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Solid-State Energetics and Electrostatics: Madelung Constants and Madelung Energies

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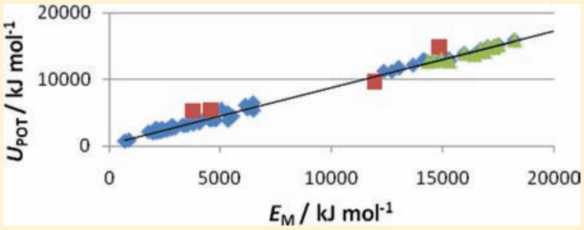
S Supporting Information



ABSTRACT: The Madelung constants of ionic solids relate to their geometry and electrostatic interactions. Furthermore, because of issues in their evaluation, they are also of considerable mathematical interest. The corresponding Madelung (electrostatic, coulomb) energy is the principal contributor to the lattice energies of ionic systems, and these energies largely influence many of their physical properties. The Madelung constants are here defined and their properties considered. A difficulty with their application is that they may be defined relative to various lattice distances, and with various conventions for inclusion of the charges, leading to possible confusion in their use. Instead, the unambiguous Madelung energy, E_M, is to be preferred in chemistry. An extensive list of Madelung energies is presented. From this data set, it is observed that there is a strong linear correlation between the lattice energies of ionic solids, U_{POT}, and their Madelung energies: U_{POT}/kJ mol^{-1} = 0.8519E_M + 293.9. This correlation establishes that the lattice energy, U_{POT}, for ionic solids is about 15% smaller than the attractive Madelung energy, the difference arising from the repulsions unaccounted for by the solely coulombic Madelung energy calculation. Correlations of U_{POT} against E_M for alkali metal hydrides and transition metal compounds, each having considerable covalency, show much reduced Madelung contributions to the lattice energy. These correlations permit ready estimation of lattice energies, and are the first to be based on actual data rather than a broad analysis. The independent volume-based thermodynamic (VBT) method, which relies on a separate correlation with the formula unit volume of the ionic material, complements these correlations.

INTRODUCTION

The lattice energy of a material is a "lattice sum"; that is, it is the sum of the interaction energies of all the contents of the system, both attractive and repulsive.[1,2] In an ionic material, the principal contributor to the total lattice energy is the charge (electrostatic or coulomb) interaction, E_M. In one form, this coulomb interaction is evaluated as the product of the reciprocal of a characteristic distance, l; the charges involved, z_+ and z_-; and a dimensionless geometric factor, M, known as the Madelung factor (or Madelung constant)[3−7] which sums the charge interaction contributions in terms of their numbers and distances, and which has a fixed value for a given invariant crystal structure type (e. g., NaCl-type, or fluorite-type, etc.).

$$E_M = \sum (1/l_o \times z_i \times z_j \times M) \tag{1}$$

Given its evaluation of the influence of the geometry of the surroundings on the electrostatics at a selected site, the coulomb lattice sum is fundamental in our understanding of the ionic solid state. As examples, the very stability of the ionic material, the relative stability of a dopant in a crystal, the influence of a crystal defect, ion diffusion, or the shifts in electronic energy spectral levels are all functions of the electrostatic interactions.

The Madelung factor, M, as a simple dimensionless geometric quantity relating to the crystal structure, is an appealing concept. A principal reason for its wide application is that it is independent of the size of the crystal unit cell, having the same value for all materials having the identical invariant symmetry. However, its evaluation is not without difficulty since the simple lattice sum is only conditionally convergent,[8] so various procedures and even subterfuges must be invoked in order to obtain a sufficiently converged value (although 1% precision is probably adequate for most chemical applications). Most current programs evaluating solid state energies obtain the electrostatic energy as a component,[9,10] and there are even self-standing programs for the purpose.[11,12]

Incidentally, it should be noted that the Madelung value is a constant only for the bulk (infinitely large) crystal. Surface and interior ion Madelung values differ from those of the bulk crystal, diverging from the bulk value as the distance to the nearest crystal surface decreases.[13,14]

A disturbing complication is that the Madelung constant is variously defined,[15,16] and then not always as simply a geometric factor, resulting in possible confusion in its application. One problem is the definition of the reference distance, l_o, which may be the following: the closest cation−anion distance, r_o, with the label M_r; a lattice constant (and different choices may be available), M_a; the cube-root of the formula-unit volume, M_δ or M_v; or even (somewhat

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mysteriously) a mean of cation−anion distances.[17] Compounding this problem, there is no clear convention as to whether or how the ion charges are to be included in the Madelung constant:[15] in some variants, the charges are simply excluded from M; in others the highest-common factor of the charges is included; finally, the full charge product may be included. These complications are particularly an issue with complex ionic solids. An additional unfortunate complication is the too-frequent misidentification of the CsCl-type structure as body-centered cubic (bcc) in place of the correct simple cubic (sc).

On the other hand, the electrostatic (Madelung) *energy* and associated *site potentials* are unambiguous, but dependent on the lattice dimensions, ion positions, and charges. They are thus unique to the associated crystalline material and its charges.

The dimensionless Madelung constant at site i is defined as

$$M_i = \sum_j \frac{z_j}{l_{ij}/l_o} \tag{2}$$

where z_j is the charge at the jth site, $l_{ij} = |l_i - l_j|$ is the distance between the i and j sites, and l_o is the chosen reference distance. The ions are generally treated as point charges.[18]

The relation between Madelung constants for different reference distances, l_o, is

$$\frac{M_{i,x}}{l_{o,x}} = \frac{M_{i,y}}{l_{o,y}} \tag{3}$$

It should be noted that each possible site in the crystal (ion, dopant, impurity, vacancy, arbitrary position) has its own value of the lattice sum.[14] The lattice energy contribution at site i, with charge z_i, is

$$E_{M,i} = \frac{z_i e^2}{4\pi\varepsilon_o l_o} M_i \tag{4}$$

where electron charge, $e = 1.6022 \times 10^{-19}$ C, and $4\pi\varepsilon_o = 1.112 \times 10^{-10}$ C^2 J^{-1} m^{-1}.

For the purpose of lattice energy calculation, the Madelung constant used is half the sum of the Madelung constants, including charge, for each independent ion of the chemical formula in the crystal, with the factor $^1/_2$ correcting for double-counting of the electrostatic interactions (as both i and j in eq 2). For an electrically neutral material, the equilibrium electrostatic energy will be negative but, in common with much of the literature, the negative sign will here be ignored as a matter of convenience.

The present paper collects together the results of published Madelung constant calculations (with charges included) for a large number of ionic solids[19−23] and demonstrates their relation to corresponding Madelung energies. Unfortunately, many of the sources of published Madelung constants for more complex materials fail to give explicitly the reference distance, l_o, to which the Madelung constant refers. This situation is here remedied by not only listing reference distances but also by listing corresponding values of M_{l_o}/l_o, which is constant for a given material, by eq 3, independent of which reference distance is used. (In fact, M_{l_o}/l_osimply represents the Madelung energy (eq 4) in units of reciprocal length, but without any energy conversion factor.)

Invariant Structures. Certain crystal structures (described as "invariant") have no free symmetry parameters, for example, some structures with cubic symmetry (but also extending to certain "idealized" tetragonal, orthorhombic, and even hexagonal symmetries[24−26]). That is, the lattice sites in these "invariant" structures are fixed by the symmetry requirements of the structure. For such materials, a most direct method for obtaining Madelung constants is that described as the Madelung−Born method. This involves treating the ionic lattice sites independently, and summing the results in accordance with Hund's potential superposition principle.[27]

An early analysis of the situation for invariant cubic lattice complexes (ICLC) is due to Naor[28,29] who showed that 17 lattice sums are sufficient to calculate M for all ICLC, while nine were believed to be independent. Subsequently, Zucker demonstrated[24,25] that only eight are independent, while only three numbers (in various linear combinations) are sufficient for many cubic materials. Naor and Zucker's treatment corresponds to the addition of sets of simple *cubic* structures of the same lattice constant and of a known Madelung constant, appropriately displaced with respect to one another, and summed. For example, the NaCl structure is calculated as the sum of a simple cubic Na^+ structure with origin at (0,0,0) together with an identical simple cubic Cl^- structure, but with origin displaced to $(^1/_2,^1/_2,^1/_2)$.

The Madelung constants of invariant structures can be further combined to yield the Madelung constants of structurally related materials. In a cubic example, the Madelung constant of fluorite (CaF_2) is a weighted sum of the values for NaCl and CsCl structures:

$$M_r(\mathrm{CaF_2}) = \frac{\sqrt{3}}{2} M_r(\mathrm{NaCl}) + 2M_r(\mathrm{CsCl}) \tag{5}$$

In fact, Hoppe asserts[5] that "there is an infinite number of such relationships for a given structure, since the Madelung constant ... can be broken down in an infinite number of ways into partial sums".

Mestechkin[27] has further simplified the analysis by considering the electrostatic interactions of *lines* with periodic charge distributions (which was also the starting point for Madelung's original summation process) having zero net charge within a period.[1] The crystal is then considered to be constructed by combining a small number of these lines, oriented and shifted appropriately. For the example of the CsCl cell, three orthogonal lines of charges are placed at staggered locations. Summing these three gives the contribution of the Cs^+ ions. The Cl^- ion has the same absolute value of its Madelung contribution, so the Madelung constant of CsCl is half the sum of these two contributions.

Only three constants are required to generate the Madelung constants of any ICLC structure. Mestechkin[27] generates the ion-site-based Madelung constants for cubic lattices from the three relations

$$\begin{aligned} a &= [M_a(\mathrm{CsCl}) - M_a(\mathrm{Cu_2O})]/3 \\ &= -2.741\,365\,174\,540\,80 \end{aligned} \tag{6a}$$

$$\begin{aligned} b &= [M_a(\mathrm{Cu_2O}) - M_a(\mathrm{NaCl})]/3 - M_a(\mathrm{CsCl}) \\ &= 0.219\,414\,438\,483\,61 \end{aligned} \tag{6b}$$

$$\begin{aligned} c &= [M_a(\mathrm{NaCl}) - M_a(\mathrm{CsCl})]/3 \\ &= 0.486\,589\,226\,6046 \end{aligned} \tag{6c}$$

Table 1. Madelung Constants and Madelung Energies for Seven Cubic Lattices:[a] Nearest-Neighbour-Based M_r, Lattice-Constant-Based M_a (Charges Included), and Madelung Energy E_M

crystal	formula[b] for M_a	M_r (Sakamoto)	r/a	M_a (Mestechkin)	a[c] /nm	E_M[d] / kJ mol^{1} = 138.94M_a/a
CsCl	$-(a + b + c)$	1.762 674 7730	$3^{1/2}/2$	2.035 361 094 5260	0.4126	685.4
NaCl	$-a - b + 2c$	1.747 564 5946	1/2	3.495 129 189 2664	0.5737	846.5
Cu_2O	$4a - b - c$	4.442 475 2098	$3^{1/2}/4$	10.259 457 033 0750	0.4627	3081
ZnS	$-6(a + b)$	1.638 055 0533	$3^{1/2}/4$	15.131 704 416 3431	0.5587	3763
CaF_2	$-5(a + b) - 2c$	5.038 784 8798	$3^{1/2}/4$	11.636 575 227 0768	0.5466	2958
$BaBiO_3$ (perovskite)	$-16(2a - b - c)$[d]	12.377 468 0325 × 2	1/4	49.509 872 113 3584 × 2	0.8836	15 572[d]
K_2PtCl_6	$4(-5a + b + 4c)$	15.872 597 2176	1/4	63.490 388 870 4239	0.9691	(9103)[e]

[a] This table is extracted from Table 1 of Mestechkin[27] and includes only the full Madelung constants. The complete table also lists site-based Madelung constants for these materials as well as Madelung constants for two fullerides. [b] $a = -2.741\,365\,174\,540\,80$, $b = 0.219\,414\,438\,483\,61$, and $c = 0.486\,589\,226\,6046$. [c] Lattice constants from AtomWorks.[32] [d] The factor 138.94 converts from the units of (e^2 nm^{-1} per molecule) to (kJ mol^{-1}), as follows: $\frac{e^2 N_A \times (\mathrm{m/nm})}{4\pi\varepsilon_0 \times (\mathrm{kJ/J})} = \frac{(1.60218\times10^{-19})^2 \times 6.02214\times10^{23}\times10^9}{(4\times3.14159\times8.85419\times10^{12})\times10^3} = 138.94$. [e] The factor 16 (the charge product for $BaBiO_3$: 2 × 4 × 2=16) has been inserted in place of Mestechkin's factor 8, in order to generate the correct Madelung energy.[10] E_M values assume fully ionic material, *e. g.*, Pt^{4+}. This may be unrealistic for ion complexes.[33]

where the individual material Madelung constants were earlier calculated to 15 significant places by Sakamoto;[30] a few of these Madelung constants, listed to 100 decimal places, can be found at *The On-Line Encyclopedia of Integer Sequences*.[31] Table 1 lists the materials, the sum formulas, and the lattice constant-based Madelung constants, M_a, for seven common cubic solids.

Although Mestechkin's analysis provides a formal process for obtaining many Madelung constants, it is complex and has not been widely applied by others. Instead, current computer programs supply the results simply, rapidly, and reliably.

Madelung Constants for other Crystal Structure Types. The Supporting Information collates a large number of Madelung energies from the literature.[19−23] Where major discrepancies were detected, the values have been recalculated using the program GULP.[10]

■ DISCUSSION AND CONCLUSIONS

The reference distances quoted in these Tables have been chosen from the most recent structure listed in the current AtomWork database.[32] These may not be exactly the same as those used in the calculation of the published Madelung constant; hence, there is some variation in the values listed in Supporting Information Tables S1 and S2. However, these are generally within the 1% range appropriate to the resulting energy calculation.

Predictive Property. Figure 1 plots the mean Born−Haber−Fajans lattice energies[34] of the tabulated ionic solids against the calculated Madelung energy for the materials, using the data in Table S1. A Born−Haber cycle calculates the lattice energy/enthalpy by comparing the standard energy/enthalpy change of formation of the ionic compound from its component elements to the energy/enthalpy required to make gaseous ions from those elements, each in their standard states.[35,36]

It can be seen that there is a good linear correlation between these values, such that lattice energies for similar materials may be estimated to a good approximation, without having to resort to a full lattice energy calculation (which requires establishment of uncertain repulsion and other parameters).[37,38]

The linear regression in Figure 1 confirms that the lattice energies, U_{POT}, for ionic solids are about 15% smaller than their attractive Madelung energies,[39−41] the difference arising because the Madelung energy only accounts for the coulombic (charge) interactions, omitting consideration of all other interactions, such as van der Waals repulsions, which generally reduce the stability of the material. Figure 1 shows the first correlation of this kind using experimental data; previous estimates of the coulombic contribution were based on estimations such as the Born−Landé division between attraction and repulsion terms $(1 - 1/n)$ selecting an average value for the repulsive exponent, n, of 9, and so yielding 89% for the attractive term.[42]

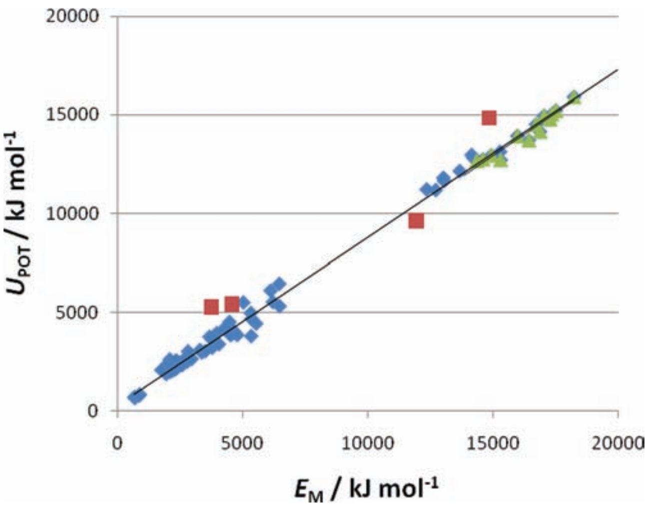

Figure 1. Plot of Born−Haber−Fajans lattice energy, U_{POT}, versus mean Madelung (electrostatic) energy, E_M, for ionic solids. The fitted least-squares linear regression line to 72 data points (blue diamonds) has the formula U_{POT}/kJ mol^{-1} = 0.8519 (±0.0073) E_M + 293.9 (±65.0), with a correlation coefficient, R^2 = 0.995. The root-mean square deviation (rmsd) of the values of U_{POT} against E_M is 345 kJ mol^{-1}. The outliers (red squares) are AsI_3, $FeCl_3$, CeO_2, and Pb_2O_3, in sequence, and have been excluded from the linear regression. The green triangles represent 13 M_2O_3 structures (extracted from the full set of 72), with a linear regression U_{POT}/kJ mol^{-1} = 0.859 (±0.0677) E_M + 54.2 (±1109.4), and a correlation coefficient, R^2 = 0.936.

The fitted intercepts (294 ± 65 and 54 ± 1109 kJ mol^{-1}) might be construed to represent the constant repulsive contribution to the lattice energy, in the absence of the coulombic term. However, the values are wildly discordant, being much influenced by the particular set of values used in the fitting process, and little should be made of their particular values, while the slope is better determined. Furthermore, the quoted values for U_{POT} come from many sources, each with its own errors, so that only broad generalizations may be made as to their accuracies; a value of 5% is suggested, but may be as small as a few kJ mol^{-1} for well-studied materials such as the alkali halides, but considerably larger for more exotic materials.[36,43]

Figure 2 plots the lattice energies of alkali metal hydrides and transition metal compounds (halides plus CuH) against the calculated Madelung energy using the data in Table S3.[44] These materials have a considerable degree of covalency, implying that the purely coulombic contribution of the Madelung energy is a smaller component of the lattice energy. This is reflected in the considerably reduced slopes of the fitted linear relations: for the alkali metal hydrides, the Madelung energy contribution is about 62%; and only about 40% for the transition metal compounds.

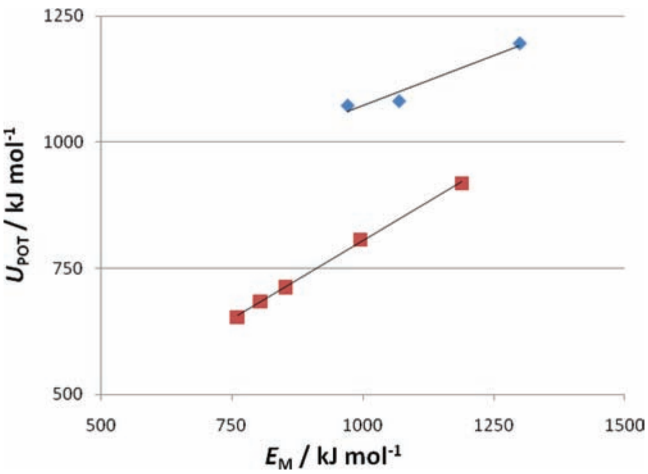

Figure 2. Plot of Born−Haber−Fajans lattice energy, U_{POT}, versus Madelung (electrostatic) energy, E_M, for alkali metal and transition metal compounds (red squares and blue diamonds, respectively). The fitted least-squares linear regression line for the alkali metal halides has the following formula: U_{POT}/kJ mol^{-1} = 0.6177 (±0.0120) E_M + 186.7 (±11.2), with a correlation coefficient, R^2 = 0.999. The root-mean square deviation (rmsd) of the values of U_{POT} against E_M is 4.2 kJ mol^{-1}. The fitted least-squares linear regression line for the transition metal halides has the following formula: U_{POT}/kJ mol^{-1} = 0.3965 (±0.0927) E_M + 675.7 (±103.9), with a correlation coefficient, R^2 = 0.948. The root-mean square deviation (rmsd) of the values of U_{POT} against E_M is 22.1 kJ mol^{-1}.

An alternative volume-based thermodynamic (VBT) estimation procedure by which to establish lattice energies has earlier been published.[45,46] An important advantage of the VBT evaluation is that a detailed crystal structure is not required (as it is for the Madelung calculation) but only the formula volume (or density), which (by implication, however) contains part of the structural information. For lattice energies less than about 5000 kJ mol^{-1}, the following formula may be used

$$U_{POT} = 2I\left(\frac{\alpha}{V_m^{1/3}} + \beta\right) \tag{7}$$

where ionic strength factor, $I = \sum_1^t n_i z_i^2$, with n_i ions each of charge z_i, summed over the t types of ions in the chemical formula. [A related factor, S (=2I), was introduced[47] in 1955 as a normalizing factor for Madelung energies but seemingly not much further applied.[22] Forty years later, I was independently found to be appropriate in order to extend energy formulas (such as the Kapustinskii equation) from binary to more complex ionic materials.[48]] The most appropriate values of the constants, α and β, are specific to the chemical formula type, M_pX_q.[49]

For materials with larger lattice energies (such as minerals with more complex chemical formulas), the following generalized formula should be used[39]

$$U_{POT} = AI(2I/V_m)^{1/3} \tag{8}$$

where A is a standard electrostatic constant with value 121.39 kJ mol^{-1} nm (and α's in eq 7 are close in value to A).

Consider the case of Pb_2O_3 (monoclinic, space group no. 14, $P2_1/c$; V_{cell} = 0.305 56 nm^3; Z = 4; I = 15). According to the lattice energy table in the *Handbook of Chemistry and Physics*,[34] the calculated U_{POT} is 14 841 kJ mol^{-1} (but this value is bracketed, as uncertain, and is, in fact, the Madelung energy value) while no Born−Haber−Fajans thermochemical cycle value is listed. Using the linear correlation for M_2O_3 of Figure 1, with V_m = 0.0764 nm^3, we calculate U_{POT} = 12 802 kJ mol^{-1} while from eq 8 (with I = 15) U_{POT} = 13 334 kJ mol^{-1}, with discrepancies of only 2.0% from the mean value of 13 069 kJ mol^{-1}. However, the latter value is to be preferred since it pertains to like materials.

The values for the other outliers may similarly be corrected, while the lattice energies of other ionic solids may easily be estimated from the linear regressions depicted.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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