

Lattice Self-Potentials and Madelung Constants for Some Compounds

Part 1

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Calculations of lattice self-potentials and lattice potentials were made for ionic compounds with the Ewald method, the formulae being modified to facilitate computer calculation. The counting procedure for ionic charges and the collection of unit cells into shells is the same as in the Evjen method for potential calculations. The significance of the use of fractional charges for ions on planes, edges or corners of the unit cell is shown. There are no symmetry restrictions for the application of the formulae.

After testing the program on some compounds whose Madelung constants are well-established in the literature, lattice self-potentials for distinct ion positions, Madelung constants and electrostatic energies were calculated for Al_2O_3 , Cr_2O_3 , $\alpha\text{-Fe}_2\text{O}_3$, Ti_2O_3 , V_2O_3 , CaCl_2 , CrCl_2 , BaHCl , BiOBr , PbFCl , SrHI , TmOI , CuFeO_2 , LiCrO_2 , NaFeO_2 , IrF_3 , MoF_3 , LaF_3 , PuBr_3 , VF_3 , AsI_3 , BiI_3 , FeCl_3 , BaTiO_3 (four modifications), TiO_2 (three modifications).

Some special applications will be discussed in a second paper.

1. Introduction

The calculation of lattice self-potentials and Madelung constants has been discussed extensively [1-3]. In spite of this, the information available [2, 4-6] is limited in two respects. (i) Most of the calculations were performed for fairly simple and rather symmetric compounds. Our interest is in more complicated compounds with a low symmetry. (ii) Most tables report Madelung constants, but not the self-potentials for the different ions. It is true that, except for the sign, the self-potentials for the positive ion equals that of the negative in simple structures and that lattice self-potentials may easily be calculated from the Madelung constant in such cases. This is no longer true in rutile, perovskite and other structures. To quote one situation: the self-potential at the O^{2-} site in perovskites depends upon the charges of the cations (3-3, 2-4, 1-5, or 0-6). These differences in self-potential are of importance in the removal of oxygen from these compounds. Other application of the differences in self-potential are in connection with the occurrence of excess of

oxygen or deficiency of oxygen in oxides, which is often related to the occurrence of p- or n-type semi-conduction. Lattice potentials are also required in solid state diffusion problems and in energy calculations involving interstitial ions.

For these reasons mentioned above a general computer program was developed for the calculation of lattice self-potential and lattice potential in a point-charge crystal. The procedure is outlined in section 2. The results of some of the calculations are summarised in section 3; some special results will be discussed in part 2. There are important limitations to the significance of electrostatic potential calculations, which assume ionic crystals with point charges. The presence of covalent bonds obviously invalidates the results although Phillips and Williams [7] and Van Arkel [8] have shown that energy values thus obtained are in better agreement with experimental evidence than might be expected. Studies in which actual size and other properties of ions have been used include the Shell-model studied by Dick and Overhauser [9] and applied to barium titanate by Havinga [10], and the

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other-than-point charges used by Birman [11], Slater and DeCicco [12]. Once the potentials are calculated, repulsive energy, London-Van der Waals forces, zero point energy and crystal field corrections must also be considered in calculating free energy. (See Tosi [1], Waddington [2], and Born and Huang [3].) Additional complications arise in the calculation of the energy needed for the creation of vacancies. (See, for example, Kröger [13].) These aspects are not discussed in this paper.

2. Formulae and Procedure

In a point-charge crystal the electrostatic potential for a particular charged point is defined as the potential for that site, after the corresponding charge has been removed. The other points remain fixed in their position for the sake of the calculation. The electrostatic potential calculated in this way is called the self-potential for the corresponding site. Lattice self-potentials refer to the collection of the lattice self-potentials for the distinguishable anion- and cation-sites. Obviously terms like "potential, anion-site", etc are a short notation for self-potential for an anion-site, etc. The electrostatic potential for some interstitial location does not need the removal of an ion for its calculation. Such a potential is referred to as lattice potential. Sometimes the term lattice potential is used quite generally. Then it describes the total collection of (interstitial) lattice potentials and lattice self-potentials.

The calculation of the electrostatic potential was done with the Ewald method [14]. In the formulation of Tosi [1] the formulas are:

$$\begin{aligned} \phi(\bar{r}_p') &= \frac{1}{\pi\Delta} \sum_h' S(\bar{h}) \bar{k}_h^{-2} \\ &\quad \exp(-\pi^2 \eta^2 \bar{k}_h^2 + 2\pi i \bar{k}_h \cdot \bar{r}_p') \\ &+ \sum_l' \sum_p' \zeta_p' \frac{1 - F(|\bar{r}_p' - \bar{r}_l - \bar{r}_p|/\eta)}{|\bar{r}_p' - \bar{r}_l - \bar{r}_p|} - \frac{2\zeta_p'}{\pi^{\frac{1}{2}} \eta} \end{aligned} \tag{1}$$

$$S(\bar{h}) = \sum_p \zeta_p \exp(-2\pi i \bar{k}_h \cdot \bar{r}_p) \tag{2}$$

$$F(t) = 2\pi^{-\frac{3}{2}} \int_0^t \exp(-t^2) dt \tag{3}$$

$$t = \frac{|\bar{r}_p' - \bar{r}_l - \bar{r}_p|}{\eta} \tag{4}$$

The symbols have the following meaning: \bar{r}_p' , ζ_p' , position vector and charge of the point at which the potential must be calculated; \bar{r}_p , ζ_p ,

position vectors and charges of other ions in the unit cell; $\bar{k}_h = h_1 \bar{a}^* + h_2 \bar{b}^* + h_3 \bar{c}^* =$ vector in the reciprocal space with basic vectors \bar{a}^* , \bar{b}^* , \bar{c}^* and integers h_1, h_2, h_3 ; $\bar{r}_l = l_1 \bar{a} + l_2 \bar{b} + l_3 \bar{c} =$ vector in normal space with basic vectors a, b, c and integers l_1, l_2, l_3 ; \sum_h' , summation over all integers values of h_1, h_2, h_3 except $h_1 = h_2 = h_3 = 0$; \sum_p , summation over all positions p (including p'); \sum_l' , summation over all integer values l_1, l_2, l_3 , except $l_1 = l_2 = l_3 = 0$ in the case where $p = p'$; η , adjustable parameter (see below); Δ , volume of the unit cell.

In order to write a simpler computer program a few changes are introduced. All calculations are made for $\bar{r}_p' = 0$. Before each calculation the unit cell is shifted so that the point under consideration is the origin of the co-ordinate system which is at the centre of the new unit cell. Co-ordinates are thus limited to those between + 0.5 and - 0.5. Since this shift is done automatically in the computer, the most convenient selection of co-ordinate axes for input data can be used.

Summations are performed as in Evjen's method [15, 16]. First \sum_p is determined for each unit cell, next the unit cells are summed over "shells".

The term "shells" refers to both the direct and the reciprocal lattice. All unit cells containing at least one value $|l_j|$ ($j = 1, 2, 3$) equal N and one value $|h_j|$ ($j = 1, 2, 3$) equal N (but no absolute values larger than N) are collected into shell $N + 1$ (the central unit cell is given a layer number of one). Consequently, for each unit cell described with \bar{k}_h there occurs a cell $-\bar{k}_h$. This means that the complex terms in equation 2 cancel. Furthermore, since summations both for direct space (\sum_l') and for reciprocal space (\sum_h') are done over the same "shell", they can be replaced by one summation \sum_n' .

In order to make all unit cells neutral and obviate the necessity for special consideration of ions which are a part of 2, 4 or 8 unit cells, the charge of ions occurring in end planes, edges or corners of the new unit cells are counted as having $\frac{1}{2}$, $\frac{1}{4}$ and $\frac{1}{8}$ respectively, of their original value (Evjen counting). The validity of this technique can be shown if one considers, for example, a charge at the corner of the unit cell. Assume this charge to be split into eight equal charges, q_m , where q_m is $\frac{1}{8}$ of original charge, q , and that each q_m occurs at a distance $|\bar{r}_m| = \delta r$ from the original point and in a different octant.

According to electrostatic theory [17, 18] the

potential at point A at a distance $|\bar{r}|$ from the charge q , due to the eight charges is shown by the following equation:

$$V_A = \sum_m \frac{q_m}{|\bar{r}|} \left[1 + \sum_{i=1}^{\infty} \left(\frac{\delta r}{|\bar{r}|} \right)^i P_i^0 \{ \cos(\bar{r}_m, \bar{r}) \} \right] \quad (5)$$

where P_i^0 are Legendre polynomials and $\cos(\bar{r}_m, \bar{r})$ is the cosine of the angle between \bar{r}_m and \bar{r} . Obviously, by making $\delta r/|\bar{r}|$ small, one can approximate the required potential $q/|\bar{r}|$, since $\sum q_m = q$. This means that calculations can be performed as if no charges at corners (also edges, end planes) occur by using eight points close to the original one, etc. This aspect is important in using Evjen fractions and it might simplify the description of situations with charges on an end plane [16].

Several values for the adjustable constant, η , have been proposed in the literature, including that of one-half the atomic distance [1], and $2(\pi)^{1/2}/a$ recommended by Dienes [19]. To find a value which gives rapid convergence, equation 1 can be rewritten to include modifications previously indicated:

$$\phi(0) = \sum_n \left[\frac{1 - \delta_{|\bar{N}^*|,0}}{\pi \Delta(\bar{N}^*)^2} \exp(-\pi^2 \eta^2 (\bar{N}^*)^2) \sum_i q_i \cos(2\pi \bar{N}^* \cdot r_i) + (1 - \delta_{|\bar{r}_i + \bar{N}|,0}) \sum_i q_i (1 - F(t))/(|\bar{r}_i + \bar{N}|) \right] - \frac{2q_j}{\pi^2 \eta} \quad (6)$$

Here $\bar{N}^* = n_1 \bar{a}^* + n_2 \bar{b}^* + n_3 \bar{c}^*$; $\bar{N} = n_1 \bar{a} + n_2 \bar{b} + n_3 \bar{c}$; $q_i =$ charge (Evjen charge) of the ions in the unit cell after lattice shifts; $q_j =$ charge at the origin, if any. In the case of self-potentials there is a charge, otherwise the value is zero. $\bar{r}_i = x_i \bar{a} + y_i \bar{b} + z_i \bar{c}$, where x_i, y_i, z_i are fractional co-ordinates of point i ; $\bar{N}^* \cdot \bar{r}_i =$ inner vector product of \bar{N}^* and $\bar{r}_i = n_1 x_i + n_2 y_i + n_3 z_i$; $\sum_n =$ summation over all values n_1, n_2, n_3 ; $\delta_{|\bar{N}^*|,0} = 1$ for $n_1 = n_2 = n_3 = 0$; zero for all other combinations of n_j ; $\delta_{|\bar{r}_i + \bar{N}|,0} = 1$ for $\bar{r}_i = 0$ when at the same time $n_1 = n_2 = n_3 = 0$. For all other values of n_j or for $i \neq j$ the value is zero.

It can be shown that the value of $\phi(0)$ in equation 6 is independent of the choice of η , at least within certain limits. A value of η acceptable in practical calculations should equalise the rate of convergence of the first two

terms as much as possible. The first term contains $\exp(-\pi^2 \eta^2 \bar{N}^{*2})$ and a good convergence is obtained for large η values. In any given shell, the most unfavourable situation occurs when the unit cell with the smallest \bar{N}^* is calculated, and that obviously depends upon the question which of the values a^*, b^* and c^* is the smallest. Let us call the smallest reciprocal lattice dimension a^*_{\min} , then the best convergence is obtained for

$$\pi \eta \bar{N}^* > 1, \text{ or } \eta = \frac{p}{\pi a^*_{\min}}, \text{ with } p > 1. \quad (7)$$

The second term can be analysed in the same way. The error function approximates the value one for large t -values and thus $1 - F(t)$ approximates zero under this condition. With $t = (|\bar{r}_i + \bar{N}|)/\eta$, good convergence here requires a small η -value. It can be shown that in this case the smallest of the three perpendicular distances in the unit cell is the applicable characteristic value. Such perpendicular distances between two end planes in the unit cell are calculated from $a_p = \Delta/bc \sin \alpha$, etc and the smallest value of the set will be indicated as a_{\min} . The condition for fast convergence becomes

$$\frac{|\bar{r}_i + \bar{N}|}{\eta} > 1, \text{ or } \eta = \frac{a_{p\min}}{q}, \text{ with } q > 1. \quad (8)$$

Giving equal weights to the convergence of each series ($p = q$) leads to

$$\eta = \left(\frac{a_{p\min}}{\pi a^*_{\min}} \right)^{\frac{1}{2}}. \quad (9)$$

Here η is expressed in the dimensions of the unit cell rather than atomic distances. This choice is better in large unit cells and complicated crystal structures where several different interatomic distances have been found.

The potentials calculated in the program are expressed in \AA^{-1} , since charges are introduced as charge numbers and distances are expressed in \AA (occasionally, in the case of averaged structures, fractions of charges are used). When potentials ϕ_j have been calculated for all different points j in the unit cell, the total electrostatic energy is

$$E \text{ (in kcal/mole)} = 332 \sum \frac{q_j p_j \phi_j}{2\kappa}. \quad (10)$$

Here q_j is the total charge number (not Evjen charge) of point j , p_j the frequency of occurrence in the unit cell of point j and κ the total number of "molecules" in the unit cell.

The Madelung constant is defined as

$$M_a = -a \sum_j \frac{q_j p_j \phi_j}{2\kappa} \quad (11)$$

where M_a is described relative to the length a of the unit cell. Again: expressing M relative to other characteristic lengths, like the atomic distance, is quite arbitrary in complex structures.

It is possible, however, to compare Madelung constants M_r expressed relative to some other distance r in the same crystal by means of formula 12

$$M_r = (r/a) M_a. \quad (12)$$

This is obvious from the energy expression:

$$E = -332 \frac{M_a}{a} = -332 \frac{M_r}{r}. \quad (13)$$

We are interested in differences between potentials rather than in the constancy of the Madelung constant for a certain structure. For that reason electrostatic potentials of lattice sites and interstitial sites were calculated, and the Madelung constant (or electrostatic energy of the compound) obtained as a by-product. If one is interested in the energy only, some short cuts can be made [20].

It should be stressed that the calculated potentials and the energy per mole are independent of the choice of the unit cell (contrary to the Madelung constant, see [12]). However, when one compares compounds with the same structure but with a different size of the unit cell, the Madelung constant is the same, but the energy and the potentials are different ($\phi_j \cdot a$ is constant).

The computer program was written in Fortran IV and was essentially based upon equation 6. Calculations were done with the Philco 212 computer*.

3. Results

3.1. Checking of the Computer Program

The simplest way to check some aspects of the program is to compare Madelung constants obtained with the program with well-established values reported in the literature. See table I for some simple compounds.

*The authors have available a limited number of copies of a paper describing in detail the program, input data and examples of printouts.

†This check does not solve the problem of different potential conventions [11]. It showed, however, that the correction proposed by Dahl [16] for potential calculations by means of the Evjen method, is not entirely correct in all cases. Applying this method of checking to a computerised version of his formulae we found that differences might occur when non-rectangular angles occur in the unit cell.

TABLE I Madelung constants for some compounds (M_a).

	This paper	Reported [1, 2]
NaCl	3.495	3.49513
CsCl	2.035	2.03536
CaF ₂	11.635	11.63657
0-6 Perovskite (ReO ₃ type)	71.632	71.616 71.6316 71.6315
1-5 Perovskite (NaTaO ₃ type)	58.537	58.53535
3-3 Perovskite (LaAlO ₃ type)	44.558	44.544 44.55489
Cu ₂ O	10.259	10.25946

This check is inadequate because in the calculation of each of the above cubic compounds, terms containing the cosines of the angles become 0 and no check of the validity of the other quantities involved in these terms can be made. There is also a possibility of a systematic error in calculating potentials which cancels out in summing up the potentials to get the Madelung constant. Both of these possible errors can be checked doing the calculation with various descriptions of the same compound, that is, using different crystallographic axes and thus different unit cells, for instance the rhombohedral and hexagonal descriptions of a crystal of the hexagonal system. A minimum requirement for the validity of the calculation is that an ion site must have the same potential in all descriptions†.

Our check was done with CsCl in six different descriptions and with Cr₂O₃, Cu₂O and CaF₂ in two descriptions. See table II for CsCl.

The unit cells used in table II are as follows (see also fig. 1).

Cubic

$$a = b = c = 4.123$$

$$\text{Cs}^+ : 0.6, 0.6, 0.6$$

$$\text{Cl}^- : 0.1, 0.1, 0.1$$

Tetragonal (2 CsCl)

$$a = b = 5.830803$$

$$c = 4.123$$

$$\text{Cs}^+ : 0.6, 0.6, 0.6 \text{ and}$$

$$0.1, 0.1, 0.6$$

$$\text{Cl}^- : 0.1, 0.6, 0.1 \text{ and}$$

$$0.6, 0.1, 0.1$$

Rhombohedral (2 CsCl)

$a = b = c = 5.830803$ Cs⁺: 0.35, 0.35, 0.35
 $\alpha = \beta = \gamma = 60^\circ$ and 0.85, 0.85,
 0.85
 Cl⁻: 0.1, 0.1, 0.1 and
 0.6, 0.6, 0.6

Triclinic (NaCl type 4 CsCl)

$a = b = c = 7.14125$ Cs⁺: 0.6, 0.6, 0.6 and
 $\alpha = \beta = 70^\circ 34'$, 0.6, 0.1, 0.1 and
 $\gamma = 109^\circ 26'$ 0.1, 0.6, 0.1 and
 0.1, 0.1, 0.6
 Cl⁻: 0.1, 0.1, 0.1 and
 0.1, 0.6, 0.6 and
 0.6, 0.1, 0.6 and
 0.6, 0.6, 0.1

Monoclinic (1 CsCl)

$a = c = 4.123$, Cs⁺: 0.1, 0.6, 0.6
 $b = 5.830803$ Cl⁻: 0.1, 0.1, 0.1
 $\alpha = \beta = 90^\circ, \gamma = 135^\circ$

Orthorhombic (3 CsCl)

$a = b = 4.123, c = 12.369$ Cs⁺: 0.6, 0.6, 0.26667
 $\alpha = \beta = \gamma = 90^\circ$ and 0.6, 0.6, 0.6
 and 0.6, 0.6,
 0.9333
 Cl⁻: 0.1, 0.1, 0.1 and
 0.1, 0.1, 0.4333
 and 0.1, 0.1,
 0.76667

The accuracy of the calculations is generally better than 0.1% and that was enough for our purpose. In some cases the potentials obtained are quite sensitive to small changes in the input data. We found, for example, that for CuO the use of eight significant figures in giving the angles of the unit cell (in radians) was required to get better than 1% precision. However, not all situations are so sensitive.

3.2. Some Results

Lattice potentials, electrostatic energy and

Madelung constants for several compounds are summarised in table III. The dimensions of the unit cells and the positions of the atoms were taken from Wyckoff's collections [21]. Since some of the compounds can occur in several crystal structures, the Wyckoff page reference is listed next to the compound name. The lattice parameter a has been listed in the footnotes to the table when it is the only variable for the type of structure under consideration. In such cases potentials and energy for other compounds of the same structure can be calculated directly from the results given here and the compound's own lattice parameter a .

3.3. Discussion

In table III there are some compounds which have a more or less characteristic structure, that is, hardly any other compounds are known to have the same structure. Examples are CuO, Pb₂O₃, ZrO₂ (baddeleyite). In other cases many compounds are found with the same structure as the examples shown in the table: for example NaCl, SnO₂, etc. The question naturally arises: is there a reasonably simple way of using the results obtained for one compound to obtain potentials and Madelung constants for related structures, or is it necessary to run the complete computer program for each compound?

For structure types where the position of the atom is completely fixed except for a proportionality factor in lattice dimensions, such as NaCl types or CsCl, CaF₂ or Cu₂O types, it can easily be seen that the potential varies inversely with the lattice parameter a . Where there are one or more additional parameters the analysis becomes more complex. An example can be found in the perovskites (NaTaO₃, SrTiO₃, etc). Here the structure is fixed, but valence state of the ions varies from one compound to another [22]. The effect of valence can be shown by fixing the

TABLE II CsCl in different descriptions.

Unit cell	Potential Cs ⁺ site	Madelung	Energy/mole	Madelung**
Cubic	- 0.4936	2.0352	163.88	2.0352
Tetragonal	- 0.4936	2.8782	163.88	2.0352
Rhombohedral	- 0.4937	2.8788	163.92	2.0352
Monoclinic (NaCl description)	- 0.4935	3.5239	163.83	2.0346
Monoclinic	- 0.4936	2.0352	163.88	2.0352
Tetragonal (triple cell)	- 0.4934	2.0345	163.82	2.0345

*Madelung*** The first three columns represent data as obtained in the computer. Since the Madelung constant is relative to the lattice dimension a , the result will be different whenever another reference distance is chosen. The last column shows the values referring all to a of the standard cell.

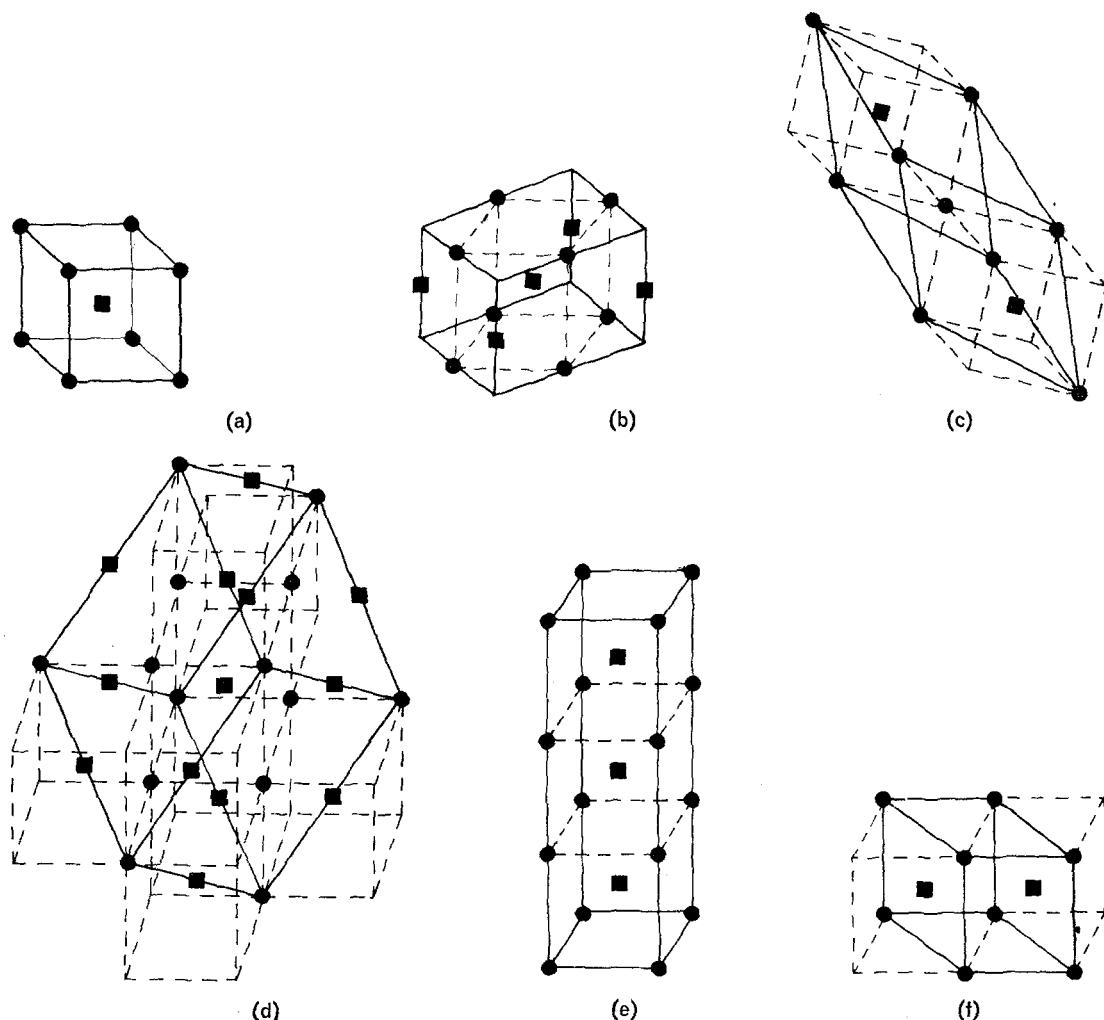


Figure 1 Some choices of the unit cell in the CsCl lattice. (a) Standard cubic; (b) tetragonal; (c) rhombohedral; (d) triclinic (NaCl type); (e) orthorhombic (triple cell); (f) monoclinic.

lattice dimensions at one constant value and varying only the valence as in table IV, where a is arbitrarily taken to be 3.881 in all four cases (3.881 is the value that is found in NaTaO_3).

It can be seen that there is a significant variation in oxygen potential as the valence of the other two ions changes. This variation will certainly influence the energy required to create an oxygen vacancy.

Formulae describing the potentials and Madelung constant as a function of one or two parameters can be derived. Waddington [2] surveyed some of these relationships in the case of Madelung constants. Similarly, relevant quantities can be calculated for artificial situations and results plotted. Fig. 3 shows this approach as applied to the rutile structure (GeO_2 , SnO_2 , and

TiO_2 of table III have this structure). In this structure two additional parameters occur: the c/a ratio of the tetragonal crystals and the parameter u in the description of the positions:

$$\begin{aligned} \text{M}^+ & (000), \left(\frac{1}{2} \frac{1}{2} \frac{1}{2}\right) \\ \text{O}^{2-} & \pm (uu0; u + \frac{1}{2}, \frac{1}{2} - u, \frac{1}{2}) . \end{aligned}$$

It should be noted that Waddington's equation (21) gives values for the Madelung constant other than those shown in fig. 2. Obviously there is an error in this equation as printed since an increase of the c/a ratio from 0.302 to 0.307 gives an increase of the Madelung constant whereas its value ought to decrease.

Groups with even more parameters include such examples as the following, all of which are included in table III. The number in parenthesis

TABLE III

Compound	Wyckoff [21]		Potential	Cation-site	Potential	Anion-site	Madelung constant M_a	Energy/mole
	Reference	Page						
$Al_2O_3^a$	II	7		- 2.540		1.832	67.258	4354.4
AsI_3^b	II	45		- 1.218		0.586	22.323	898.3
$BaHCl^c$	I	294		- 1.135	Cl ⁻ H ⁻	0.537 0.655	7.633	574.9
$BaTiO_3$				See table V				
BiI_3^b	II	45		- 1.236		0.576	22.090	902.1
$BiOBr$	II	45		- 1.893	O ²⁻ Br ⁻	1.532 0.514	18.129	1537.0
$CaCl_2$	I	252		- 1.111		0.638	10.918	580.9
CaF_2^d	I	240		- 1.385		0.745	11.635	707.1
Ce_2O_2S	II	2		- 1.928	(0, 0, 0) ($\frac{1}{3}, \frac{2}{3}, 0.64$)	1.048 1.557	39.830	3302.6
$CrCl_2$	I	253		- 1.185		0.711	11.326	629.4
$Cr_2O_3^e$	II	6		- 2.426		1.764	62.260	4172.4
$Cr_2O_3^a$	II	6		- 2.427		1.764	67.268	4174.4
$CsCl^f$	I	103		See Table II				
CuO	I	140		- 1.684		1.662	15.570	1110.9
Cu_2O^g	I	331		- 0.886		1.517	10.259	797.7
$CuFeO_2$	II	292	Cu ₂ ⁺	- 1.122		1.423	36.704	2044.9
			Fe ₂ ⁺	- 2.191				
			Cu ⁺	- 0.860				
			Fe ³⁺	- 2.453		1.690	44.636	2486.8
$FeCl_3^b$	II	45		- 1.488		0.703	22.218	1091.5
$\alpha-Fe_2O_3^a$	II	7		- 2.416		1.731	67.346	4130.2
GeO_2^h	I	251		- 3.240		1.871	44.930	3394.1
IrF_3^i	II	48		- 2.064		0.868	23.834	1460.5
LaF_3	II	60		- 1.894	(2b) (4f)	0.747 0.661	16.074	1286.5
					(1a) (2d)	1.384 1.388		
La_2O_3	II	1		- 2.012			40.152	3385.6
$LiCrO_2$	II	292	Li ⁺	- 1.281		1.692	36.611	2383.3
			Cr ³⁺	- 2.103				
MoF_3^i	II	48		- 2.140		0.960	26.347	1543.8
$NaCl^k$	I	85		- 0.621		0.621	3.495	206.2
$NaFeO_2$	II	292	Na ⁺	- 0.763		1.688	42.057	2497.8
			Fe ³⁺	- 2.510				
			Na ⁺	- 0.864				
$NaTaO_3^l$	II	393	Ta ⁵⁺	- 3.714		1.789	58.537	5007.6
$PbFCl$	I	296		- 1.185	Cl ⁻ F ⁻	0.534 0.753	7.508	607.1
					0 (1) 0 (2) 0 (3)	1.483 1.390 1.473		
Pb_2O_3	II	14	Pb (1) Pb (2)	- 2.276 - 1.949		1.483 1.390 1.473	75.320	3547.0
					Br (1) Br (2)	0.445 0.600	36.027	946.3
$PuBr_3$	II	62		- 1.352		1.268		
					S ²⁻ I ⁻	0.481	32.422	1267.9
$SbSI$	I	385	Sb ³⁺	- 1.541		0.163	3.611	141.2
					S ⁰ I ⁻	0.428		
$SbSI$	I	385	Sb ⁺	- 0.423		1.709	44.385	3110.6
SnO_2	I	251		- 2.976		0.589	7.313	555.5
$SrHI$	I	295		- 1.109	H ⁻ I ⁻	0.540		
$SrTiO_3^m$	II	394	Sr ²⁺ Ti ⁴⁺	- 1.380 - 3.170		1.653	49.512	4209.4

Compound	Wyckoff [21] Reference Vol. Page	Potential	Cation-site	Potential	Anion-site	Madelung constant M_a	Energy/mole
TiO ₂ ⁿ	I 251		- 3.107		1.797	45.055	3256.3
TiO ₂ ^o	I 253		- 3.081		1.839	37.246	3267.0
TiO ₂ ^p	I 254		- 3.093	(1) (2)	1.800 1.820	90.056	3255.5
Ti ₂ O ₃ ^a	II 7		- 2.336		1.710	65.934	4030.6
TmOI	I 295		- 1.804	O ²⁻ I ⁻	1.753 0.458	18.258	1556.3
VF ₃	II 48		- 2.121		0.938	24.659	1523.7
V ₂ O ₃ ^a	II 7		- 2.318		1.692	67.929	3993.4
ZnO	I 111		- 1.668		1.668	10.843	1107.8
ZrO ₂ ^r	I 244		- 2.938	O ²⁻ (1) O ²⁻ (2)	1.586 1.698	47.131	3041.0

(a) Rhombohedral description; (b) rhombohedral description, positions slightly idealised, where $x = -0.25, y = 5/12, z = 1/12$; (c) H in (2a); (d) $a = 5.46295$; (e) hexagonal description; (f) caesium chloride structure, $a = 4.123$; (g) $a = 4.2696$; (h) rutile structure; (i) VF₃ structure; (k) sodium chloride structure, $a = 5.62779$; (l) cubic modification, $a = 3.881$; (m) $a = 3.9051$; (n) rutile; (o) anatase; (p) brookite; (r) baddeleyite.

TABLE IV Perovskites ABO₃^a

Type	Composition	ϕ_A	ϕ_B	ϕ_o	Madelung constant	Energy/mole
ReO ₃	(A ^o) B ⁶⁺ O ₃ ²⁻	- 0.340 ^b	- 4.238	1.914	71.692	6127.8
NaTaO ₃	A ⁺ B ⁵⁺ O ₃ ²⁻	- 0.864	- 3.714	1.789	58.537	5007.6
SrTiO ₃	A ²⁺ B ⁴⁺ O ₃ ²⁻	- 1.371	- 3.150	1.643	49.512	4091.9
LaAlO ₃	A ³⁺ B ³⁺ O ₃ ²⁻	- 1.913	- 2.665	1.538	44.558	3811.7

(a) a is taken to be 3.881 in all four cases. A at (000), B at ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$), O at ($\frac{1}{2}\frac{1}{2}0$), ($\frac{1}{2}0\frac{1}{2}$) and ($0\frac{1}{2}\frac{1}{2}$); (b) this site is empty.

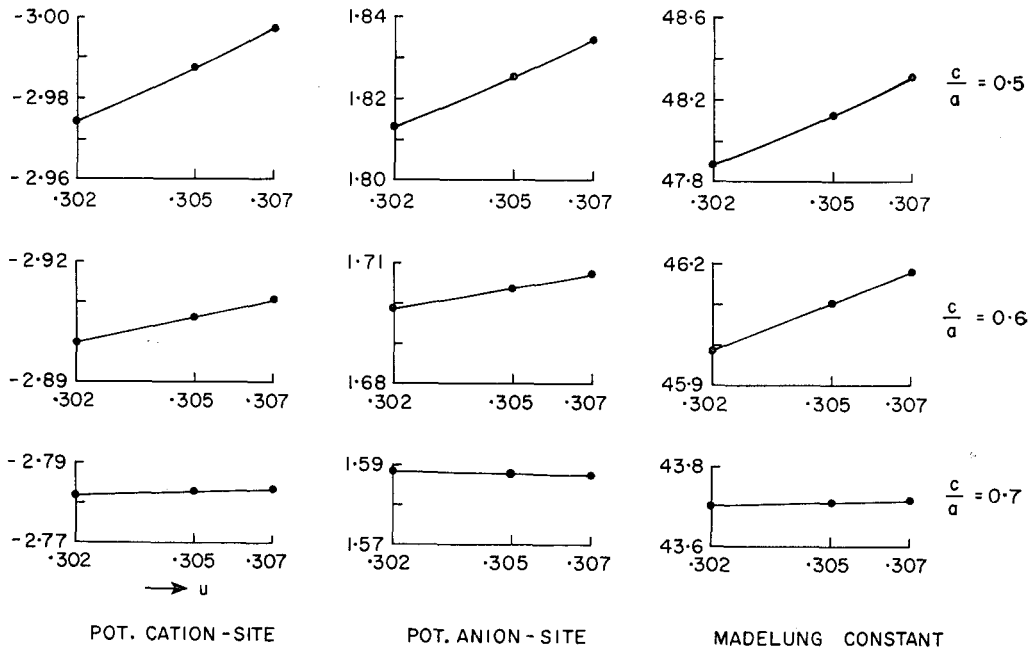


Figure 2 Potential at cation-site and anion-site and Madelung constants for some rutile structures, $a = 5\text{\AA}$ in all situations, u is position parameter.

indicates the number of parameters in addition to lattice parameter a .

1. Al_2O_3 , Cr_2O_3 , $\alpha\text{Fe}_2\text{O}_3$, Ti_2O_3 , V_2O_3 (3).
2. AsI_3 , BiI_3 , FeCl_2 (5).
3. BaHCl , BiOBr , PbFCl , SrHI , TmOI . This group has the PbFCl arrangement. Wyckoff quotes about fifty compounds in this group (3).
4. CaCl_2 , CrCl_2 (4).
5. CuFeO_2 , LiCrO_2 , NaFeO_2 (2 or 3 depending on whether ionisation is obvious or not. See $\text{Cu}^{2+} \text{Fe}^{2+} \text{O}_2^{2-}$ and $\text{Cu}^+ \text{Fe}^{3+} \text{O}_2^{2-}$ in table III). Wyckoff mentions about thirty-five compounds in this group.

Obviously one could make plots like that shown in fig. 2 for all these situations, but the value of this approach is doubtful if used solely to obtain potential and energy values for other members of a group. It would be more efficient simply to feed the data for the other compound into the computer.

Problems in materials research are often centred about small differences in related compounds. Even when they belong to the same space group, three or more variables make for a unique structure for each compound. The concept of any constant, Madelung constant or otherwise, stresses what is common to the group. The Madelung constant is, for instance, of great value in describing the energy of highly symmetric compounds like CsCl , NaCl , etc. In less symmetric compounds, those with several parameters, the difference in potentials at lattice sites and interstitial sites is frequently more germane to the purpose of the research. An example is found in BaTiO_3 with its four structures. The results of calculations are reported in table V.

It is stressed that the appearance of material in table III should not be taken to mean that the compound really is ionic. Some quite certainly are covalent in character. SbSI , for example, can be considered as having SbS chains, separated by

I^- ions. (The same structure occurs with some other Sb and Bi compounds.) The calculations are significant only in that they show that the potential at the I^- site is not particularly dependent on the separation of charges in the Sb/S chains, as long as the effective charge remains the same. The potential, $\phi(\text{I}^-)$, is 0.481 if chains are assumed to be $\text{Sb}^{3+} \text{S}^{2-}$ and 0.428 if Sb^+S^0 chains are postulated.

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TABLE V Potentials of four BaTiO_3 structures.

Structure	Wyckoff Page	ref.	Potential Ba^{2+} site	Potential Ti^{4+} site	Potential O^{2-} site	Madelung constant	Energy/mole
Cubic	II	391	- 1.3431	- 3.0854	1.6092	49.512	4097.4
Tetragonal	II	401	- 1.3445	- 3.0858	(1) 1.5959	49.262	4094.2
					(2) 1.6099		
Orthorhombic	II	405	- 1.3448	- 3.0970	(1) 1.6139	49.428	4112.8
					(2) 1.6176		
Hexagonal	II	414	(1) - 1.2748	(1) - 3.2585	(1) 1.6904	70.883	4103.4
			(2) - 1.3414	(2) - 2.9853	(2) 1.5986		

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