Inorg. Chem. **2003**, *42*, 2465–2469

Inorganic Chemistry Article

Lattice Energy Estimation for Inorganic Ionic Crystals

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Received July 24, 2002

An empirical method based on chemical bond theory for the estimation of the lattice energy for ionic crystals has been proposed. The lattice energy contributions have been partitioned into bond dependent terms. For an individual bond, the lattice energy contribution made by it has been separated into ionic and covalent parts. Our calculated values of lattice energies agree well with available experimental and theoretical values for diverse ionic crystals. This method, which requires detailed crystallographic information and elaborate computation, might be extended and possibly yield further insights with respect to bond properties of materials.

Introduction

The lattice energy of ionic crystals plays an important role in diverse thermodynamic analysis of the existence and stability of ionic crystals. It is one of the most important quantities in elucidating the structure, character, and behavior (reactivity) of solids. Considering a crystal with a general formula A_mB_n, the lattice energy can be defined as an energy change for the process

$$A_mB_n(c) \rightarrow mA^{\alpha n^+}(g) + nB^{\alpha m^-}(g) \qquad (1)$$

where α is the multiplicator accounting for the actual valence of both ions. Although lattice energy can be determined experimentally from the Born–Haber thermochemical cycle,[1] direct measurement is very difficult. Therefore, computation or estimation of lattice energy is of considerable interest in modern materials science.

Theoretical studies on lattice energy have been carried out almost since the beginning of 1900s, and a variety of estimation methods for lattice energies were available.[2−12] Born and Lande[2] proposed the Born–Lande equation for the lattice energy calculation for ionic solids, which was later improved by Born and Mayer.[3] The disadvantage of their equations is that they can only be applied to binary systems. On the basis of their work, Kapustinskii developed these equations[4−7] to permit evaluation of the lattice energy of any simple ionic crystal not yet investigated by X-ray measurement. Although it is only an approximation of Born and Mayer's equation,[3] it opens up a way for extending the evaluation of lattice energy to various scientific investigations. Jenkins,[8,10−12] Glasser,[9−12] etc. have explored a series of simple approaches in recent years. Based on crystal formula, molecular (formula unit) volume,[10,11] and density,[12] their methods can be applicable for lattice energy estimation for more complex ionic solids.

In this study, based on a new idea, we have proposed an empirical approach on the basis of the chemical bond theory for the estimation of the lattice energy for both binary and complex ionic crystals. In this method, the lattice energy contributions have been divided into bond dependent terms. For an individual bond, the lattice energy contribution can be separated into ionic and covalent parts. These two parts of energies may be related to some special bond properties in future studies, such as force constants. In ionic crystals, van der Waals interactions, the zero-point energy, and the nonbonding interactions are neglected because of their relatively small contributions to the lattice energy. The stronger the ionicity of the bond, the better the results should be when using this method. Therefore, the lattice energies of many ionic materials, e.g., superconductor and colossal magnetoresistant materials that mainly comprise electrovalent bonds, can be calculated with good accuracy using this method.

Theoretical Method

Ionic crystals are made up of positive and negative ions, and the strongest interactions (ionic bonds) result from the

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10.1021/ic025902a CCC: $25.00
Published on Web 03/06/2003

nearest oppositely charged ions. The lattice energy contribution mainly originates from these nearest interactions; in other words, the sum of the "lattice energies" of these interacting ion pairs constituting ionic bonds would well represent the total lattice energy of the multibond crystals. It is known that there is no pure ionic bond in ionic crystals; even for CsF, the ionicity is about 0.96−0.97, not 1. This means that a cation cannot completely lose all its valence electron(s); there is more or less overlap of the electron clouds of the two nearest-neighbor atoms. Therefore, every bond will have nonzero ionicity and covalency in ionic crystals.

On the basis of the above ideas and our previous research on chemical bond theory,[15,17] we assume that the lattice energy of a single-bond crystal can be separated into ionic and covalent parts. The ionic contribution to the crystal lattice energy mainly results from electrostatic interactions and repulsive interactions of the ion pairs, and the covalent contribution arises from the overlap of electron clouds. In the following paragraphs, we will first establish the model for many single-bond binary crystals, and then extend it to complex (multibond) crystals. Two examples are also presented to illustrate how to make a calculation.

(i) Binary Ionic Crystals. The total lattice energy U_{cal} of a binary crystal with only one type of bond can be separated into the ionic part U_i and the covalent part U_c as follows:

$$U_{cal} = U_i + U_c \qquad (2)$$

To calculate the ionic contribution to the lattice energy, originally, we directly use Kapustinskii equation[5] multiplied by fractional ionicity f_i, but one will find that the parameters in our equation (eq 3) are different from those of Kapustinskii's.[5] In fact, our parameters, including B, C, and D, appearing in the following equation (eq 4), are obtained by fitting the lattice energies of about 50 binary compounds with only one type of bond when the best agreement between the calculated and experimental lattice energies is reached. These single-bond compounds that mainly comprise electrovalent bonds include alkali halides, alkaline earth chalcogenides, and some other binary crystals. They are not purely highly ionic, but partially covalent.

For a single-bond binary ionic crystal with a formula A_mB_n, the ionic part of its lattice energy U_i is given by the relation

$$U_i = \frac{1270(m+n)Z_+Z_-}{d}\left(1 - \frac{0.4}{d}\right) f_i \qquad (\text{kJ mol}^{-1}) \quad (3)$$

where d is the bond length (nearest-neighbor distance). Z_+ is the normal valence of the cation A. Z_- is obtained according to the neutral principle of the binary crystal. For binary crystal A_mB_n, Z_- is calculated from $Z_- = mZ_+/n$. For instance, for binary crystal with one type of bond like NaCl, we can easily get $Z_+ = 1.0$, $Z_- = 1.0$. For a more complex example like ZrO_2, we have $ZrO_2 = Zr_{3/7}O(1) + Zr_{4/7}O(2)$ (concerning the method to decompose ZrO_2 into the sum of binary crystals, see ref 17); for $Zr_{3/7}O(1)$, $Z_+ = 4.0$; then $Z_- = {}^3/_7 \times 4 = 1.7143$. Similarly, for $Zr_{4/7}O(2)$, $Z_+ = 4.0$, $Z_- = {}^4/_7 \times 4 = 2.2857$. So the entire charge of oxygen would be $1.7143 + 2.2857 = 4.0$, as meets the neutral principle of the molecule.

The covalent part of the lattice energies U_c should be related to f_c (fractional covalency of the bond), the electron charges on the cation Z_+, and the bond length d. It is expressed as follows:

$$U_c = Bm\frac{Z_+^{\,C}}{d^D} f_c \qquad (\text{kJ mol}^{-1}) \qquad (4)$$

where $B = 2100$, $C = 1.64$, and $D = 0.75$.

The definition of ionicity f_i and covalency f_c can be found in diverse literature both for binary crystals[12−16] and for complex crystals.[17−20] Therefore, only a brief discussion is given in this paper. Usually there are two ways to calculate f_i and f_c depending on the availability of dielectric constant or index of refraction. If the dielectric constant or index of refraction of the materials is not available, we can calculate f_i and f_c in the following way:

The fractional ionicity f_i^μ and the covalency f_c^μ of any individual bond μ in a multibond crystal can be defined as follows:

$$f_i^\mu = \frac{(C^\mu)^2}{(E_g^\mu)^2} \qquad f_c^\mu = \frac{(E_h^\mu)^2}{(E_g^\mu)^2} \qquad (5)$$

where E_g^μ is the average energy band gap and is composed of homopolar E_h^μ and heteropolar C^μ parts,

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2 \qquad (6)$$

where

$$E_h^\mu = \frac{39.74}{(d^\mu)^{2.48}} \qquad (\text{eV}) \qquad (7)$$

$$C^\mu = 14.4 b^\mu \exp(-k_s^\mu r_0^\mu)\left[\left(\frac{(Z_A^\mu)^*}{r_0^\mu} - (n/m)\frac{(Z_B^\mu)^*}{r_0^\mu}\right)\right] \qquad (\text{eV}) \quad (\text{if } n > m) \quad (8)$$

$$C^\mu = 14.4 b^\mu \exp(-k_s^\mu r_0^\mu)\left[(m/n)\frac{(Z_A^\mu)^*}{r_0^\mu} - \frac{(Z_B^\mu)^*}{r_0^\mu}\right] \qquad (\text{eV}) \quad (\text{if } m > n) \quad (8')$$

where b^μ is a correction factor that is proportional to the square of the average coordination number N_c^μ,

$$b^\mu = \beta(N_c^\mu)^2 \qquad (9)$$

This correction factor β depends on a given crystal structure;

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for general binary crystals it is approximately a constant and equal to 0.089.[15]

$$N_c^\mu = \frac{m}{m+n} N_{CA}^\mu + \frac{n}{m+n} N_{CB}^\mu \quad (10)$$

N_{CA}^μ is the coordination number of μ type of bond for cation A, and N_{CB}^μ is the coordination number of μ type of bond for anion B.

$\exp(-k_s^\mu r_0^\mu)$ is the Thomas−Fermi screening factor,

$$k_s^\mu = \left(\frac{4k_F^\mu}{\pi a_B}\right)^{1/2} \quad (11)$$

$$k_F^\mu = [3\pi^2 (N_e^\mu)^*]^{1/3} \quad (12)$$

where a_B is the Bohr radius and has the value 0.5292 Å and r_0^μ is the average radius of A and B in angstroms, which is equal to a half of the nearest-neighbor distance,

$$r_0^\mu = d^\mu/2 \quad (13)$$

$(N_e^\mu)^*$ is the number of valence electrons of μ bond per cubic centimeter:

$$(N_e^\mu)^* = \frac{(n_e^\mu)^*}{v_b^\mu} \quad (14)$$

The number of effective valence electrons $(n_e^\mu)^*$ per μ bond is

$$(n_e^\mu)^* = \frac{(Z_A^\mu)^*}{N_{CA}^\mu} + \frac{(Z_B^\mu)^*}{N_{CB}^\mu} \quad (15)$$

where $(Z_A^\mu)^*$ is the effective number of valence electrons on the cation A and $(Z_B^\mu)^*$ is the effective number of valence electrons on the anion B. It should be indicated that they are different from Z_+ and Z_- appearing in eqs 3 and 4. Again take NaCl as an example, $(Z_A^\mu)^* = 1$, $(Z_B^\mu)^* = 7$. For more discussion on $(Z_A^\mu)^*$ and $(Z_B^\mu)^*$, see refs 15 and 17. The bond volume v_b^μ for the bond of μ type is

$$v_b^\mu = \frac{(d^\mu)^3}{\sum_\nu (d^\nu)^3 N_b^\nu} \quad (16)$$

where the denominator is a normalized factor and the summation over ν extends over all the different types of bonds. N_b^μ is the number of bonds per cubic centimeter, which can be obtained from the crystal structural data.

In the case that the dielectric constant ϵ or index of refraction n is available, we will first calculate the linear susceptibility χ by

$$\epsilon = n^2 = 1 + 4\pi\chi \quad (17)$$

$$\chi = \sum_\mu F^\mu \chi_b^\mu = \sum_\mu N_b^\mu \chi_b^\mu \quad (18)$$

where χ^μ is the total macroscopic susceptibility which a crystal composed entirely of bonds of type μ would have. F^μ is the fraction of bonds of type μ composing the actual complex crystal, and χ_b^μ is the susceptibility of a single bond of type μ.

According to the Phillips−van Vechten theory, the susceptibility of any bond μ is expressed as

$$\chi^\mu = \frac{1}{4\pi}\left(\frac{\hbar\Omega_p^\mu}{E_g^\mu}\right)^2 \quad (19)$$

where Ω_p^μ is the plasma frequency,

$$(\Omega_p^\mu)^2 = \frac{4\pi (N_e^\mu)^* e^2 D_\mu A_\mu}{m} \quad (20)$$

where D_μ and A_μ are the coordination factors defined in ref 15. e and m are the electronic charge and mass, respectively.

After $(N_e^\mu)^*$ is obtained from crystal structural data (eqs 14−16), considering that A_μ depends on E_g,[15] substitute Ω_p^μ into eq 19; then E_g can be obtained after solving eq 19. Using eqs 6 and 7, C^μ can be determined. Therefore, f_i and f_c can be calculated using eq 5. It should be pointed out that, for a binary crystal with only one type of bond like NaCl, it is relatively easy to calculate f_i, but for the complex (multibond) crystal, elaborate computation is required to obtain f_i^μ; for more discussion see refs 15 and 17.

(ii) Complex Ionic Crystals. From our previous study, it is known that complex crystals can be decomposed into the binary crystals.[17−20] On the basis of this idea, the total lattice energy U_{cal} of a complex crystal can be written as

$$U_{cal} = \sum_\mu U_b^\mu \quad (21)$$

$$U_b^\mu = U_{bc}^\mu + U_{bi}^\mu \quad (22)$$

$$U_{bc}^\mu = 2100m \frac{(Z_+^\mu)^{1.64}}{(d^\mu)^{0.75}} f_c^\mu \quad (23)$$

Z_+^μ and Z_-^μ are the valence states of cation and anion that

$$U_{bi}^\mu = 1270 \frac{(m+n) Z_+^\mu Z_-^\mu}{d^\mu}\left(1 - \frac{0.4}{d^\mu}\right) f_i^\mu \quad (24)$$

constitute bond μ. U_b^μ is the lattice energy of the corresponding binary crystals. The summation runs over all the bonds in the complex crystal.

(iii) Examples. In order to illustrate how to make a calculation, we will give two examples. One is the binary crystal NaCl, and the other is complex ionic crystal $LaCrO_3$.

(1) Binary Crystal NaCl. The evaluation of bond ionicity f_i is not the emphasis of this paper, so we give only a brief description of how it is calculated. For more details, see refs 15 and 17. In this part, the superscript μ is omitted since there is only one type of bond in NaCl. The dielectric constant of NaCl is 2.3,[15] and the unit cell constant is $a =$

Table 1. Bond Lengths (d in Å), Bond Ionicity (f_i), and Calculated Values of U_c, U_i, and U_{cal} (All in kJ mol^{-1}) of Some Simple Crystals (with Only One Type of Bond)[a]

crystal	d[b]	f_i[c]	U_c	U_i	U_{cal}	U_{ref}[d]	U_{exp}[d]
LiF	2.01	0.914	107	925.2	1032	1028	1036
NaCl	2.82	0.936	62	723	785	805	786
KI	3.53	0.948	42	605	647	656	649
RbCl	3.29	0.956	38	648	686	690	689
CsBr	3.62	0.965	28	602	630	625	631
CuCl	2.34	0.882	131	794	925	921	996
BeS	2.105	0.611	1457	2389	3846	3927	3910
MgTe	2.77	0.589	1253	1848	3101	2878	3081
CaO	2.405	0.916	295	3215	3510	3414	3401
SrS	3.01	0.917	238	2684	2922	3006	2848
BaTe	3.179	0.897	283	2506	2789	2721	2843
MnO	2.22	0.887	406	3325	3731	3724	3745
CoO	2.13	0.858	527	3324	3851	3837	3910
MgF_2	1.992	0.911	347	2785	3132	2913	2957
$SrCl_2$	2.99	0.968	92	2137	2229	2127	2156
LaN	2.65	0.759	1477	5559	7036	6876	6793
NbN	2.35	0.720	1877	5812	7689	7939	8022
GeO_2	1.88	0.730	3430	9317	12748	12828	
SnO_2	2.054	0.784	2735	9201	11936	11807	

[a] U_{ref} is the value by other theoretical methods. U_{exp} (thermochemical cycle lattice energy) is the experimental value. [b] References 15, 22, and 23. [c] References 15 and 16. [d] References 23 and 24.

Table 2. Bond Lengths (d^μ in Å), Bond Ionicity (f_i^μ) and Calculated Values of U_{bc}^μ, U_{bi}^μ, U_b^μ, and U_{cal} (All in kJ mol^{-1}) of Some Complex Crystals[a]

crystal	bond type	d^μ	f_i^μ	U_{bc}^μ	U_{bi}^μ	U_b^μ	U_{cal}[b]	U_{ref}[c]
ZrO_2	Zr−O(1)	2.088[d]	0.707[b]	1475	3406	4881		
	Zr−O(2)	2.206	0.842	1017	5702	6719	11600	11188
Al_2O_3	Al−O(1)	1.969[d]	0.797[b]	1554	6144	7699		
	Al−O(2)	1.856	0.792	1665	6377	8042	15740	15916
$MgAl_2O_4$	Mg−O	1.954[e]	0.566[e]	1719	2340	4059		19269
	Al−O	1.901	0.857	2248	13562	15810	19869	19192
$Y_3Al_5O_{12}$	Y−O	2.367[f]	0.934[f]	1320	16866	18186		59795
	Al(1)−O	1.937	0.869	2031	13563	15594	62280	58006
	Al(2)−O	1.761	0.688	7792	20707	28499		
$LaCrO_3$	La−O(1)	2.765[g]	0.9753	49	1724	1773		
	La−O(2)	2.757	0.9755	97	3457	3555		14608
	Cr−O(1)	1.975	0.8437	398	2596	2994	14316	13678
	Cr−O(2)	1.971	0.8417	807	5188	5995		
$NdFeO_3$	Nd−O(1)	2.8049[h]	0.9259[h]	145	1617	1763		14521
	Nd−O(2)	2.7820	0.9316	269	3277	3547	14190	13854
	Fe−O(1)	2.0106	0.8572	359	2602	2961		
	Fe−O(2)	2.0112	0.8557	725	5195	5920		

[a] U_{ref} is the value by other theoretical methods. [b] This work. [c] References 11 and 24. [d] Reference 21. [e] Reference 25. [f] Reference 26. [g] Reference 20. [h] Reference 18.

5.64056 Å ≈ 5.64 Å,[21] so $d = 2.82$ Å. The unit cell volume is $V_c = a^3$, $(Z_A)^* = 1$, $(Z_B)^* = 7$, and $N_{CA} = N_{CB} = 6$. Therefore, using eq 15, we have $(n_e)^* = 4/3$. Since there are four NaCl molecules and 24 bonds per unit cell, we have $N_b = 24/V_c$; the bond volume v_b from eq 16 is $v_b = V_c/24$. Thus using eq 14, $(N_e)^* = (n_e)^*/v_b = 24(n_e)^*/a^3 = 1.784 \times 10^{23}$ cm^{-3}. From eq 17, we get $\chi = 1.3$. $D = 1.0$.[15] Take $(N_e)^*$ and D into eq 20, and then Ω_p into eq 19; solving eq 19, we obtain $E_g = 12.0$ eV. Other parameters are $A = 0.7627$ and $\Omega_p = 2.08 \times 10^{16}$ s^{-1}. Since from eq 7, we get $E_g = 3.04$ eV, then using eq 6 we have $C = 11.62$ eV. Finally, from eq 5 we get $f_i = 0.936$. These results are exactly the same as those obtained by Levine.[15] Because Z_+, Z_-, f_i, and d have been obtained, using eqs 2, 3, and 4, we have $U_c = 62$ kJ mol^{-1}, $U_i = 723$ kJ mol^{-1}, and $U_{cal} = 785$ kJ mol^{-1}.

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Table 3. Bond Lengths (d^μ in Å), Bond Ionicity (f_i^μ), and Calculated Values of U_{bc}^μ, U_{bi}^μ, U_b^μ, and U_{cal} (All in kJ mol^{-1}) of Some Complex Crystals in Which Experimental Lattice Energies Are Not Available

crystal	bond type	d^μ	f_i^μ	U_{bc}^μ	U_{bi}^μ	U_b^μ	U_{cal}[a]
$ZnFe_2O_4$	Zn−O	1.97[b]	0.310[a]	2716	1274	3990	
	Fe−O	2.04	0.682	4742	10240	14982	18972
$FeAl_2O_4$	Fe−O	1.969[c]	0.506[c]	1945	2081	4026	
	Al−O	1.916	0.824	2751	12965	15715	19741
$YAlO_3$	Y−O	2.469[d]	0.923[d]	498	5570	6068	
	Al−O	1.911	0.800	1566	6936	8502	14570
$PrMnO_3$	Pr−O(1)	2.8565[e]	0.9209[e]	153	1584	1737	
	Pr−O(2)	2.7902	0.9210	310	3232	3542	
	Mn−O(1)	1.9539	0.8047	505	2515	3020	14084
	Mn−O(2)	2.0493	0.8052	965	4819	5784	
$YBa_2Cu_3O_6$	Ba−O(1)	2.773[f]	0.922[f]	238	2529	2767	
	Ba−O(2)	2.911	0.923	113	1216	1329	
	Ba−O(3)	2.911	0.923	113	1216	1329	
	Y−O(2)	2.399	0.947	175	3290	3465	22224
	Y−O(3)	2.399	0.947	175	3290	3465	
	Cu(1)−O(1)	1.786	0.163	1460	488	1948	
	Cu(1)−O(2)	2.471	0.811	234	1131	1365	
	Cu(2)−O(1)	1.940	0.780	654	2624	3278	
	Cu(2)−O(2)	1.940	0.780	654	2624	3278	

[a] This work. [b] Reference 27. [c] Reference 25. [d] Reference 26. [e] Reference 28. [f] Reference 19.

(2) Complex Crystal $LaCrO_3$. For $LaCrO_3$, the bond parameters, including bond ionicity f_i^μ, bond length d^μ, etc., are taken from our previous study.[20] The compound can be decomposed into many binary crystals as follows:

$$LaCrO_3 = La(1)Cr(1)O(1)O_2(2)$$
$$= La_{1/3}O_{2/3}(1) + La_{2/3}O_{4/3}(2) + Cr_{1/3}O_{1/3}(1) + Cr_{2/3}O_{2/3}(2)$$

For the $La_{1/3}O_{2/3}(1)$ bond, $f_i^\mu = 0.9753$. $d^\mu = 2.765$ Å, $Z_+^\mu = 3.0$, and $Z_-^\mu = 1.5$. According to eqs 22−24, we have $U_{bi}^\mu = 1724$ kJ mol^{-1}, $U_{bc}^\mu = 49$ kJ mol^{-1}, and $U_b^\mu = 1773$ kJ mol^{-1}. Similarly, for the $La_{2/3}O_{4/3}(1)$ bond, $f_i^\mu = 0.976$. $d^\mu = 2.757$ Å, $Z_+^\mu = 3.0$, $Z_-^\mu = 1.5$, and we can obtain $U_{bi}^\mu = 3457$ kJ mol^{-1}, $U_{bc}^\mu = 97$ kJ mol^{-1}, and $U_b^\mu = 3555$ kJ mol^{-1}. Lattice energies of $Cr_{1/3}O_{1/3}(1)$ and $Cr_{2/3}O_{2/3}(1)$ have also been calculated in a similar way; eventually, the total estimated lattice energy U_{cal} from eq 21 is 14316 kJ mol^{-1} for $LaCrO_3$. All these results are listed in Table 2.

Results and Discussion

On the basis of the current method, the lattice energies of more than 60 binary crystals which contain only one type of bond have been calculated. A portion of the results is listed in Table 1. The estimated lattice energies of some complex crystals are listed in Tables 2 and 3. As shown in Tables 1 and 2, our calculated values agree well with the available experimental and other theoretical values; the errors of 90% crystals are within 5%. The results are very acceptable. The lattice energies of some complex oxides whose lattice energies have not been reported, including $ZnFe_2O_4$, $FeAl_2O_4$, $YAlO_3$, $PrMnO_3$, and $YBa_2Cu_3O_6$, have been predicted in Table 3.

The present approach for the evaluation of the lattice energy of ionic crystals, which is based on the dielectric chemical bond theory, is rather complicated for detailed crystallographic data, and much computational labor is required. But as a new approach, this method needs to be developed, and it seems worthwhile to extend these fruitful ideas.

Acknowledgment. The authors are grateful for the referees' fruitful suggestions and comments.

IC025902A

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