the range of temperatures so ΔH is not known. In addition, the microscopic nature of the Mg and Fe coordination sites of intermediate orthopyroxenes has not been determined, but they are certainly not identical to the end member geometries assumed. A refinement of the ionic model calculation must await a better description of these microscopic structures. Once this information has been obtained, we can also include the difference of M1 and M2 crystal field stabilization energies, estimated to be less than 1 kcal/mole (Burns, 1970, p. 104).

Table 7. Comparison of Mineyeva (1974) and MEG site energies for Fe,Mg ordering in ludwigite

Site	Coulombic[a] Energy	kcal/mole	Repulsion Energy Mineyeva	Repulsion Energy Present	Total Site Energy Mineyeva	Total Site Energy Present
M1	-1960		297	251	-1663	-1709
M2	-2068		333	256	-1735	-1812
M3	-2166		599	270	-1567	-1896

a. from Mineyeva (1974)

Mineyeva (1974) has also used a semiempirical version of the ionic model to explain the distribution of Fe and Mg among the M1, M2, and M3 positions in ludwigite, $(Mg,Fe^{2+})_2(Fe^{3+},Al)BO_3O_2$. He had earlier concluded that Fe^{2+} ions preferentially entered positions with less negative site potentials. The total site potentials (ionic + repulsive) which he calculated were least negative for the M3 site, consistent with the preferential occupation of M3 by Fe observed in Mössbauer spectroscopy (Kurash *et al.*, 1972). However, using Mineyeva's Coulombic potentials and the crystal structure of Mokeyeva and Alexandrov (1968) to calculate MEG short-range Mg^{2+}–O^{2-} energies for the three sites, the M1 and M2 sites actually have less negative potentials than does the M3, suggesting that Fe should prefer them. These results are compared with Mineyeva's in Table 7. A careful inspection of Mineyeva's procedure suggests that the difference of results arises from his choice of different wavefunctions for oxygens depending upon whether or not they form part of a BO_3^{3-} group; the overlap repulsion with Mg is assumed to be much greater if the oxygens are not in a BO_3^{3-} group. Since four of the six oxygens in the M1 and M2 sites and only two of six for M3 are part of a borate group, the overlap repulsion effect is consequently greater for M3. This assumption is qualitatively reasonable and could be tested by performing MEG calculations on the Mg^{2+}–BO_3^{3-} ion pair in different orientations. Such work is planned for the future. It is also clear that a more rigorous way to approach the problem would be to calculate site potentials for Fe^{2+} ions in the Fe end member of the series and to then compare M1, M2, and M3 site potential differences for Mg^{2+} and Fe^{2+}, as was done for the orthopyroxenes. Such a procedure must await further crystallographic work on the ludwigites.

Covalency corrections

An additional area for future work will be in the development of covalency corrections to the MEG model. With a sound ionic model basis, such corrections could be made in a semiempirical way by fitting differences of calculated and experimental heats of formation to atomic properties. For example, the error in ΔH_f° per oxygen for these oxides seems to be qualitatively related to the differences of metal and oxygen electronegativities (Fig. 4). There is, however, considerable scatter of the points from either a linear or a quadratic plot. More fruitful semiempirical approaches may include the dielectric approach to bond character developed by Phillips and Van Vechten (1970) or spectroscopic approaches focusing upon valence orbital ionization potential differences (Kowalczyk *et al.*, 1974; Tossell, 1976).

An approach more in keeping with the rigor of the MEG method and with its concentration upon electron density as the primary physical quantity in the description of the chemical bond would be to evaluate the difference between the experimental electron distribution and the superimposed ion electron distribution and to estimate the energetic effect of this difference. Experimentally, one can combine X-ray and neutron diffraction to obtain total valence electron densities (Coppens, 1977) from which superimposed free ion densities can be subtracted. *Ab initio* Hartree–Fock self-consistent-field (SCF) quantum-mechanical calculations have also often yielded differences of total electron densities and superimposed free atom or ion densities in agreement with experiment. The difference densities so obtained could be used with density functional theory to estimate the covalency correction (Payne, 1978). SCF calculations, starting with a superimposed free ion charge distribution, could give directly the stabilization due to covalency. By such a rigorous separation of ionic and covalent contributions to the electron density and the total energy, we would obtain a considerably more detailed understanding of the nature of covalency in these oxides.

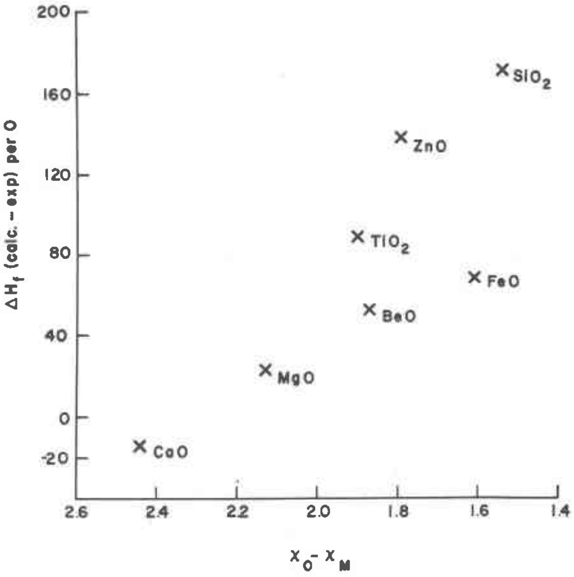

Fig. 4. Difference (per oxygen) of experimental and calculated heats of formation for metal oxides *vs.* electronegativity difference of metal and oxygen $\Delta\chi$ (+1 stabilized O^{2-} results used; electronegativities from Pauling, 1960).

Conclusions

The MEG method makes possible the purely theoretical quantitative prediction of bond distances, heats of formation, and preferred coordination numbers in ionic compounds such as the alkali halides and, to a lesser extent, in BeO, MgO, and CaO. For compounds possessing appreciable covalency, such as ZnO, SiO_2, and TiO_2 the method provides an ionic limit reference point, allowing a quantitative estimate of the covalency contribution to ΔH_f°. The method in its present form may well yield useful predictions of element site distributions. However, reliable means for estimating covalency contributions must be developed before accurate energies can be obtained for the vast majority of silicate minerals.

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