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Interpolation Determination of the Lattice Energy of Ionic Crystals within the Framework of Stereoatomic Model

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Abstract—A new method based on graph theory was suggested for interpolation calculation of the lattice energy *U* of ionic crystals. The method is based on revealing matrix correlation between the ionic radii and *U* values for MX compounds, where M is a metal and X is halogen, hydrogen, or chalcogen. A new formula was obtained for calculating the lattice energy solely from the ionic radii, without introduction of abitrary factors. The mean error of determining *U* for alkali metal halides is 0.49%. The lattice energies were calculated for a large group of inorganic substances. The accuracy of the interpolation calculation of the lattice energy of ionic crystals depends on the degree of ionicity of the bond: With an increase in the covalent contribution, the error increases.

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Determination of the crystal lattice energy *U* of inorganic compounds is one of basic problems of the composition–property chemistry and is important for understanding the nature of chemical bond in solids and for predicting its properties.

This problem has been analyzed in detail in monographs and reviews [1–10]. The problem of experimental and theoretical determination of the lattice energy of ionic crystals was solved from the standpoints of quantum chemistry, physical chemistry, thermodynamics, and thermochemistry, and also using a purely empirical approach. Numerous formulas and methods allowing calculation of *U* for ionic crystals have been considered. For example, good results in calculation of the lattice energy of binary compounds MX were obtained with the first Born–Lande theoretical equation expressing the inverse relationship between the ion repulsion energy and the interatomic distance *R* (without taking into account van der Waals forces):

$$U = -A/R + B/R'' . \qquad (1)$$

In this formula, the first term is the attractive Madelung energy, and the second term describes the repulsion; *B* and *n* are repulsion parameters; and *R* is interatomic distance [1].

Later Born refined the form of this repulsive term and suggested a new, complete equation for calculating the lattice energy of ionic compounds (Born–Mayer equation):

$$U = -A/R + B_2\exp(-R/\rho - C/R_6 - D/R_8 + 9/8mh\nu_{\max}). \qquad (2)$$

In this equation, the first term is the attraction energy; the second term, repulsion energy; the terms C/R^6 and D/R^8 express the dipole–dipole and dipole–quadrupole interactions; and the last term is the zero-point vibration energy [1].

Later Ladd and Lee [5] transformed this equation for equilibrium distances R_0, and Urusov [9] modified the repulsion potential by including the zero-point vibration energy.

Urusov [9] suggested a new form of the repulsion potential:

$$U = -A/R + B_4R^{-1}\exp(-\lambda R). \qquad (3)$$

It can be readily seen that the second terms of Eqs. (1)–(3) for the lattice energy have no rigorous mathematical substantiation. Therefore, the development of theoretical aspects of the problem of lattice energy consisted mainly in improvement of the form of the repulsion function and fitting of empirical formulas for decreasing the calculation error. For example, the repulsive term (*RT*) after Prakash and Thakur [11] has the form

$$RT = a + pR^{-n}. \tag{4}$$

In [12], this term for alkali metal halides is given by the expression

$$RT = AR^{-m}\exp[-B(R^{n} - 1)]. \tag{5}$$

Yadav [11] expressed the repulsive potential via compressibility:

$$U = -(e^{2}Z_{1}Z_{2}\alpha/R) + AR^{-n}e^{-R\lambda}. \tag{6}$$

Analysis shows that the theoretical formulas are mainly related to the calculation of U for typical representatives of binary ionic crystals, Group Ia metal halides. It can be readily seen that these equations (as well as other equations, not cited here) include empirical parameters. This leads to the fact that all the theoretical methods for calculating the lattice energy are, to a certain extent, heuristic [9], i.e., they include an indefinite components, which complicates their use for subsequent transformations. Many authors directly used semiempirical fitting.

For example, Kapustinskii [13] calculated the lattice energy U of a crystal from the radii of ions and their number (Σn) in formula unit:

$$U = 287.2(Z_{c}Z_{a}\Sigma n)/(R_{c} + R_{a})[1 - 0.345/(R_{c} + R_{a})], \tag{7}$$

where Z_i are charges and R_i are radii (Å) of the cation (subscript c) and anion (subscript a) in 6-coordination.

Numerous formulas with arbitrary coefficients of unclear physical sense are used for theoretical calculation of the lattice energy of ionic crystals. Their drawback is that they are mainly intended for application to diatomic systems MX. Rigorous basis for the construction of recurrence formulas for multiatomic systems is lacking. Calculations of U for such systems involve significant simplifications and appreciable errors. In such calculations, a large number of chemical and crystallophysical characteristics of molecules should be taken into account. Often the required data are insufficiently accurate or lacking. Therefore, minimization of the set of parameters used for calculating U is an urgent problem. In this connection, it is very important to develop a new versatile, simple, and reliable procedure for determining the lattice energy of ionic crystals with a minimal set of the required parameters of atoms and ions, which would also be applicable to multiatomic systems.

In this study, instead of introducing new arbitrary parameters into the calculation equation, I suggest a new, principally different approach to calculating the crystal lattice energy of ionic compounds. Namely, I suggest to use elements of topological algebra, in particular, the mathematical apparatus and concepts of the graph theory allowing pictorial presentation of the interconnections of elements of any finite set at a minimal number of parameters to be taken into account.

A graph G [14] is any set of points connected with each other by various ribs or arcs. If an arc issues from a point (graph node) and returns to the same node without passing any other nodes, it is termed loop.

Let us apply this concept to the structure of a simplest diatomic molecule MX and present this molecule as a graph G(MX):

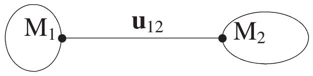
$$\mathrm{M}\,\overset{\mathbf{u}_{\mathrm{MX}}}{\rule{4em}{0.4pt}}\,\mathrm{X}.$$

Here M and X are atoms or ions of a molecuyle, bound to each other with a certain nonoriented bond, rib $\mathbf{u}_{\mathrm{MX}}$. To describe molecules, it is more convenient to number these nodes of graph G and present them as M_1 and M_2.

Let us use one more notion of the graph theory, adjacency matrix A of graph G. I suggest to diverge from the traditional concepts of the graph theory and replace topological values of elements a_{ij} (0 or 1) of the adjacency matrix A by other physicochemical quantities. The essence of the replacement is as follows.

It is known that the nature of chemical bond is determined by Coulomb-type electrostatic forces [4, 16, 17]. According to the Coulomb law, the force of electrostatic attraction between two charged particles is given by the expression $F_{12} = k(Z_1Z_2/R_2)$. Let us rewrite this formula as product of certain physicochemical potentials: $F_{12} = k(Z_1/R)(Z_2/R)$.

Assume that graph $G(\mathrm{M}_1\mathrm{M}_2)$ has loops at each node M_i. In the case of a diatomic molecule MX (or $\mathrm{M}_1\mathrm{M}_2$), this graph with loops $\mathbf{l}_i$ will have the following form:



Let us now present these potentials (Z_i/R) of charged particles (ions) M_1 and M_2 in the form of maps

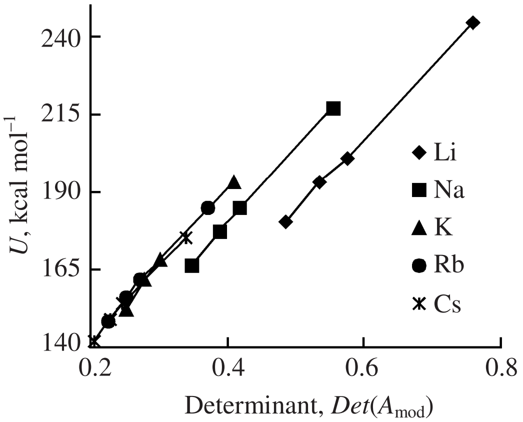


Fig. 1. Lattice energy U of ionic crystals as a function of the determinant (12) of the modified adjacency matrix of the graph representing a diatomic molecule.

of graph loops incident to the corresponding nodes. Here for each node it is logical to take into account the radius of the corresponding ion R_i, rather than the internuclear distance R. Then the symbol (map) of the loop at node M_i of graph G in its adjacency matrix will have the form Z_i/R_i (remember the Cartledge potential Z/R [18]). Thus, the diagonal element a_{ii} of the leading diagonal of the adjacency matrix A of graph G, representing the molecular core, will have the value of Z_i/R_i, instead of the traditional topological value of 0 or 1.

Let us turn to presentation of the connection between nodes M_1 and M_2 of graph $G(M_1M_2)$, i.e., of the chemical bond between atoms or ions M_1 and M_2 in an M_1M_2 molecule. According to graph theory [14], the connection between nodes M_i and M_j of a graph in its adjacency matrix A is represented by nondiagonal elements a_{ij}, and they usually have values of 0 (no connection) or 1 (connection exists), although the values of 2, 3, etc. are also possible. Let us introduce the similar corrections to this concept also and, when describing the element connecting the graph nodes (atoms of molecule), i.e., rib a_{ij}, let us take into account the ionic radii R_i and charges Z_i in the form of potential function Z_i/R_i.

To preserve the dimension of charge and the sense of the Coulomb law, for characterizing the bond, let us take in the numerator of the matrix descriptor of the rib element the geometric mean of the charges of two chemically bonded ions, ($\sqrt{Z_1Z_2}$). When estimating the denominator of this descriptor, let us take into account the fact that the strength of a bond between atoms (ions) of a molecule is inversely proportional to the interatomic distance, which is assumed for ions to be equal to the sum of their ionic radii, i.e., $R_{ij} = R_i + R_j$. Thus, the second correction is that the con-nection (rib) between nodes of graph $G(M_1M_2)$ will be presented in the adjacency matrix as the descriptor $\sqrt{Z_1Z_2}/(R_1 + R_2)$.

Now we can write down the modified adjacency matrix A_{mod} of graph $G(M_1M_2)$, representing a molecule M_1M_2 (or MX), in the final form:

$$A_{\mathrm{mod}} = \begin{pmatrix} Z_1/R_1 & \sqrt{Z_1Z_2}/(R_1+R_2) \\ \sqrt{Z_1Z_2}/(R_1+R_2) & Z_2/R_2 \end{pmatrix}. \qquad (8)$$

The determinant Det of this modified adjacency matrix A_{mod} of graph $G(M_1M_2)$ is expressed by

$$Det(A_{\mathrm{mod}}) = Z_1Z_2[1/R_1R_2 - 1/(R_1 + R_2)^2]. \qquad (9)$$

This expression can be transformed as follows:

$$Det(A_{\mathrm{mod}}) = Z_1Z_2/R_1R_2[1 - R_1R_2/(R_1 + R_2)^2]. \qquad (10)$$

Equation (10) exhibits an interesting analogy with the form of key terms in the Ladd–Lee equation for equilibrium R_0 [5] and especially with the Kapustinskii equation (7). Hence, it is logical to assume that the determinant of the modified adjacency matrix $Det(A_{\mathrm{mod}})$ of this graph-molecule can be the basis for the construction of a new equation for the lattice energy, i.e., there may be a rigidly deterministic correlation between U and $Det(A_{\mathrm{mod}})$: $U \sim K_{\mathrm{gen}}Det(A_{\mathrm{mod}})$, where K_{gen} is a certain generalizing coefficient based on the ionic radii.

To find the accurate form of K_{gen}, which is a functional of the ionic radii, we considered the dependence $U = f[Det(A_{\mathrm{mod}})]$ for alkali metal halides. The ionic radii were taken after Shannon [19]. The plot (Fig. 1) consists of a group of approximately straight lines arranged stepwise one over another. These groups of lines correspond to crystals of halides with the same cation of Group IA metal. This fact indicates that it is necessary to take into account the number of period of an atom or any other directly related quantity, e.g., the principal quantum number or the cationic radius.

In view of the approximately linear, though stepwise, character of the function $U = f(Det)$, it seemed appropriate to find a general, desirably universal, expression of the form $U = K_{\mathrm{gen}}Det(A_{\mathrm{mod}})$. Therefore, our next goal was to obtain a satisfactory mathematical expression for the generalizing coefficient K_{gen} that would describe and take into account the stepwise character of the dependence with the aim to eliminate it and linearize the whole function $U = f[Det(A_{\mathrm{mod}})]$, i.e., to present it in the general form as $U = f(R_{1,2})$.

To determine the form of the generalizing coefficient K_{gen}, we analyzed various dependences of $U/Det(A_{\mathrm{mod}})$ on terms contained in the expression for determinant (10).

Analysis of the plots shows that the functions $U = f[Det(A_{\mathrm{mod}})/(R_1 + R_2)]$ and $U = f[Det(A_{\mathrm{mod}})R_1R_2]$ form several families of lines that preserve the stepwise character but show essentially opposite trends (Figs. 2a, 2b). Therefore, I decided to consider the plot (Fig. 2c) of a new dependence including both parameters of the radii: $U = f[Det(A_{\mathrm{mod}}R_1R_2/(R_1 + R_2)]$.

It is seen that the dependence $U = f[Det(A_{\mathrm{mod}})R_1R_2/(R_1 + R_2)]$ lost its stepwise character, which was compensated by opposite trends of the initial curves, and can be fairly accurately approximated by an equation of a straight line. Thus, the desired generalizing coefficient K_{gen} can be expressed as $K_{\mathrm{gen}} = K_uR_1R_2(R_1 + R_2)$, and a simple mathematical expression for calculating the lattice energy of ionic crystals can be obtained in the form of the linear dependence of U on the determinant of the adjacency matrix of the graph:

$$U = KDet(A_{\mathrm{mod}})R_1R_2/(R_1 + R_2), \tag{11}$$

where K is a common constant of proportionality. After substituting in (11) the determinant from (10), canceling like terms, and determining K by traditional methods from experimental values of U_{exp}, the equation for calculating the lattice energy of ionic crystals will take the following form:

$$U = KZ_1Z_2/(R_1 + R_2)[1 - R_1R_2/(R_1 + R_2)^2], \tag{12}$$

where $K = 695.514$.

Formula (12) is similar to universal Kapustinskii formula (7), but it gives lower error in calculation of the lattice energy of crystalline alkali metal halides: deviation from the experimental values is 3.06%, against 4–5% for the Kapustinskii equation [9]. This fact stimulated us to look for a more accurate expression for calculating the lattice energy of ionic crystals.

Remember that Yatsimirskii [20] attempted to reduce the error of theoretical calculation of U by introducing a correction for polarization of the elec-

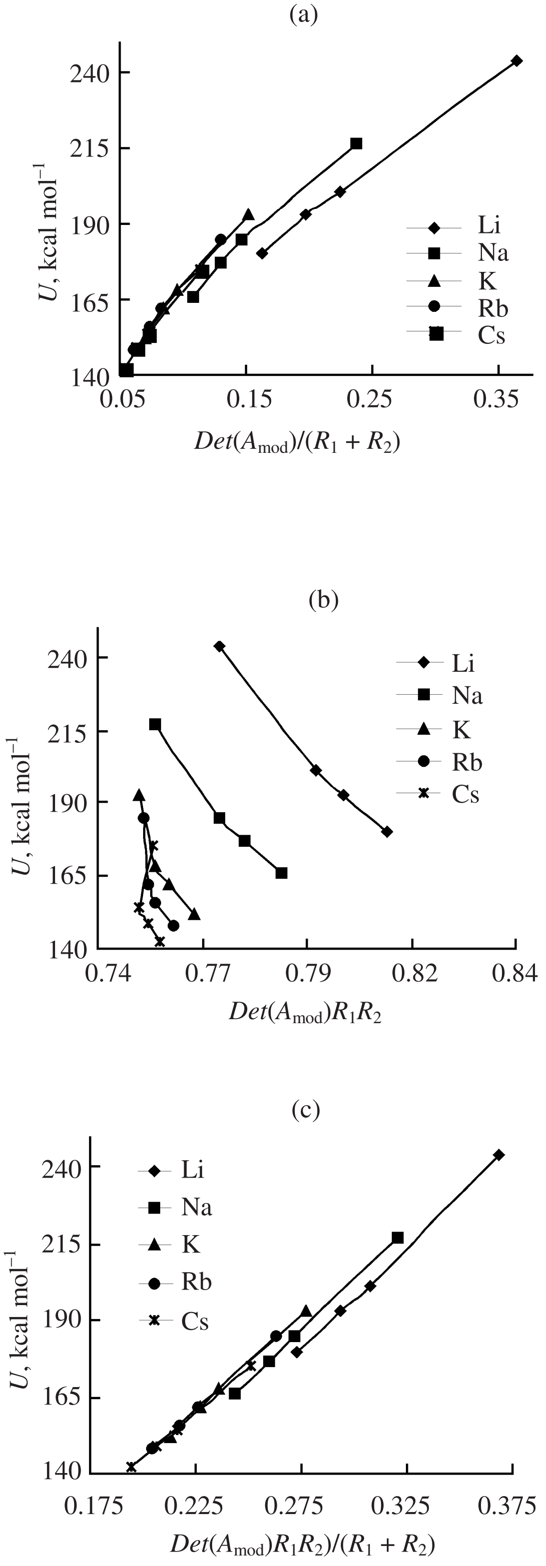


Fig. 2. Functions (a) $U = f[Det(A_{\mathrm{mod}})/(R_1 + R_2)]$ (b) $U = f[Det(A_{\mathrm{mod}})R_1R_2]$, and (c) $U = f[Det(A_{\mathrm{mod}})R_1R_2/(R_1 + R_2)]$.

Table 1. Lattice energies (kcal mol^{-1}) of alkali metal halides, calculated by formula (14) and determined experimentally [5, 6]

Salt	U_{exp}	U_{calc}	Error, %	Salt	U_{exp}	U_{calc}	Error, %
LiF	244	241.91	–0.85	KBr	162	160.90	–0.68
LiCl	201	202.57	0.78	KI	152	151.86	–0.09
LiBr	193	192.87	–0.06	RbF	185	183.58	–0.76
LiI	180	179.19	–0.45	RbCl	162	161.47	–0.33
NaF	217	216.74	–0.12	RbBr	156	155.76	–0.15
NaCl	185	184.99	–0.005	RbI	148	147.47	–0.35
NaBr	177	177.01	0.007	CsF	175	175.88	0.50
NaI	166	165.63	–0.22	CsCl	154	155.93	1.25
KF	193	191.53	–0.76	CsBr	149	150.75	1.17
KCl	168	167.15	–0.50	CsI	142	143.20	0.84

tron clouds of interacting ions in the end efficient of formula (7):

$$U = 287.2(Z_cZ_a\Sigma n)/(R_c + R_a) \\ \times[1 - 0.345/(R_c + R_a) + 0.0087(R_c + R_a)]. \qquad (13)$$

I believe that it is more appropriate to improve the accuracy of determining U by introducing an additional correction into the under-charge denominator without altering the expression for $Det(A_{\mathrm{mod}})$, because specifically this determinant is the basis for deriving the formula for the lattice energy. Therefore, to reduce the calculation error and eliminate weak curvature of the function $U = f[Det(A_{\mathrm{mod}}R_1R_2/(R_1 + R_2)]$, let us introduce into the denominator of Eq. (12) a diminishing correction for curvature as a function of the same smoothing parameter $R_1R_2/(R_1 + R_2)$. Formula (14) appeared to give the best results (calculation error 0.49%):

$$U = 600\,\frac{Z_1Z_2}{R_1 + R_2 - \dfrac{\pi}{4}\left(\dfrac{R_1R_2}{R_1 + R_2}\right)^2} \times \left(1 - \frac{R_1R_2}{(R_1 + R_2)^2}\right), \qquad (14)$$

where U is the crystal lattice energy (kcal mol^{-1}); 600, refined constant of proportionality; Z_i, ion charges; and R_i, ionic radii (Å) for coordination number 6, according to [13].

Table 2. Comparison of the lattice energies (kcal mol^{-1}) of alkali metal astatides and francium halides, calculated by formula (14) and by other methods [5]

Salt	U_{calc} from [5]	U_{calc} determined by (14)	Error, %
LiAt	172	173.06	0.62
NaAt	157	160.48	2.21
KAt	147	147.71	0.49
RbAt	142	143.66	1.17
CsAt	140	139.71	–0.21
FrF	169–171	169.77	0.46÷–0.72
FrCl	150–151	151.50	1.00–0.33
FrBr	144–146	146.74	1.90–0.51
FrI	137–139	139.77	2.02–0.56
FrAt	137	136.54	–0.33

Using Eq. (14), I calculated the lattice energies for alkali metal halides (Table 1). Here and hereinafter, I used as basis quantities the Shannon ionic radii for 6-coordination [19]. As seen from Table 1, the values I obtained closely coincide with the experimental data [5, 6]: The mean error is as low as 0.49%, and the maximal error does not exceed 1.25%. To compare, the complete Born–Mayer equation (2) provides an accuracy of about 4% [9]; Kapustinskii equation (7), 4–5% [9]; and Yadav equation (6), 2.1% [11]. In [21], I used in the denominator of the equation for calculating U a more complex expression, and the error was 0.99%.

Owing to good agreement between the calculation results and experimental data, I estimated the lattice energy of Group IA metal astatides and of francium halides (Table 2). The At^- ionic radius was taken equal

Table 3. Lattice energies (kcal mol^{-1}) of alkali metal hydrides, hydroxides, and hydrosulfides: calculation by formula (14) and experimental data [5, 6, 23]

Compound	U_{exp}	U_{calc}	Error, %	Compound	U_{exp}	U_{calc}	Error, %
LiH R_{H^-} 1.3 Å	220	244.93	11.33	RbH R_{H^-} 1.3 Å	164	185.23	12.94
LiH R_{H^-} 1.5 Å		226.24	2.83	RbH R_{H^-} 1.5 Å		174.94	6.67
LiH R_{H^-} 1.53 Å		223.69	1.68	RbH R_{H^-} 1.53 Å		173.52	5.80
LiH R_{H^-} 2.08 Å		185.78	–15.55	RbH R_{H^-} 2.08 Å		151.50	–7.62
LiOH	234	238.01	1.72	RbOH	183	181.45	–0.85
LiSH		190.45		RbSH	155	154.31	–0.44
NaH R_{H^-} 1.3 Å	194	219.14	12.96	CsH R_{H^-} 1.3 Å	156[a]	177.36	13.69
NaH R_{H^-} 1.5 Å		204.19	5.25	CsH R_{H^-} 1.5 Å		168.10	7.76
NaH R_{H^-} 1.53 Å		202.14	4.20	CsH R_{H^-} 1.53 Å		166.82	6.93
NaH R_{H^-} 2.08 Å		171.13	–11.79	CsH R_{H^-} 2.08 Å		146.87	–5.85
NaOH	211[a]	213.63	0.55	CsOH	172[a]	173.96	1.14
NaSH	178	175.00	–1.68	CsSH	149	149.43	0.29
KH R_{H^-} 1.3 Å	172	193.35	12.41	FrH R_{H^-} 1.3 Å		169.98	
KH R_{H^-} 1.5 Å		181.98	5.80	FrH R_{H^-} 1.5 Å		161.47	
KH R_{H^-} 1.53 Å		180.41	4.89	FrH R_{H^-} 1.53 Å		160.33	
KH R_{H^-} 2.08 Å		156.24	–9.16	FrH R_{H^-} 2.08 Å		143.90	
KOH	189	189.17	0.09	FrOH		166.80	
KSH	155	159.31	2.78	FrSH		145.78	

[a] Values of U calculated by Ladd and Lee [5].

to 2.32 Å (estimation according to [22]). Analysis shows that the results well agree with the Ladd and Lee's calculations [5]: The mean deviation is 0.8%.

I also calculated the lattice energies for Group IA metal hydrides, hydroxides, and hydrosulfides (Table 3). The radii of these anions were taken from [23–25]. As the radius of the H^- ion strongly differs according to data of different authors (from 1.3 to 2.08 Å), the lattice energies of the hydrides were calculated for all the reported values of $R(H^-)$. The experimental values of U and those calculated by other methods were taken from [5, 6, 23]. The calculated lattice energies for the francium compounds are also given in Table 3.

Comparison of the results (Table 3) shows that the calculated and experimental data are in reasonable argeement for hydroxides and hydrosulfides but noticeably differ for hydrides. This is apparently associated with uncertain radius of the H^- ion. Calculations with $R(H^-)$ = 1.53 Å give results that better agree with the experiment. Hence, knowing the lattice energy, it is possible to refine the ionic radius.

I also calculated the lattice energy of Cu(I), Ag(I), Au(I), and Tl(I) halides and of salts of these elements with other single-charged anions (Table 4). The ionic radius of H^- was taken equal to 1.53 Å. It can be seen that, for halides of these elements, the calculated values are considerably smaller than the experimental values: The deviation varies from 7–9% for Tl(I) compounds to 32–38% for Au(I) compounds. For hydrides and hydroxides, the U_{calc} values are also smaller than the experimental values [4–6]. The discrepancies are apparently associated with the contibution of covalent bonding. The degrees of bond ionicity ε calculated by the Urusov equation [9]

$$\varepsilon = \left| \frac{I_A + F_A - I_B - F_B}{I_A - F_A + I_B - F_B} \right| \qquad (15)$$

Table 4. Lattice energies (kcal mol^{-1}) of compounds of Group IB metals and thallium(I), calculated by formula (14) and determined experimentally [4–6]

Compound	U_{exp}	U_{calc}	Error, %	ε
CuF	–	240.78	–	0.582
CuCl	234	201.79	–13.76	0.481
CuBr	228	192.17	–15.71	0.418
CuI	226	178.59	–20.98	0.330
CuAt		172.50		0.239
CuH	241	222.73	–7.58	0.279
CuOH	240	236.92	–1.28	
CuSH		189.76		
AgF	226	206.67	–8.31	0.592
AgCl	214	177.88	–16.72	0.493
AgBr	211	170.60	–18.84	0.429
AgI	208	160.14	–23.05	0.341
AgAt		155.39		0.249
AgH	223	193.47	–13.24	0.286
AgOH	219	203.86	–6.91	
AgSH		168.76		
AuF	–	192.13	–	0.447
AuCl	246	167.58	–31.88	0.310
AuBr	246	161.28	–34.44	0.238
AuI	247	152.19	–38.39	0.140
AuAt		148.02		0.037
AuH	247	180.93	–26.75	0.143
AuOH		189.76		
AuSH		159.69		
TlF	198	184.67	–6.73	0.728
TlCl	173	162.25	–6.10	0.667
TlBr	169	156.47	–7.41	0.611
TlI	164	148.08	–9.49	0.533
TlAt		144.22		0.451
TlH	178	174.46	–1.99	0.420
TlOH	168	182.51	8.64	
TlSH		155.00		

are also given in Table 4. In Eq. (15), I_A and I_B are the ionization energies of atoms A and B in molecule AB; F_A and F_B are their electron affinities. The quantities ε were calculated using data from [25].

Correlation of the error of calculating U with the degree of bond ionicity ε (Fig. 3) shows that, the lower the degree of bond ionicity in the crystal, the larger the error Δ of determining the lattice energy. The correlation is approximately linear, with the correlation coefficient of –0.95.

For example, for potassium halides the degree of bond ionicity is close to 0.9, and the error of calculating U is less than 0.8%. For Tl(I) halides, ε varies within 0.73–0.53, and the error of calculating U reaches 7–9%. For Au–Hlg bonds, ε is 0.44–0.14, i.e., the bonds are essentially covalent, and in this case the error of calculating U is as large as 32–38%.

It is interesting that the structures of these halides (except AgF, AgCl, and AgBr) differ essentially from the NaCl-type and related structures characteristic of alkali metal halides, hydrides, and hydrosulfides [24], for which the error of calculating U is small. For example, copper(I) halides crystallize in the zinc blende structural type, and AuI consists of chain-like molecules (for the other Au(I) halides, structural data are lacking [24]). Compounds TlHlg have a distorted NaCl-type structure and a CsCl-type configuration [24, 26]. Only AgF, AgCl, and AgBr crystallize in the NaCl structural type [24], but the relative error of determining their lattice energy is large (Table 4).

Using Eq. (14), I also calculated the energies U for Group IIA metal chalcogenides (Table 5). The Be^{2+} ion was taken with coordination number 4, and the Ra^{2+} ion, with coordination number 8 [19]. The corresponding experimental data and the calculated lattice energies [5, 6] (in cases when experimental data were lacking) are also given in Table 5. It can be seen that the calculated energies U for alkaline-earth metal chalcogenides are in reasonable agreement with the experiment [5, 6]; the calculation error does not exceed 5%, being 1.70% on the average. It can be readily seen that the calculation error somewhat decreases from Be to Ra, i.e., as the sum of the radii of the cation and anion, $R_c + R_a$ (and hence the internuclear distance), increases, the error of calculating the lattice energy decreases. However, the error may also arise from the neglect of the ion coordination mode in the corresponding crystal.

Note that these chalcogenides have a NaCl structure, except Be(II) compounds characterized by the sphalerite and wurtzite structures with 4-coordination of Be [24, 26].

I also calculated the lattice energies of binary chalcogenides of transition metals, Sn(II), and Pb(II). The Sn^{2+} ionic radius was taken equal to 0.93 Å after Ahrens [23]. Comparison of the calculated values of U

Table 5. Comparison of the lattice energies (kcal mol^{-1}) of alkaline-earth metal chalcogenides, calculated by formula (14) and found experimentally [5, 6, 23]

Compound	U_{exp}	U_{calc}	Error, %	Compound	U_{exp}	U_{calc}	Error, %
BeO	1080	1113.31	3.08	SrO	791	799.10	1.02
BeS	893[a]	923.99	3.47	SrS	687	699.55	1.83
BeSe	855[a]	876.72	2.54	SrSe	667	673.27	0.94
BeTe	795[a]	808.82	1.74	SrTe	630	634.27	0.68
MgO	940	958.45	1.96	BaO	747	756.70	1.30
MgS	778	814.94	4.75	BaS	656	668.50	1.90
MgSe	757[a]	778.17	2.80	BaSe	638	645.01	1.10
MgTe	720[a]	724.57	0.63	BaTe	606[a]	609.97	0.65
CaO	853	851.80	–0.14	RaO	751[a]	727.91	–3.07
CaS	722	737.95	2.21	RaS		647.32	
CaSe	699	708.20	1.32	RaSe		625.74	
CaTe	666[a]	664.35	–0.25	RaTe	593[a]	593.40	0.07

[a] Calculated data from [5, 6].

with the experimental values taken from [5, 6] shows (Table 6) that they are in reasonable agreement.

The mean calculation error is 6.29%, although the errors vary in a wide range: from 1% for Sn(II) and Ni(II) chalcogenides to 11–18% for Hg(II) chalcogenides, and they are appreciably larger than for alkaline-earth metal chalcogenides. The largest calculation error is observed with the heaviest metals: Hg(II) and Pb(II). It is interesting that better agreement is attained when the ionic radii of Cr(II), Mn(II), Fe(II), and Co(II) are taken for their low-spin states. It can also be seen that the calculation error increases with an increase in the atomic number of the anion (going from oxides to tellurides), which is apparently associated with a decrease in the bond ionicity.

Good agreement of the calculation results with the experiment (relative error Δ 1–2%) is attained for compounds with different lattice types [24, 26]: face-centered cubic (NaCl type) for oxides of Ni(II), Fe(II), Co(II), Mn(II), and V(II); tetragonal (antifluorite type) for SnO; and hexagonal (wurtzite type) for ZnO. At the same time, for isostructural SnO and PbO the calculation errors strongly differ: 1.6 and 7.7%. For CdO (NaCl type), the calculation error reaches 7%. The accuracy of calculating *U* for rhombic SnS (Δ 1.2%) is higher than for PbS and PbSe (NaCl-type cubic lattice, Δ 8.6 and 10.6%), for cubic or hexagonal CdS and CdSe (Δ ~9%), and especially for cubic (sphale-rite-type) HgS and HgSe (Δ 16 –18%).

To check the feasibility Eq. (14) for calculating the lattice energy of polyatomic ionic crystals, I calculated *U* for Group II metal halides. The results are given in Table 7. In so doing, I introduced into Eq. (14) an arbitrary correction for the number of ions in the formula unit of the crystal, Σn, similar to the corresponding Kapustinskii correction in Eq. (7), i.e., instead of a constant equal to 600 I used $300\Sigma n$.

As seen from Table 7, the calculated lattice energies U_{calc} of alkaline-earth metal halides reasonably agree with the experimental data and calculation results of other authors (error 3.6%), with my calcula-

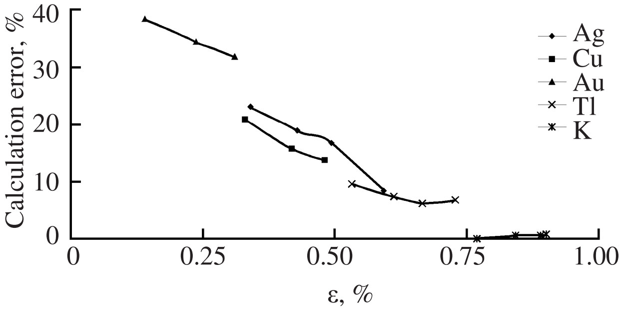


Fig. 3. Error of calculating the lattice energy of ionic crystals *U* as a function of the degree of bond ionicity ε.

Table 6. Lattice energies (kcal mol^{-1}) of *p*- and *d*-metal chalcogenides, calculated by formula (14) and determined experimentally [5, 6, 23]

Compound	U_{exp}	U_{calc}	Error, %	Compound	U_{exp}	U_{calc}	Error, %
SnO	883	875.12	–0.89	CoO	964	992.12	2.92
SnS	765	754.88	–1.32	CoS	850	838.98	–1.30
SnSe		723.60		CoSe		799.96	
SnTe		677.62		CoTe		743.28	
PbO	852	796.43	–6.52	NiO	966	972.44	0.67
PbS	759	697.60	–8.09	NiO	863	824.95	–4.41
PbSe	750	671.49	–10.47	NiO		787.24	
PbTe		632.74		NiO		732.37	
TiO	949	900.43	–5.12	PdO	969	900.43	–7.08
TiS		773.20		PdS		773.20	
TiSe		740.25		PdSe		740.25	
TiTe		691.96		PdTe		691.96	
VO	947	928.06	–2.00	CuO	925	953.92	3.13
VS		793.13		CuS	887	811.70	–8.49
VSe		758.36		CuSe		775.22	
VTe		707.54		CuTe		722.04	
CrO		953.92		ZnO	964	949.46	–1.51
CrS		811.70		ZnS	878	808.50	–7.92
CrSe		775.22		ZnSe	864	772.32	–10.61
CrTe		722.04		ZnTe		719.55	
MnO	926	982.13	6.06	CdO	926	868.27	–6.23
MnS	807	831.86	3.08	CdS	827	749.91	–9.32
MnSe	794	793.51	–0.06	CdSe	791	719.08	–9.09
MnTe		737.75		CdTe		673.72	
FeO	945	1013.10	7.21	HgO	944	845.46	–10.44
FeS	840	853.87	1.65	HgS	869	733.34	–15.61
FeSe		813.44		HgSe	860	704.01	–18.14
FeTe		754.83		HgTe		660.74	

tion giving slightly overestimated results. For Group IIB metal halides, the calculated values of *U*, on the contrary, are noticeably underestimated relative to the experimental data. Increased calculation error for this group of halides can be accounted for by increased contribution of covalent bonding, similarly to crystals of Group IB metal halides. However, final conclusions can only be made after a rigorous recurrence equation will be obtained for calculating the lattice energy of polyatomic crystals.

Table 7. Lattice energies (kcal mol^{-1}) of Group II *s*- and *d*-metal halides, calculated by formula (14) with the correction Σn and determined experimentally [6]

Compound	U_{exp}	U_{calc}	Error, %	Compound	U_{exp}	U_{calc}	Error, %
MgF_2	696	739.82	6.30	ZnF_2	710	732.68	3.19
$MgCl_2$	597	617.47	3.43	$ZnCl_2$	646	612.53	–5.18
$MgBr_2$	576	587.41	1.98	$ZnBr_2$	633	582.96	–7.90
MgI_2	550	545.06	–0.90	ZnI_2	612	541.27	–11.56
CaF_2	624	655.24	5.01	CdF_2	663	668.28	0.80
$CaCl_2$	535	558.50	4.39	$CdCl_2$	602	567.66	–5.70
$CaBr_2$	515	534.22	3.73	$CdBr_2$	578	542.49	–6.14
CaI_2	493	499.61	1.34	CdI_2	577	506.68	–12.19
SrF_2	588	613.54	4.34	HgF_2	668.74[a]	650.22	–2.77
$SrCl_2$	507	529.10	4.36	$HgCl_2$	633.60[a]	554.97	–12.41
$SrBr_2$	489	507.67	3.82	$HgBr_2$	628.11[a]	531.04	–15.45
SrI_2	465	476.90	2.56	HgI_2	623.80[a]	496.88	–20.35
BaF_2	566	580.04	2.48	Li_2O	693	705.54	1.81
$BaCl_2$	483	505.33	4.62	Na_2O	616	634.09	2.94
$BaBr_2$	466	486.19	4.33	K_2O	556	562.35	1.14
BaI_2	441	458.56	3.98	Rb_2O	548	539.68	–1.52
				Cs_2O	535	517.68	–3.24

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