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Lattice Energies of Crystals with Multiple Ions: A Generalized Kapustinskii Equation

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A remarkably successful empirical equation for the evaluation of the lattice energies of binary ionic crystals has been developed by Kapustinskii[1] and extended by himself and Yatsimirskii.[2] This equation was based on the Born−Landé or (more reliably) the Born−Mayer equation for a 1:1 system of charges, consisting of a coulomb attractive term and an overlap repulsive term:

$$U = \frac{ALe^2}{4\pi\epsilon_o}\frac{z_+z_-}{r_o}\left(1 - \frac{\varrho}{r_o}\right) \tag{1}$$

Here A = Madelung constant for the crystal lattice, L = Avogadro's constant, e = electronic charge, z_+, z_- = cation, anion charges in electron units, r_o = center-to-center spacing of ions = $r_+ + r_-$ = sum of cation and anion radii, ϱ = "softness" parameter. Kapustinskii's insight was to note that A/n (where n = sum of ions per formula unit) is approximately constant for a number of crystal structures, and that (A/nr_o) is even less variable. Hence, it becomes possible to replace the factor (A/nr_o) for any binary (not necessarily 1:1) ionic structure by the corresponding value for the six-coordinate sodium chloride structure, while using the six-coordinate values for the actual ion radii, r_+ and r_-. This substitution yields

$$U = \frac{Bz_+z_-n}{(r_+ + r_-)}\left[1 - \frac{0.345}{r_+ + r_-}\right] \tag{2}$$

where ϱ = 0.345 Å is chosen as a representative value for the alkali metal NaCl-type structures, and B = (2427.8/2) kJ Å mol^{-1} (where the divisor 2 compensates for the introduced factor, n).

This equation provides excellent estimates of lattice energies[3−5] in conjunction with Goldschmidt ionic radii,[3] often to better than 5% of the experimental value but generally on the low side.[5] Among the most significant uses of lattice energy estimation was in the prediction by Bartlett[6] of the stability of the xenon complex, $XePtF_6$. The Kapustinskii concept has also been extended to complex salts, treated as binary systems, by assigning notional "thermochemical radii" to complex ions, such as sulfate.[4,5,7]

There are two principal problems with the Kapustinskii equation. First, r_o is simply treated as the sum of cation and anion radii without consideration of structural details[5] such as noncontact of the ions. Second, the form of the equation does not permit extension to mixed ion systems, such as $Ca_2Fe_2O_5$ or Fe_3O_4 (which contains Fe^{2+}, Fe^{3+}, and O^{2-} ions); this second restriction does not seem to have been commented on before. The following generalization of the Kapustinskii equation overcomes the second problem.

A quantity characterizing the interactions among a system of charges is the sum

$$\sum_{i>j}^{n} z_iz_j$$

where n = number of charges in the system. If we deal with a neutral chemical formula unit, for example, $A_{n_1}B_{n_2}X_{n_3}Y_{n_4}$—with obvious generalizations—having corresponding ionic charges, z_1, z_2, ..., then it is possible to count and sum the various interaction terms, to yield the result

$$\sum_{i>j}^{n} z_iz_j = -{}^1/_2\sum_{k}^{t} n_kz_k^2 \tag{3}$$

where t = number of types of ion in the formula unit, each of number, n_k, and charge z_k.

It may be noted that the term on the right corresponds to the negative of the ionic strength, I; the ionic strength is a standard quantity in electrochemical theory[8,9] (but not usually acknowledged in solid-state theory) and is a measure of the intensity of the electrical field due to the set of ions.[9] Equation 3 seems not to have previously been noted. Further, for a neutral binary ionic system, $A_{n+}X_{n-}$, eq 3 simplifies as follows:

$$-{}^1/_2\sum_{i} n_kz_k^2 = {}^1/_2 z_+z_-n \tag{4}$$

This is exactly the term introduced into the Born−Mayer equation by Kapustinskii and has the necessary property of proportionality to the size of the formula unit. This suggests substitution of the ionic strength expression for the Kapustinskii term, to yield the generalized equation

$$U/\text{kJ mol}^{-1} = -\frac{1213.9}{\langle r\rangle}\left(1 - \frac{\varrho}{\langle r\rangle}\right)\sum n_kz_k^2 \tag{5}$$

where $\langle r\rangle$ = weighted mean ion radius sum.

The mean radius sum which must be used in eq 5 is rather nebulous, and it might be expected to include terms for all the (unknown, in principle) actual ion−ion distances. Experimentation with various possibilities, such as the mean radius sum (including cation−anion, cation−cation, and anion−anion terms), a weighted mean radius sum, and weighted mean cation−anion radius sum, have shown the last to be the only reliable measure. The weighting consists of the number of each kind of cation−anion pair (for example, in $MgAl_2O_4$ there are four Mg−O pairs and eight Al−O pairs). The following results are based on this last measure.

For binary systems, the generalized form of the equation is identical to the Kapustinskii form. Therefore, Table 1 provides a test of the generalized equation beyond binary systems, using the Ti−O series, which (except for TiO) we have recently studied by crystal structure modeling techniques using the

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Table 1. Evaluation of Lattice Energy Predictions

Ti−O series	$\langle r\rangle^a$/Å	ionic strength, $I = -\frac{1}{2}\sum n_k z_k^2$	lattice energy/kJ mol^{-1}			$(U_K - U_M/U_M)$/%
			predicted, $-U_K$ (eq 5)	modeled,[b] $-U_M$	lit.,[c] U_L	
TiO	2.12	−4	3835		3832 (3810−4013)	
TiO_2: rutile	1.96	−12	12248	11830	12150	3.5
anatase				11860	(10163−12351)	
brookite				11820		
TiO_2(II)				11810		
Ti_2O_3	2.01	−15	15008	14820	14702 (14258−14990)	1.3
Ti_3O_5: low temp	1.99	−27	27193	26580		2.3
high temp				26560	(24594)	
Ti_4O_7	1.99	−39	38409	38490	35445[d]	−0.2

[a] $\langle r\rangle$ = weighted mean cation−anion radius sum (using Goldschmidt radii)[3], for use in the generalized Kapustinskii equation, (5). [b] Modeling of structures in Ti−O series by H. le Roux and L. Glasser: details to be published. [c] Jenkins, H. D. B. in *Handbook of Chemistry and Physics*, 73 ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1992. Ranges in parentheses were provided in a personal communication by H. D. B. Jenkins (Warwick). [d] Data from ref 11.

program WMIN,[10] generating lattice energies in the process. The model we use consists of a "shell" model for the oxide ion, repulsive terms for $Ti^{4+}-O^{2-}$ and $Ti^{3+}-O^{2-}$ (the latter over two ranges to allow for ferroelectric interactions), together with a coulomb sum for the ions (including an Ewald summation to accelerate convergence). The potential parameters, which have been simultaneously optimised over the full set of structures, yield relaxed unit cell volumes within 2% of the experimental values for all the structures, while all lattice constants lie within 4% of the experimental values. Details of these calculations will be published in due course.

As can be seen in Table 1, the generalized equation (using Goldschmidt 6-coordinate radii and the NaCl-type Madelung constant) yields excellent agreement with the modeled results; the generally larger Pauling radii are not as successful. (Of course, the Kapustinskii equations cannot distinguish among polymorphs.)

It now becomes possible to predict the lattice energies of a host of ionic structures containing multiple ionic species. We report in Table 2 on a series of ternary oxides recently modeled by Bush *et al.*,[12] who have developed a consistent set of pair potentials for a large group of binary and ternary oxides, also yielding lattice energies. Table 2 shows that the generalized Kapustinskii equation successfully predicts these results, with very little error.

Table 2 also reports some predictions for iron oxides, which match the literature values rather well. On this basis, we predict in Table 2 the lattice energy of Fe_3O_4—which does not appear in the literature.

Table 2. Lattice Energy Predictions for Complex Oxides

ternary oxides	$\langle r\rangle^a$/Å	ionic strength, $I = -\frac{1}{2}\sum n_k z_k^2$	lattice energy/kJ mol^{-1}		
			predicted, $-U_K$ (eq 5)	modeled,[b] $-U_M$	$(U_K - U_M/U_M)$/%
$Ca_2Fe_2O_5$	2.19	−23	21521	21811	−1.3
$MgAl_2O_4$	1.96	−19	19392	19269	0.6
$LaAlO_3$	2.22	−15	13880	13856	0.2
$NdFeO_3$	2.23	−15	13804	13856	−0.4
$Y_3Fe_5O_{12}$	2.14	−60	57176	56504	1.2
$Y_3Al_5O_{12}$	2.07	−60	58558	58006	1.0

iron oxides	$\langle r\rangle^a$/Å	ionic strength, $I = -\frac{1}{2}\sum n_k z_k^2$	lattice energy/kJ mol^{-1}		$(U_K - U_L/U_M)$/%
			predicted, $-U_K$ (eq 5)	lit.,[c] U_L	
FeO	2.14	−4	3806	3795 (3849−3988)	0.3
Fe_2O_3	1.99	−15	15127	14309 (15121−15361)	5.7
Fe_3O_4	2.04	−19	18788		

[a] $\langle r\rangle$ = weighted mean cation−anion radius sum (using Goldschmidt radii)[3], for use in the generalized Kapustinskii equation, (5). [b] Data from ref 12. [c] Jenkins, H. D. B. in *Handbook of Chemistry and Physics*, 73 ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1992. Ranges in parentheses were provided in a personal communication by H. D. B. Jenkins (Warwick).

In summary, the newly-generalized Kapustinskii equation, (5), provides a means of predicting, within a few percent, lattice energies of crystals containing multiple ions based on their ionic radii or using thermochemical radii for complex ions.

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