

Lattice Self-Potentials and Madelung Constants for Some Compounds

Part 2 *Some Applications*

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The computerised potential and electrostatic energy calculations described in Part 1 can be used as the first step in more sophisticated calculations, four types of which are described. (i) The results obtained by calculating the actual crystal field in a sodium vacancy in NaCl are compared to the results of the familiar approximation for that situation. (ii) CaF₂ and β -alumina are used as examples of compounds in which there is remarkable similarity between some of the interstitial and some of the lattice sites. A complete calculation of all the self-potentials and the Madelung constant of β -alumina is included. (iii) In a discussion of p- and n-type semiconduction in simple binary compounds, self-potentials are used to show that many structures have a built-in preference for a deviation from stoichiometry, although other factors (not considered in this paper) can obscure this preference. (iv) The concept of a solid-state energy storage using compounds with two different cations in non-interacting sublattices is explored, using the mineral quenselite (PbMnO₂(OH)), as an example. The computer program is used to evaluate this mineral with respect to its energy density.

1. Introduction

Part 1 of this series of papers summarised the results obtained with a computer program for calculating lattice potentials, Madelung constants and electrostatic energy. This paper shows how its applicability can be stretched beyond the mere collection of data. The program assumed a crystal lattice with point-charges and none of the corrections or changes needed for the free energy calculations are included. In that sense, the material reported here constitutes an essential first step rather than a final result.

Most of the problems discussed here have actually come up in the course of material evaluation. Interstitial sites with a lattice site character, for example, are found in β -alumina and CaF₂. The defect chemistry of the latter is of importance in studying its fluorescence and ion conduction [1, 2]. Some evidence has been brought forward which shows the importance of the interstitial sites in explaining the mechanism

of sodium-ion diffusion in β -alumina [3]. Potential calculations which can be applied to interstitial sites with lattice site character are discussed in section 3.

The influence of crystal structure on the predominance of p- or n-type conduction in ionic compounds [4, 5] is another area where potential calculations can provide an important first step. In section 4, previously calculated potentials are arranged to point out such influences.

Section 5 contains some calculations bearing on the possibility of energy storage in a solid phase containing two cations with changeable valency. Since this approach to energy storage has not yet been described in the literature, a somewhat more detailed discussion will be given.

Before dealing with the problems of material selection, it might be helpful to show the actual calculation of electrostatic potentials in a vacant lattice site as compared to the familiar approxi-

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mations for such a potential. Such figures are of importance when a transition metal ion is substituted at the vacant site and the crystal field is used to calculate the possible transitions in the substituted ion [6, 7].

2. Electrostatic Potential in a Vacancy

Without the aid of a computer, calculation of the electrostatic field at some point in a crystal can be so tedious and involved that approximation formulas have been developed. A first approximation can be obtained by considering only the immediate neighbours of the point. The formulae reported by Hutchings [8] can then be applied.

With the computer program described briefly in Part 1, actual potentials can be calculated and a comparison made with the approximations as described above.

Assuming that, in NaCl, the Na⁺ and Cl⁻ are present at (0.5 0.5 0.5) and (000) respectively, the potential calculated at (0.5 0.5 0.5) does not include any contribution from the Na⁺ ion at that site. However, in calculating a potential at a nearby interstitial site, e.g. (0.6 0.6 0.6), there will be an important contribution from the Na⁺ site. In order to get the potential near a Na⁺ vacancy, at (0.5 0.5 0.5), the vacancy must be "created" in the calculation by subtracting the contribution due to the sodium ion at that location from the potential as given by the computer. In this manner calculations were performed for various interstitial sites in the (100), (110), and (111) directions.

The Hutchings' formula (1.2) ([8] p. 231), used a distance a which is one-half of the unit cell dimension a and distances x, y, z and r expressed in Ångstroms rather than fractional description. It can be rewritten

$$V(x, y, z) = (12q/a) [1 + (70/3)(x^4 + y^4 + z^4 - (3/5)r^4) - 56\{x^6 + y^6 + z^6 + (15/4)(x^2y^4 + x^2z^4 + y^2x^4 + y^2z^4 + z^2x^4 + z^2y^4) - (15/14)r^6\}] \quad (1)$$

where $V(x, y, z)$ is the potential to be calculated; a is the lattice parameter of NaCl = 5.62779 Å; q is the charge on the surrounding six ions (-1); x, y, z are fractional co-ordinates, measured from (0.5 0.5 0.5); $r^2 = x^2 + y^2 + z^2$. The results of the calculations are summarised in table I. The pertinent question is where the approximation starts to deviate appreciably from the complete calculation. The comparison is done in two ways. First, the difference of the answers of the two calculations is considered. It represents the potential of the remainder of the crystal after removing the six ions surrounding the vacancy. The constant value of this difference is a criterion for the applicability of the approximation. The table shows that this condition is fulfilled up to about 1.5 Å, depending somewhat upon the direction in the crystal. The second method is based upon the fact that variations in the potential in the vacancy are of importance rather than its absolute value. By adding 0.6210 to the calculated potential and 2.1323 to the approximated potential, these variations can be com-

TABLE I Potentials in a sodium vacancy in NaCl.

r^a	Calc. pot. ^b	Approx. pot. ^c	Remainder ^d	Calc. pot. + 0.6210	Approx. pot. + 2.1323	Direction
0.0	- 0.6210	- 2.1323	+ 1.5113	0.0000	0.0000	} (100)
0.5	- 0.6222	- 2.1333	+ 1.5111	- 0.0012	- 0.0010	
1.0	- 0.6422	- 2.1527	+ 1.5105	- 0.0212	- 0.0204	
1.5	- 0.7399	- 2.2388	+ 1.4989	- 0.1189	- 0.1065	
0.5	- 0.6206	- 2.1320	+ 1.5114	0.0004	0.0003	} (110)
1.0	- 0.6149	- 2.1264	+ 1.5115	0.0061	0.0059	
1.5	- 0.5859	- 2.0972	+ 1.5113	0.0351	0.0351	
2.5	- 0.3120	- 1.7255	+ 1.4135	0.3090	0.4068	
0.5	- 0.6201	- 2.1315	+ 1.5114	0.0009	0.0008	} (111)
1.0	- 0.6088	- 2.1200	+ 1.5112	0.0122	0.0123	
2.0	- 0.4902	- 1.9818	+ 1.4916	0.1308	0.1505	
3.0	- 0.3544	- 1.7568	+ 1.4024	0.2666	0.3755	

^a(a) distance in Å from point (0.5 0.5 0.5); ^b(b) potential as calculated; ^c(c) potential according to Hutchings' formula; ^d(d) remainder = (calc. pot.) - (approx. pot.).

pared immediately. In the situation under consideration the nearest neighbours are at the following distances: 100-direction 2.81 Å, 110-direction 3.98 Å, and 111-direction 4.86 Å. Summarising, one can state that the variation of the potential in the vacancy according to the approximation deviates about 10% from the exact value half-way between the central point and the nearest neighbours. Further away the deviation increases fast. This result confirms the correctness of Hutchings' formula under the conditions for which it was derived.

3. Interstitial Sites with Lattice Site Character

In many compounds the character of interstitial sites is quite different from that of lattice sites. The volume of the ion that can be accommodated at an interstitial site is usually severely restricted for one thing. In some compounds, however, there is no essential difference between lattice sites and some interstitial positions. In CaF_2 , for instance, the calcium ion at (000) and interstitial position at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ are both surrounded by eight fluoride ions. In fact, this structure could be described as a CsCl structure in which one-half of the Cs sites were empty. Obviously such empty sites can play an important role in defect chemistry and diffusion properties, since they can accommodate ions of the same type as the occupied sites, if charge neutrality is maintained by other substitutions.

In CaF_2 , the calculated potential for the empty position $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ is -0.1053 when all the ions are in position. If one Ca^{2+} at $(\frac{1}{2}\frac{1}{2}0)$ is removed, the potential at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ becomes -0.8376 . The self potential at $(\frac{1}{2}\frac{1}{2}0)$ is -1.3848 . The two numbers demonstrate the negative nature of the two positions. More calculations are required to confirm the model in which F^- exists at interstitial sites. This is the model used by Short and Roy [9] for the interpretation of density and lattice parameters of $\text{CaF}_2 - \text{YF}_3$ mixed crystals.

Some computer calculations were performed for β -alumina, which is the name usually given to the compound $\text{Na}_2\text{O} \cdot 11 \text{Al}_2\text{O}_3$. Its structure is reported by Wyckoff [10] and the ions in table II are described in accordance with his conventions. (The calculation is done for ten different reference points and up to eighty ions in the unit cell, about six minutes work for the computer.) The Madelung constant for the compound, as described, is 821.4 and the electrostatic energy 48 740 kcal/mole of $\text{Na}_2\text{O} \cdot 11 \text{Al}_2\text{O}_3$.

TABLE II Self-potentials in " β - Al_2O_3 ".

Site occupation	Position			Regular structure	Anti-structure
Empty ^a	0	0	1/4	-0.4307	-0.9082
Na^+ ^a	1/3	2/3	3/4	-0.8851	-0.4077
Al (1)	0	0	0	-2.1374	-2.1352
Al (2)	1/3	2/3	0.022	-2.5337	-2.5342
Al (3)	1/6	1/3	0.894	-2.4097	-2.4097
Al (4)	1/3	2/3	0.178	-2.7382	-2.7382
O (1)	1/6	1/3	0.050	2.0179	2.0194
O (2)	1/3	2/3	0.950	2.0485	2.0437
O (3)	0	0	0.144	1.7845	1.8597
O (4)	1/2	0	0.144	1.7961	1.7732
O (5)	1/3	2/3	1/4	1.7017	1.7017

(a) In the anti-structure Na^+ is at $(00\frac{1}{4})$ and $(\frac{1}{3}\frac{2}{3}\frac{3}{4})$ is empty.

β -alumina shows a high conductivity for Na^+ ions [3]. In their report Yao and Kummer discuss some evidence for a diffusion mechanism using interstitial sites. These interstitial sites are another example of sites with a lattice site character. When all sodium ions are placed in the interstitial sites, the so-called anti-structure is obtained. Its self-potentials are also reported in table II. This anti-structure has a Madelung constant of 821.6 and the electrostatic energy differs but little from that of the normal structure (48 755 kcal/mole). Potentials were then calculated for interstitial positions between $(\frac{2}{3}\frac{1}{3}\frac{1}{4})$, which is a normal Na^+ position and $(10\frac{1}{4})$, which is the (empty) anti-position. The results are shown in fig. 1. Curve (a) gives the potentials when Na^+ is present at its normal site $(\frac{2}{3}\frac{1}{3}\frac{1}{4})$. Curve (c) shows the potential when one Na^+ ion is placed in $(10\frac{1}{4})$ leaving $(\frac{2}{3}\frac{1}{3}\frac{1}{4})$ empty. Curve (b) refers to the situation in which the two sites are empty. The changes are made at one local spot in the crystal; the other plane containing sodium ($Z = \frac{3}{4}$) and all the other unit cells are unchanged.

These calculations demonstrate mainly the nearly complete equivalence of the lattice site and the interstitial site. This equivalence makes it possible that real crystals may have a more complicated structure than the ideal, at least as far as the position of the Na^+ is concerned. One of the obvious suggestions is that the Na^+ ions occur with a certain degree of disorder which is a 2-dimensional analogue of the stacking-fault disorder occurring in ZnS and SiC [11, 12].

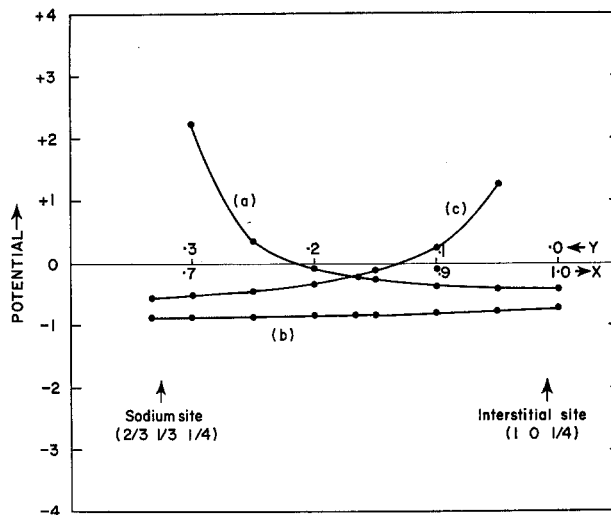


Figure 1 Electrostatic potential between Na^+ site and interstitial site in " $\beta\text{-Al}_2\text{O}_3$ ". (a) Na^+ in $(\frac{2}{3} \frac{1}{3} \frac{1}{4})$, (b) both sites empty, (c) Na^+ in $(1 \ 0 \ \frac{1}{4})$.

4. p- and n-Type Character of Binary Compounds

Whether a simple compound becomes p- or n-type when its defect chemistry is changed is a complex question. Changing preparation conditions can change the defect chemistry. Thus, with simple metal oxides, a high oxygen pressure during preparation may increase the excess of oxygen in the compound, while a high metal pressure (if possible) may cause an oxygen deficiency. In general, although not always, an excess of oxygen tends to make the compound a p-type semiconductor, whereas a metal excess may lead to n-type conduction. The many exceptions include some in which the materials have metallic conduction [13, 14].

The question then becomes whether there is some reference condition in which the intrinsic nature of the compound shows up and what are the factors determining the tendency to p-type or n-type conduction. The question of the reference condition has been discussed by one of us elsewhere ([14], Chapter 6). There it is demonstrated that the relationship between conduction type and the heat of formation as found by Rudolph [4, 5] is largely controlled by preparation conditions. The intrinsic tendency of a given compound toward either conduction type will emerge when the materials are compared at the minimum vapour pressure, as in vacuum or an inert gas atmosphere (see Kröger [13] for a detailed discussion). After excluding the influence of the surrounding atmospheres as described, the

problem resolves itself into calculation of free energies of reaction such as

$$\begin{aligned} M_M &= M_a + V_M \\ O_0 &= \frac{1}{2}O_2 + V_0 \end{aligned}$$

and the other competing reactions. At present it is not possible to perform calculations with sufficient accuracy to explain small differences between members of a series of materials.

The use of electrostatic energy considerations will prove helpful in some, but not all cases. In a compound of two ions located in symmetrically equivalent positions, such as NaCl or ZnO , the electrostatic energy required to remove one of the ions from the lattice, which is otherwise immobilised, is the same as that required for the other. Thus, electrostatic energy cannot be an important factor in explaining why ZnO is found to be n-type and other explanations must be sought (see the calculations summarised by Kröger [13]).

However, in compounds whose component ions are at non-equivalent sites, the structure itself can make one site more favourable than another for the removal of an ion. This tendency to a deviation from stoichiometry is expressed by the self-potentials of the lattice site. Obviously, other factors must also be considered and these may indicate opposing tendencies. Tables III and IV summarise data for some halides and some oxides in such a way as to show the tendencies based on self-potential. The values originally come from table III of Part 1, but have

been recalculated to refer to a charge of ± 1 on the lattice site, giving a comparison of electrostatic energy required for the removal of a monovalent ion. It is suggested that materials with a high ϕ anion/ $|\phi$ cation $|$ ratio have a built-in tendency towards p-conductivity and that a low ratio indicates a tendency toward n-conductivity.

TABLE III ϕ Anion/ $|\phi$ cation $|$ for some halides.

Compound	Cation	Anion	$\frac{\phi \text{ Anion}}{ \phi \text{ Cation} }$
PuBr ₃ ^a	- 0.451	0.445	0.987
CrCl	- 0.494	0.494	1.000
NaCl	- 0.621	0.621	1.000
LaF ₃ ^a	- 0.631	0.661	1.047
CaF ₂	- 0.692	0.745	1.075
CaCl ₂	- 0.550	0.638	1.162
CrCl ₂	- 0.592	0.711	1.215
IrF ₃	- 0.688	0.868	1.261
VF ₃	- 0.707	0.938	1.325
MoF ₃	- 0.713	0.960	1.346
FeCl ₃	- 0.496	0.703	1.418

(a) For PuBr₃ and LaF₃ the F⁻ ion with the lowest energy was used.

TABLE IV ϕ Anion/ $|\phi$ Cation $|$ for some oxides.

Compound	ϕ Cation	ϕ Anion	$\frac{\phi \text{ Anion}}{ \phi \text{ Cation} }$
Cu ₂ O	- 0.886	0.758	0.856
CuO	- 0.842	0.831	0.998
ZnO	- 0.834	0.834	1.000
La ₂ O ₃ ^a	- 0.671	0.692	1.030
ZrO ₂ ^a	- 0.744	0.793	1.065
Pb ₂ O ₃ ^a	- 0.650	0.695	1.069
Cr ₂ O ₃	- 0.809	0.882	1.091
V ₂ O ₃	- 0.773	0.846	1.095
Ti ₂ O ₃	- 0.779	0.855	1.098
Al ₂ O ₃	- 0.847	0.916	1.121
SnO ₂	- 0.744	0.854	1.148
GeO ₂	- 0.810	0.935	1.152
TiO ₂	- 0.777	0.898	1.155

(a) The lowest (absolute) values were used whenever two or more non-equivalent sites occur for one ion.

Unfortunately, a comparison with experimental results is not yet possible. Very few of the compounds in the tables have been evaluated at minimum vapour pressure and the purity of those has not always been ascertained. Impurities can easily override the intrinsic tendency toward conduction type.

The use of anion and cation potentials by themselves, rather than the ratios, could lead to

difficulties. The ranges of values are as follows: halides, cation 0.451 to 0.692, anion 0.445 to 0.960 (ratio range 0.987 to 1.418); oxides, cation 0.650 to 0.886, anion 0.692 to 0.935 (ratio range 0.856 to 1.155). A low value for an oxygen self-potential means that only a small amount of electrostatic energy is required for the removal of O²⁻ and would seem to imply that the number of oxygen vacancies would be large. It must be pointed out that such absolute predictions are more prone to be modified by additional effects than conclusions drawn from the ratios.

5. Solid State Energy Storage

Because the concept of solid state energy storage as used in this paper is not as familiar as the other concepts discussed, some explanations are given below to clarify the significance of the reported calculations.

Solid state energy storage can be approached in two different ways. In one the starting point is a rechargeable battery. Suppose, for example, that the two electrodes consist of PbO and Mn₂O₃ respectively and that charging the batteries leads to PbO₂ and MnO. The valence state of the two cations is changed: Pb²⁺ → Pb⁴⁺ and Mn³⁺ → Mn²⁺, and the corresponding amount of O²⁻ must be transported from the Mn₂O₃ electrode to the PbO electrode. (Charge accumulation in each electrode can be neglected.) The essential charging steps are oxygen diffusion in the solid electrodes, oxygen diffusion through the electrolyte and electron transport in the two electrodes. It is also required that the process runs smoothly in the opposite direction to discharge the battery.

Such requirements are difficult to fulfill at room temperature and as a consequence, most existing batteries are more complicated than the example given here, which, incidentally, does not actually work.

In solid state energy storage the two electrodes are combined in one solid phase and the need for an electrolyte removed. Materials containing two cations with changeable valence states, and in which those cations are located in two sublattices which are separated from each other electrically, could act as such a battery.

A second description starts with a normal capacitor. If the thickness of the metal plates is reduced to a monatomic layer and the distance between two neighbouring electrodes also reduced to atomic dimensions, the same situation as above is obtained. On an atomic scale there is no difference between a capacitor and a re-

chargeable battery. The possibility of recharging ions in one solid phase has been demonstrated many times by means of the glow curves observed in fluorescent materials [15, 16].

The evaluation of this approach to energy storage has not yet been done. The readily apparent advantages of solid state energy storage cannot be fully appraised until the following three problems are solved: 1. What are the conditions needed for the appropriate interaction between the two cationic subsystems and their surroundings? 2. To what extent can the battery be charged without short-circuiting on an atomic scale? 3. What materials can be used to evaluate this concept?

Only the third of these questions will be discussed here, since it is in this challenging materials selection problem that the energy calculations are of value. Two simple structural forms are possible: either the two cations are located in different planes, or they occur in different chains giving a two- or one-dimensional electrode. A two-dimensional electrode is used here as an example. Calculations were made for the mineral quenselite, $\text{PbMnO}_2(\text{OH})$ [17]. It has a layer structure with the sequence $\text{Mn} | \text{O} | \text{Pb} | \text{OH} | \text{Pb} | \text{O} | \text{Mn}$. Potential calculations for the ions are summarised in table V. More interesting for energy storage evaluation is the change in the value of total electrostatic energy when the valence states of the lead and manganese are changed. Assuming that lead is present as Pb^{2+} and manganese Mn^{3+} , the electrostatic energy is -2836 kcal/mole. Recharging to Pb^{3+} and Mn^{2+} without changing the position of the ions gives an energy of -2442 kcal/mole. If the O^{2-} ions are shifted 0.91 \AA in the direction of the Mn^{2+} ions, the electrostatic energy becomes -2678 kcal/mole. Since the ionisation energy in going from the $2+$ to $3+$ state is almost the same for lead as manganese, these energy differ-

ences represent total stored energy, corresponding to 680 Wh/lb^* for fixed position and 270 Wh/lb when the lattice is polarised (O^{2-} shift). The values are sufficiently high to justify further evaluation.

It should be pointed out that usually the one- or two-dimensional pattern occurs in compounds where there is an appreciable amount of covalency or metal-metal interaction. The value of the ionic approach is therefore limited. On the other hand, when covalency prevails in one or two directions the changes in energy are not necessarily different from those calculated with the completely ionic model.

It is also true that the interesting materials frequently have a rather low symmetry, which makes hand calculations lengthy and tedious and which made it necessary to write a computer program which was independent of symmetry considerations.

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TABLE V Self-potentials in quenselite.

Ion	Position			Pot.	Remarks
Mn^{3+} (1)	0	1/8	0	- 2.456	Same pot. for Mn^{3+} (4)
Mn^{3+} (2)	0	5/8	0	- 2.452	Same pot. for Mn^{3+} (3)
Pb^{2+} (1)	0.342	0	0.264	- 1.294	Same pot. for other Pb^{2+} -ions
O^{2-} (1)	1/9	1/8	0.32	1.611	Same pot. for O^{2-} (4)
O^{2-} (2)	1/9	5/8	0.32	1.523	Same pot. for O^{2-} (3)
OH^- (1)	1/2	1/8	0	0.841	Same pot. for OH^- (4)
OH^- (2)	1/2	5/8	0	0.888	Same pot. for OH^- (3)

*1.0 lb = 0.4536 kg.

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