Reconstruction of NaCl Surfaces from a Dipolar Solution to the Madelung Problem

Dieter Wolf

Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 26 December 1991)

Based on the manner in which large Coulomb terms with opposite signs cancel each other at long range, it is proposed that most ionic-crystal surfaces undergo a simple zero-temperature reconstruction, a prediction validated by computer simulation of surfaces in rocksalt-structured materials.

PACS numbers: 61.50.−f, 68.35.Md

The classic Madelung problem, i.e., the divergence associated with the r^{-1} term in the Coulomb potential of condensed systems [1], and its consequences for the physics of ionic crystals and liquids have received considerable attention throughout this century. The mathematical problems associated with the handling of conditionally convergent series have led to computationally expensive summation methods which, based mostly on Ewald's solution [2], are now in common use for the simulation of ionic materials. These problems have also given rise to a widespread belief that certain "typically ionic" phenomena, such as the long-range charge ordering in ionic liquids or the space-charge effects at ionic surfaces and interfaces, are a consequence of the long-ranged Coulomb interactions. However, as evidenced, for example, by Evjen's solution [3,4] and by extensive simulations of ionic liquids [5], in many instances Coulombic effects seem to cancel almost completely at long range. Here, by describing a direct solution to the Madelung problem involving shell-wise lattice summation over *dipolar* molecules with integral ionic charges, we demonstrate that the effective Coulomb potential in a perfect ionic crystal at zero temperature decreases as r^{-5}. In contrast with earlier direct-summation solutions [6–9], this approach obviously requires a polarization correction [10] to obtain the correct Madelung constant. It has the advantage, however, of avoiding (i) the assumption that the basis molecule must have at least a vanishing dipole [6] or even higher multipole moments [7–9] and (ii) the assignment of fractional ionic charges to the summation unit [2,7,8]. These simplifications are shown to lead naturally to the prediction, illustrated here for the case of materials with the NaCl structure, that most ionic-crystal surfaces should be reconstructed at zero temperature.

The main difficulty in the evaluation of Madelung's constant by direct summation arises from the fact that all shells of the *crystal* lattice are charged and that, therefore, it is virtually impossible to terminate the summation in a way that renders the system as a whole neutral [4]. As illustrated in Fig. 1, this problem may be simply overcome by summing over neutral shells of molecules, i.e., shells of the *Bravais* lattice with subsequent attachment of the neutral basis molecule (such as NaCl, with charges $\pm q$). This results in the generation of two identical, oppositely charged crystal lattices displaced relative to each other by the basis vector **b**. The total "molecular" Coulomb energy $E_{\mathrm{mol}}^{\mathrm{tot}}$ of some ion i at the origin is then given by

$$E_{\mathrm{mol}}^{\mathrm{tot}} = -q^2/b + q^2 \sum_{j \neq i} \sum_{j'} (1/r_{ij} - 1/r_{ij'}) = E_{\mathrm{intra}} + \sum_{r_s} E_{\mathrm{inter}}(r_s) , \qquad (1)$$

where the first term represents its "intramolecular" (i-i') interaction while the second is the "intermolecular" interaction of ion i with the molecules in shells with radii $r_{ij} \equiv r_s$ (see Fig. 1).

Intuitively one would expect the double sum in Eq. (1) to converge rapidly for the following reasons. Within a given shell of the Bravais lattice (i.e., for a fixed value of r_{ij}), the values of $1/r_{ij} - 1/r_{ij'}$ vary between positive (for $\vartheta_{j'} > 90°$; see Fig. 1) and negative (for $\vartheta_{j'} < 90°$) because the direction of **b** is fixed while that of $\mathbf{r}_{ij}$ is averaged over a discrete set of Bravais points on a sphere. In contrast to a sum over charged shells of the *crystal* lattice (involving very large $\pm 1/r_{ij}$ terms), Eq. (1) involves the averaging over two types of very small differences. First, as in the multipole expansion the differences $1/r_{ij} - 1/r_{ij'}$ within a given shell are small compared to $1/r_{ij}$. Second, when summing these already small positive and negative differences over Bravais shells, the weak correlation between the directions of $\mathbf{r}_{ij}$ and **b** which exists for small distances ($r_{ij} \approx b$) is lost rapidly with increasing shell radius, thus quickly averaging to zero.

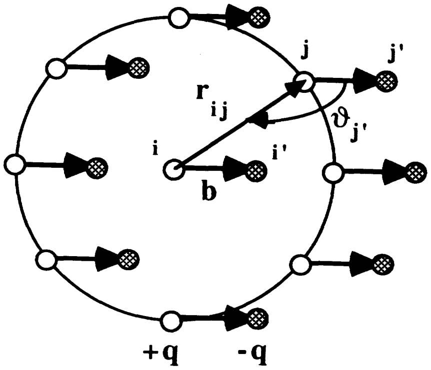

FIG. 1. Dipolar shells of a Bravais lattice (schematic).

The rapid convergence of the total sum $E_{\mathrm{mol}}^{\mathrm{tot}}$ in Eq. (1) is illustrated in Fig. 2 (open symbols, left scale) for an fcc Bravais lattice with a dipolar NaCl basis [with $\mathbf{b}=(a/2,0,0)$, where a is the cubic lattice parameter]. Moreover, the contributions $E_{\mathrm{inter}}(r_s)$ from complete dipolar shells fluctuate about zero while decreasing rapidly with increasing shell radius (solid symbols, left scale).

For a formal investigation of this convergence behavior we consider the multipole expansion of the intermolecular terms in Eq. (1) with subsequent summation over the dipolar shells of the Bravais lattice. Introducing the angle $\vartheta_{j'}$ between $\mathbf{r}_{ij}$ and $\mathbf{b}$ (see Fig. 1), these terms may be written in the familiar manner as

$$1/r_{ij}-1/r_{ij'}=(1/r_{ij})\{1-[1+(b/r_{ij})^2-2(b/r_{ij})\cos\vartheta_{j'}]^{-1/2}\}. \qquad (2)$$

For $b/r_{ij}\ll 1$, the square root can be expanded into a power series and inserted into Eq. (1). We define the angular sums over complete dipolar Bravais shells with radii r_s by

$$\langle\cos^n\vartheta\rangle_{r_s}=[N(r_s)]^{-1}\sum_{j'(r_s)}\cos^n\vartheta_{j'}, \qquad (3)$$

where $N(r_s)$ is the number of Bravais sites (i.e., NaCl molecules) in a given shell, labeled by $j'(r_s)$.

Because of the inversion symmetry of Bravais lattices, all odd powers of the cosine summed over the dipolar shell vanish identically. With the exception of the quadratic term (for which $\langle\cos^2\vartheta\rangle_{r_s}=\frac{1}{3}$), the even powers vary from one shell to another, and no simple r_s-independent values attain. Using these geometrical properties and inserting the power series obtained from Eq. (2) together with Eq. (3) into Eq. (1), it is readily seen that the leading r_s-dependent term in $E_{\mathrm{mol}}^{\mathrm{tot}}$ is of fifth order,

$$E^{(5)}=(7q^2/8b)\sum_{r_s}N(r_s)(b/r_s)^5(1-5\langle\cos^4\vartheta\rangle_{r_s}), \qquad (4)$$

while the next higher-order terms are $E^{(7)}\sim r_s^{-7}$ and $E^{(9)}\sim r_s^{-9}$, etc. The convergence of the Coulomb energy in Eq. (1) is therefore determined by $E^{(5)}$, an assertion validated by means of our direct lattice summations. According to Eq. (4), $E^{(5)}$ vanishes identically for all shells for which $\langle\cos^4\vartheta\rangle_{r_s}=0.2$, and its sign for each shell is given by the deviation from 0.2. A detailed investigation for cubic lattices shows that the shell-by-shell values of $\langle\cos^4\vartheta\rangle_{r_s}$ scatter practically randomly about 0.2, giving rise to the fluctuations about zero in $E_{\mathrm{inter}}(r_s)$ in Fig. 2.

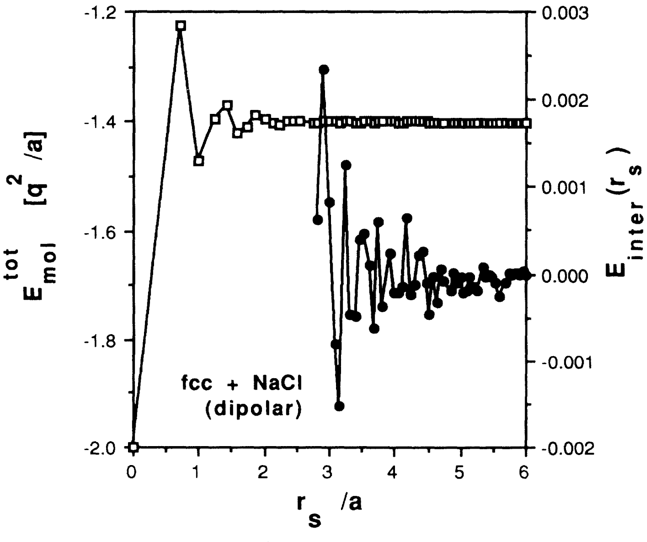

FIG. 2. Solid symbols (right scale): Shell-by-shell contributions to the dipolar energy in Eq. (1). Open symbols (left scale): Sum of all shell contributions.

A problem with the above approach is that the dipolar sums in Eqs. (1) and (4) do not converge to the correct Madelung constant ($\alpha_{\mathrm{Mad}}=-3.49513q^2/a$ for the NaCl lattice, in contrast with the value $\alpha_{\mathrm{dip}}=-1.40074q^2/a$ in Fig. 2). As is obvious from the geometry in Fig. 1, a sum over shells of dipoles cannot be terminated without rendering the system as a whole polarized. In order to obtain the correct Madelung energy E_{Mad}, the surface-dipole contribution has to be eliminated by subtracting the corresponding polarization energy E_{pol} of the system [10], i.e.,

$$E_{\mathrm{Mad}}=E_{\mathrm{mol}}^{\mathrm{tot}}-E_{\mathrm{pol}}. \qquad (5)$$

Since each molecule contributes a dipole moment of qb to the polarization, the related dipole energy per unit volume is given by $E_{\mathrm{pol}}=(2\pi/3\Omega)(qb)^2$ [10], where Ω is the molecular volume. In the fcc lattice, $\Omega=a^3/4$; with the primitive basis of length $b=a/2$ of the NaCl lattice, we obtain $E_{\mathrm{pol}}=(2\pi/3)q^2/a$ which, when subtracted from α_{dip}, gives the correct Madelung constant, $\alpha_{\mathrm{Mad}}=\alpha_{\mathrm{dip}}-2\pi/3$. That the surface-dipole correction of de Leeuw, Perram, and Smith [10] is, indeed, correct was validated further by evaluating $E_{\mathrm{mol}}^{\mathrm{tot}}$ and E_{pol} for various nonprimitive NaCl basis molecules and for the CsCl lattice.

One might consider avoiding the polarization correction altogether by choosing a basis molecule without a di-

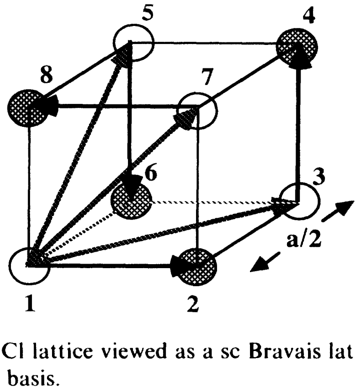

FIG. 3. NaCl lattice viewed as a sc Bravais lattice with octopolar $(\mathrm{NaCl})_4$ basis.

pole moment [6–9]. Thus, instead of viewing the NaCl lattice as an fcc Bravais lattice with a dipolar basis molecule, one could choose the simple cubic (sc) Bravais lattice with the $(NaCl)_4$ basis shown in Fig. 3. Having thus avoided generating a long-range polarization of the system, the direct Coulomb sum based on Eq. (1) (in which, however, dipolar molecules and shells are replaced by octopolar ones) gives the Madelung energy directly, i.e., without the correction of de Leeuw, Perram, and Smith, as shown in Fig. 4.

The comparison with the dipolar energy of Fig. 2 [corrected, however, according to Eq. (5)] demonstrates that both sums converge equally fast and to identical values. This suggests that the sum over octopoles may be broken down into the contributions due to the four dipoles 1-2 to 7-8 forming the octopole (see Fig. 3). As seen from the values listed in Table I, summing the four dipole potentials at the site of ion i reproduces, indeed, the correct Madelung constant.

An interesting property of the direct-summation method involving octopolar molecules is that the intramolecular contribution (see Fig. 3),

$$E_{\rm intra}=(q^2/a)[-6+3\sqrt{2}-2/\sqrt{3}] \approx -2.91206(q^2/a)\,, \qquad (6)$$

is identical to that obtained from Evjen's method [3] while avoiding the ambiguities associated with the assignment of fractional charges to ions at different sites in the crystallographic unit cell; moreover, its r^{-5} convergence behavior is identical to that of the Evjen sum [5]. Therefore, while it appears that the direct dipolar sum reproduces Evjen's method (if an octopolar molecule is chosen), it avoids some of the ambiguities of the latter, a property particularly important when considering defected ionic crystals (see below).

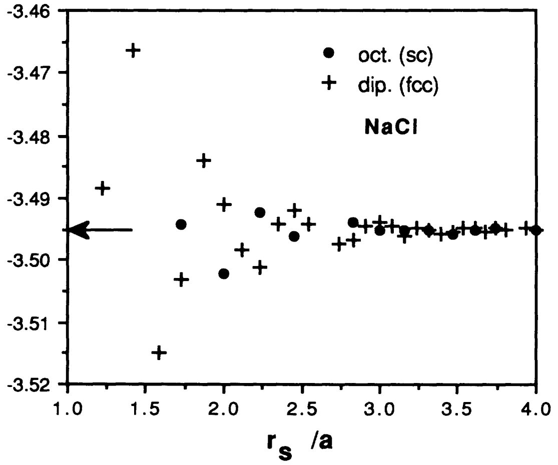

FIG. 4. Comparison of the energies of the octopolar (sc) and dipolar (fcc) lattice sums. The latter is the same as in Fig. 2 (open symbols, left scale) corrected, however, according to Eq. (5).

TABLE I. Determination of the Madelung energy of the NaCl lattice as a sum of the potentials from four interpenetrating simple cubic Bravais lattices with the dipolar bases 1-2 to 7-8 sketched in Fig. 3.

Dipole	$E^{\rm tot}_{\rm mol}(q^2/a)$
1-2	−2.21775
3-4	+0.74293
5-6	−1.01015
7-8	−1.01015
Total ($E_{\rm Mad}$)	−3.49512

That a direct evaluation of the Madelung energy of the NaCl lattice involving octopolar molecules is possible merely with pencil and paper was pointed out also by Lacman [9]. His "octopolar approximation" is based on the fact that the interaction between complete octopolar molecules decreases as r_s^{-7}. The above analysis demonstrates that it is not necessary to consider the interactions only between complete octopoles. Instead, while avoiding the surface-dipole problem altogether, this approximation follows from the more fundamental convergence behavior of the summation involving dipolar shells of the Bravais lattice.

Assuming that the destruction of the octopolar building blocks adversely affects the rapid convergence of his octopolar Coulomb summation method, Lacman postulated that all surfaces in the NaCl structure should be reconstructed such that the finite crystal terminates with only complete $(NaCl)_4$ molecules. Shi and Wortis [11] have recently used this idea to determine the finite-temperature shape of NaCl-structured crystals. Unfortunately, neither study considered the effects of lattice relaxation [9,11].

Table II gives the fully relaxed zero-temperature energies of the three principal surfaces in NaCl and NiO for both the atomically "flat" structure and the octopolar reconstruction. These energies were determined both via direct dipolar lattice summation (with a cutoff radius for

TABLE II. Relaxed energies γ (in mJ/m^2) of octopolar and flat surfaces (in parentheses) of NaCl and NiO simulated via the potentials of Catlow, Diller, and Norgett (so-called type 2) [12] and Stoneham and Sangster [13], respectively. For NaCl, the unrelaxed energies γ^u are also given; these agree well with values obtained by Shi and Wortis [11] for the same potential.

	NaCl		NiO
Surface	γ	γ^u	γ
(100)	223 (223 [a])	225 (225)	1741 (1741)
(110)	367 (458 [a])	384 (472)	2950 (3984)
(111)	541 (∞)	693 (∞)	4284 (∞)

[a] These energies are slightly larger than those given by Tasker [14] due to his use of the shell model.

the Bravais shells of $3a$) and by means of Ewald's method, with no differences in either the energy, the surface stress, or the detailed atomic structure. Whereas in the case of (001), the two structures are obviously identical (see Fig. 3), the lowering of the energy by octopolar reconstruction, accompanied by a reduction in surface stress, is considerable for the remaining surfaces. (The unrelaxed geometries of these surfaces, both flat and octopolar, were discussed in detail earlier [9,11].) The effect is particularly pronounced for the charged (111) surface whose energy is infinite due to the long-range dipole moment in the ⟨111⟩ direction. By contrast, the octopolar structure provides a simple thermodynamic ground state that does not require point defects or kinetic phenomena (such as the adsorption of impurities) for its stabilization.

Concerning the physical reason for these reconstructions, however, we mention that, contrary to Lacman's assumption, the convergence of the sum over octopoles is not destroyed when the octopoles are broken up into neutral fragments. Instead, the breakup will usually lead to the creation of surface charges or dipoles and the associated energy increase. Based on this analysis one can expect the surfaces of all ionic crystals with a dipolar basis molecule to be reconstructed in such a way as to eliminate, or at least minimize, the surface-dipole problem.

The complete agreement with Ewald's method for the case of free surfaces demonstrates that the direct dipolar evaluation of the Coulomb energy is not limited to undefected perfect crystals at zero temperature, while offering hope that an extension to finite temperatures and, hopefully, liquids, may be possible. While its computational efficiency as compared to Ewald's method would enable the study of substantially larger systems, the surface reconstructions predicted on the basis of its convergence behavior promise to provide new insights into the basic structure and properties of defects in ionic materials.

I have benefited from discussions with J. Eggebrecht, J. A. Jaszczak, D. D. Koelling, R. Kulver, S. R. Phillpot, and M. Wortis. This work was supported by the U.S. Department of Energy, BES-Materials Sciences under Contract No. W-31-109-Eng-38.

[1] E. Madelung, Z. Phys. **19**, 524 (1918).
[2] P. Ewald, Ann. Phys. (Leipzig) **64**, 253 (1921).
[3] H. M. Evjen, Phys. Rev. **39**, 675 (1932).
[4] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College, Philadelphia, 1976), p. 404.
[5] See, for example, J. H. R. Clarke, W. Smith, and L. V. Woodcock, J. Chem. Phys. **84**, 2290 (1984).
[6] F. E. Harris, Theor. Chem. **1**, 147 (1975).
[7] V. R. Marathe, S. Lauer, and A. X. Trautwein, Phys. Rev. B **27**, 5162 (1983).
[8] J. V. Calara and J. D. Miller, J. Chem. Phys. **65**, 843 (1976).
[9] R. Lacman, Colloq. Int. C. N. R. S. **152**, 195 (1965).
[10] S. W. de Leeuw, J. W. Perram, and E. R. Smith, Proc. R. Soc. London A **27**, 373 (1980); see also M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987), Sec. 5.5.
[11] A.-C. Shi and M. Wortis, Phys. Rev. B **37**, 7793 (1988).
[12] C. R. A. Catlow, K. M. Diller, and M. J. Norgett, J. Phys. C **10**, 1395 (1977).
[13] A. M. Stoneham and M. J. L. Sangster, Philos. Mag. B **43**, 609 (1981).
[14] P. W. Tasker, Philos. Mag. A **39**, 119 (1979).

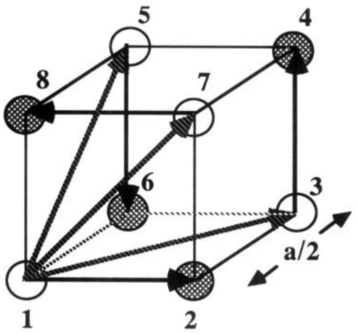

FIG. 3. NaCl lattice viewed as a sc Bravais lattice with octopolar $(NaCl)_4$ basis.