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**Simulation of Ionic Surfaces from an Absolutely
Convergent Solution of the Madelung Problem***

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Simulation of Ionic Surfaces from an Absolutely Convergent Solution of the Madelung Problem

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Abstract. The classic Madelung problem is cast into an absolutely convergent form that is readily evaluated by direct lattice summation, revealing a net r^{-5} range of the net Coulomb potential in ionic crystals and liquids. The realization that Coulomb interactions in condensed systems can actually be rather short ranged (provided the system is overall neutral) leads to the prediction, verified by computer simulations for rocksalt-structured surfaces, that all surfaces in predominantly ionic crystals should be fundamentally reconstructed. The work also provides a conceptual framework for the theoretical treatment of polar surfaces, as demonstrated for the case of the (111) surfaces of NaCl and MgO.

1. Introduction

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 - and physically not very transparent - 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 divergence of the energies of polar surfaces or the long-range charge ordering in ionic liquids, are a consequence of the long-ranged Coulomb interactions. [3] However, as evidenced, for example, by Evjen's solution of the Madelung problem [4] and by extensive simulations of ionic liquids [3], in many instances Coulombic effects seem to cancel almost completely at long range.

The convergence problems encountered when simply summing the Coulomb potential, $\pm r^{-1}$, over shells of the rocksalt lattice are illustrated in Fig. 1. Figure 1(a) (left half) reveals large oscillations of the apparent Madelung energy thus obtained between large positive and negative values; its value depends strongly on the terminating crystal shell, with no indication of convergence towards the dashed line which gives the correct value, $E_{\text{Mad}} = -3.495116a^{-1}$ (where a is the cubic lattice parameter). Figure 1(b) (right half), showing the apparent Madelung energy as a

function of the difference between the total number of cations and anions up to a given shell, $N(+)-N(-)$, gives some indication as to the origin of this behavior since $N(+)-N(-)$ is proportional to the net charge of the crystal up to the distance r . In fact, when the system is neutral or almost neutral, values close to the correct Madelung energy are obtained. Three such data points are marked by the arrows in Fig. 1(a), corresponding to the following shell radii and values of $N(+)-N(-)$ (in parentheses): $0.866a$ (-2), $2.739a$ (-2) and $3.464a$ (0). These observations suggest that the large oscillations of the apparent Madelung energy arise directly from the fact that the crystal lattice is practically never neutral when terminated by complete *crystal* shells.

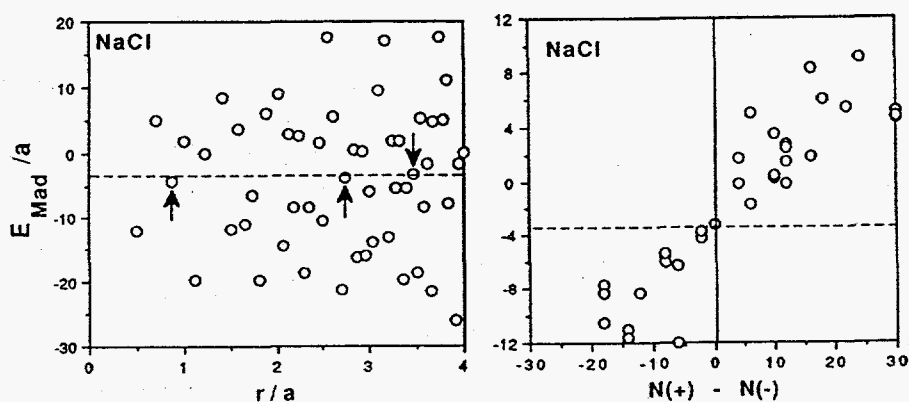


Fig. 1. Total apparent Madelung energy, E_{Mad} (in units of the inverse lattice parameter, a^{-1}) obtained by simply summing the Coulomb potential, $\pm r^{-1}$, over shells of the rocksalt lattice. (a) (left half): E_{Mad} against shell radius, r (in units of the cubic lattice parameter, a); (b) (right half): E_{Mad} against the difference, $N(+)-N(-)$, between the total number of cations and anions up to a given shell of radius r .

Based on the above observation, in the present work a simple, absolutely convergent solution of the Madelung problem involving direct r^{-1} lattice summation, is presented. (For a preliminary report, see Ref. [5].) As illustrated in Sec. 2, operationally the "trick" is to sum over the *neutral* shells of the *Bravais* lattice and not, as in Fig. 1, over the *charged* shells of the *crystal* lattice. The convergence analysis presented in Sec. 3 demonstrates that the effective Coulomb potential in ionic crystals and liquids decreases as r^{-5} . This realization leads naturally to the prediction, illustrated here for materials with NaCl structure, that most ionic-crystal surfaces should reconstruct in a manner that involves "molecular" building blocks (see Sec. 4). The insights gained from understanding the nature of this convergence also provide a conceptual framework for the theoretical treatment of polar surfaces, another long-standing problem in the physics of ionic materials (see Sec. 4).

2. A Dipolar Model

As illustrated above, the main difficulty in the evaluation of Madelung's constant by direct lattice summation arises from the fact that most 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. Figure 2 demonstrates how operationally this problem may be overcome by simply summing over *neutral* shells of basis 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 sublattices displaced relative to each other by the basis vector \mathbf{b} . The total "molecular" Coulomb energy, $E_{\text{mol}}^{\text{tot}}$, of some ion i at the origin is then given by [5]

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

where the first term represents the "intra-molecular" (i - i') interaction while the second is the "inter-molecular" interaction of ion i with the molecules in shells with radii $r_{ij} \equiv r_s$ (see Fig. 2).

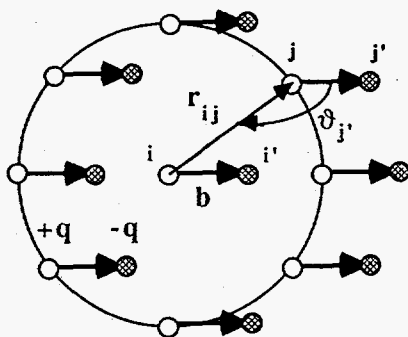


Fig. 2. Neutral shells of NaCl "molecules" are obtained by attachment of the NaCl basis dipoles to the sites of the fcc *Bravais* lattice (schematic). $r_s \equiv r_{ij}$ denotes the radii of the shells of the Bravais lattice.

Intuitively one would expect the double sum in Eq. (1) to converge rapidly for the following two reasons. First, because the direction of \mathbf{b} is fixed while that of r_{ij} is averaged over a discrete set of Bravais points on a sphere, within a given Bravais-lattice shell (i.e., for a fixed value of $r_{ij} \equiv r_s$), the values of $1/r_{ij} - 1/r_{ij'}$ vary between small positive and negative (for $\delta_j > 90^\circ$ and $\delta_j < 90^\circ$, respectively; see Fig. 2). By contrast with a sum over *charged* shells of the *crystal* lattice (involving very large, non-compensated $\pm 1/r_{ij}$ terms), the sum in Eq. (1) over Bravais shells therefore involves differences between very small terms. Second, these already small positive or negative net values obtained for each shell are summed over the entire Bravais lattice, with rapidly decreasing small negative and positive values as r_s increases.

The rapid convergence of the total sum, $E_{\text{mol}}^{\text{tot}}$ in Eq. (1) is illustrated in Fig. 3 for an fcc Bravais lattice with a dipolar NaCl basis (see also Fig. 2). Notice that the contributions from complete dipolar shells in Eq. (1), $E_{\text{inter}}(r_s)$ (right scale in Fig. 2), indeed fluctuate about zero while decreasing rapidly with increasing shell radii.

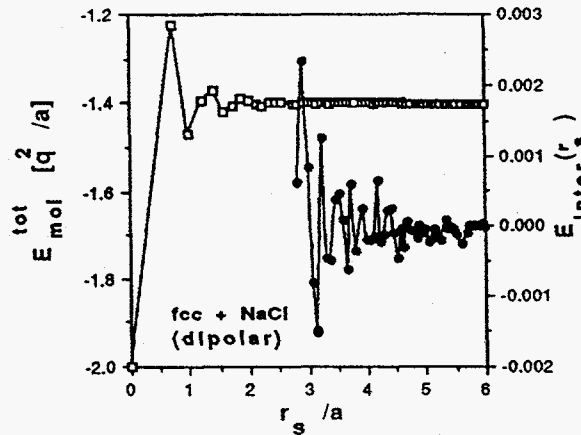


Fig. 3. Evaluation of Eq. (1) for an fcc Bravais lattice with dipolar NaCl basis. [5] Filled circles (right scale): shell-by-shell contributions to the energy in Eq. (1). Open squares (left scale): sum of all shell contributions. The point at $r_s=0$ corresponds to the intra-molecular energy, $-1/0.5a = -2/a$.

An apparent problem with the dipolar sum in Fig. 3 is that it does not converge to the correct Madelung energy, $E_{\text{Mad}} = -3.49513 q^2/a$; instead, the value $E_{\text{dip}} = -1.40074 q^2/a$ is obtained. However, a sum over shells of dipoles *cannot* be terminated without rendering the system as a whole polarized (see Fig. 2). To obtain the correct Madelung energy, the polarization energy, E_{pol} , has to be subtracted; i.e.,

$$E_{\text{Mad}} = E_{\text{mol}}^{\text{tot}} - E_{\text{pol}} . \quad (2)$$

Since each molecule contributes a dipole moment of qb to the polarization (Fig. 2), the related dipole energy per unit volume is given by [6]

$$E_{\text{pol}} = (2\pi/3\Omega) (qb)^2, \quad (3)$$

where Ω is the "molecular" volume. In the fcc lattice, $\Omega = a^3/4$; with $|b| = a/2$ for the NaCl basis molecule, we obtain $E_{\text{pol}} = (2\pi/3) q^2/a = 2.09439$ which, when subtracted from $E_{\text{mol}}^{\text{tot}}$ in Fig. 3, gives the correct Madelung energy.

By choosing a basis molecule without a dipole moment, this polarization correction can be avoided altogether. Thus, instead of viewing the NaCl lattice as an fcc Bravais lattice with a *dipolar* basis, one can choose the simple cubic (sc) Bravais lattice with the cube-shaped *octopolar* $(\text{NaCl})_4$ basis shown in Fig. 4. Avoiding thus

the generation of a long-range polarization of the system, the direct r^{-1} Coulomb sum based on Eq. (1) (in which, however, dipolar molecules and shells are replaced by octopolar ones) gives the Madelung energy directly, as demonstrated in Fig. 5.

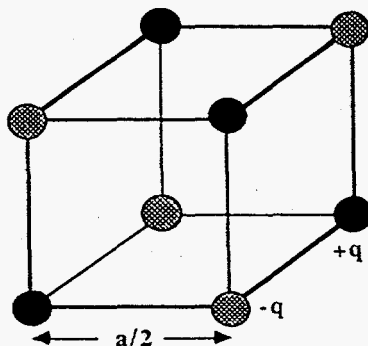


Fig. 4. Octopolar, dipole-moment-free $(\text{NaCl})_4$ building block of the rocksalt lattice viewed as a simple-cubic Bravais lattice. a is the cubic lattice parameter.

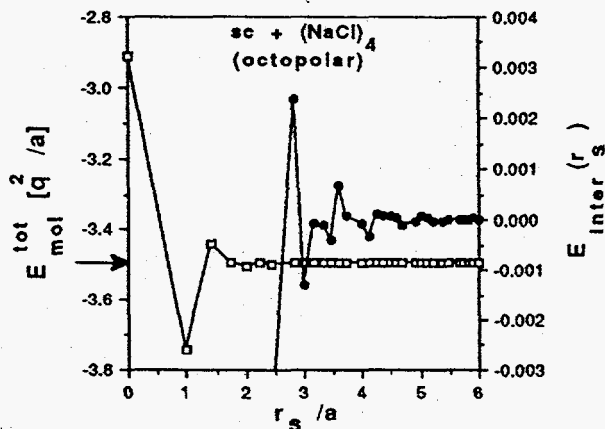


Fig. 5. Evaluation of Eq. (1) for an sc Bravais lattice with the octopolar $(\text{NaCl})_4$ basis in Fig. 4. [5] Filled circles (right scale): shell-by-shell contributions in Eq. (1) against shell radius, r_s . Open squares (left scale): sum of all shell contributions, including the intramolecular contribution (see also Fig. 3.) The arrow indicates the correct Madelung energy.

An interesting property of the direct-summation method involving octopolar molecules is that the intra-molecular contribution (see Fig. 4),

$$E_{\text{intra}} = (q^2/a) [-6 + 3\sqrt{2} - 2/\sqrt{3}] \approx -2.91206 (q^2/a) \quad (4)$$

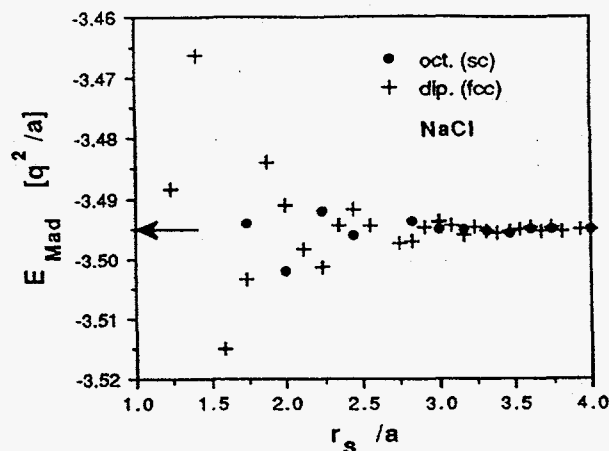


Fig. 6. Madelung energy against cutoff radius obtained by direct lattice summation involving either a dipolar (fcc) basis (Figs. 2 and 3 with Eqs. (2) and (3)) or an octopolar (sc) basis (Figs. 4 and 5). The arrow indicates the correct Madelung energy.

is identical to that obtained from Evjen's method [4,7] while avoiding the ambiguities associated with the assignment of fractional charges to the ions in the unit cell. The latter is particularly important when considering defected ionic crystals.

The above results are summarized in Fig. 6 showing the Madelung energy obtained by direct summation for rocksalt viewed as (a) an fcc Bravais lattice with dipolar NaCl basis (see Fig. 3 and Eq. (2)) and (b) an sc Bravais lattice with octopolar $(\text{NaCl})_4$ basis. In the latter case, $E_{Mad} \equiv E_{mol}^{tot}$ (see Eqs. (1) and (2), with $E_{pol} \equiv 0$). This comparison demonstrates that the dipolar and octopolar sums converge 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. 7). As seen from the values listed in Table 1, summing the four dipole potentials at the site of any ion reproduces, indeed, the correct Madelung constant.

Table 1. Determination of the octopolar Madelung energy of the (sc) NaCl lattice as a sum of the potentials of four interpenetrating sc Bravais lattices with the dipolar bases 1 - 2 to 7 - 8 sketched in Fig. 7.

dipole	$E_{mol}^{tot} [q^2/a]$
1 - 2	-2.21775
3 - 4	+0.74293
5 - 6	-1.01015
7 - 8	-1.01015
Total [E_{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 earlier by Lacman [8]. His "octopolar approximation" is based on the fact that the interaction between complete octopolar molecules decreases as r_s^{-7} [9]. The above analysis demonstrates that it is not necessary to consider the interactions only between complete octopoles. Instead, while avoiding the polarization problem, this "approximation" follows from the more fundamental r_s^{-5} convergence behavior for the summation involving dipolar shells of the Bravais lattice (see the next section).

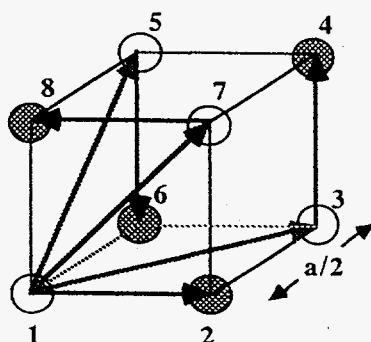


Fig. 7. Breakdown of the sum over octopoles into four contributions from dipoles labeled 1 - 2 to 7 - 8; see also Table 1.

3. Convergence

A formal investigation of the convergence behavior of Eq. (1) with Fig. 2 starts with a power expansion of the inter-molecular terms with subsequent summation over the dipolar shells of the Bravais lattice. Introducing the angle ϑ_j between r_{ij} and b (see Fig. 2), these terms may be written in the familiar manner as

$$1/r_{ij} - 1/r_{ij}^* = (1/r_{ij}) \{1 - [1 + (b/r_{ij})^2 - 2(b/r_{ij}) \cos \vartheta_j]^{-1/2}\}. \quad (5)$$

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 by

$$\langle \cos^n \vartheta \rangle_{r_s} = \frac{1}{N(r_s)} \sum_{j'(r_s)} \cos^n \vartheta_{j'}, \quad (6)$$

where $N(r_s)$ is the number of Bravais sites (i.e., NaCl molecules) in a given shell, labeled by $j'(r_s)$. Equation (1) may then be written as follows [5]:

$$E_{\text{mol}}^{\text{tot}} = -\frac{q^2}{b} \left\{ 1 + \sum_{r_s} N(r_s) \left[\left(\frac{b}{r_s}\right)^2 \langle \cos \vartheta \rangle_{r_s} - \frac{1}{2} \left(\frac{b}{r_s}\right)^3 (1 - 3 \langle \cos^2 \vartheta \rangle_{r_s}) - \frac{1}{2} \left(\frac{b}{r_s}\right)^4 (3 \langle \cos \vartheta \rangle_{r_s} - 5 \langle \cos^3 \vartheta \rangle_{r_s}) + \frac{1}{8} \left(\frac{b}{r_s}\right)^5 (3 - 30 \langle \cos^2 \vartheta \rangle_{r_s} + 35 \langle \cos^4 \vartheta \rangle_{r_s} + \dots) \right] \right\}. \quad (7)$$

Because of the inversion symmetry of Bravais lattices, all odd powers of the cosine summed over the dipolar shells vanish identically. With the exception of the quadratic term (for which $\langle \cos^2 \vartheta \rangle_{r_s} = 1/3$), the even powers in Eq. (6) vary from one shell to another, and no simple r_s -independent values attain. However, using these properties, the leading r_s -dependent term in Eq. (7) is found to be of 5-th order, [9]

$$E_{\text{mol}}^{\text{tot}} \approx E^{(5)} = \frac{7q^2}{8b} \sum_{r_s} N(r_s) \left(\frac{b}{r_s}\right)^5 (1 - 5\langle \cos^4 \vartheta \rangle_{r_s}), \quad (8)$$

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 $E^{(5)}$.

A shell-by-shell comparison of the analytical expression for $E^{(5)}$ in Eq. (8) and the sum of the three lowest-order terms, $E^{(5)} + E^{(7)} + E^{(9)}$, with the results determined by direct evaluation of Eq. (1) is shown in Fig. 8 (for the fcc Bravais lattice with dipolar basis). According to Fig. 8, for Bravais-shell radii $r_s > a$, the lowest-order analytical results obtained from Eq. (8) agree completely with the direct results.

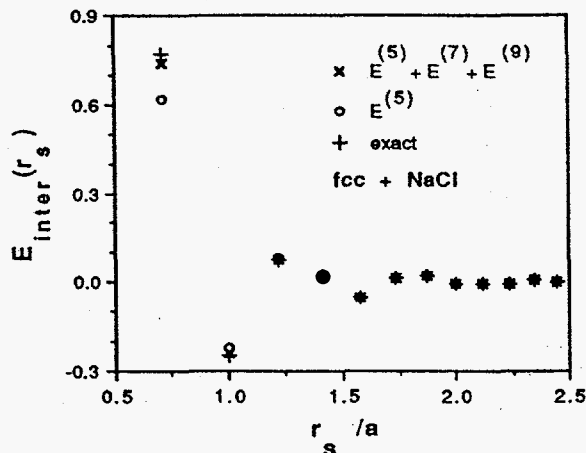


Fig. 8. Coulomb energy for Bravais shells of radii r_s determined analytically from Eq. (8) for $E^{(5)}$, from Eqs. (7) and (8) for the sum of the three lowest-order terms, $E^{(5)} + E^{(7)} + E^{(9)}$, and numerically (i.e., exact results) by directly evaluating Eq. (1) for the fcc Bravais lattice with dipolar basis (see also Fig. 3, right scale).

According to Eq. (8), $E^{(5)}$ vanishes identically for any shell for which $\langle \cos^4 \vartheta \rangle_{r_s} = 0.2$, and the signs of any non-vanishing contributions are given by the deviation from this value. As seen from Fig. 9, 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 $E_{\text{inter}}(r_s)$ in Figs. 3 (right scale) and 8. We finally mention that, since the order in which the individual r^{-1} terms in Eq. (1) are summed does not matter, the direct summation sketched in Fig. 2 and Eq. (1) is absolutely convergent.

That the above arguments are not limited to a perfect crystal lattice is readily seen. For example, Coulomb interactions in liquids are usually evaluated by using 3-

d periodic cell borders [2]. By considering the entire simulation cell as the "molecule" attached to the sc lattice of the periodic cell images, the problem is reduced to one analogous to Fig. 2 and Eq. (1). Even in a liquid the r^{-5} convergence therefore attains, an assertion verified by recent molecular-dynamics simulations of liquids.

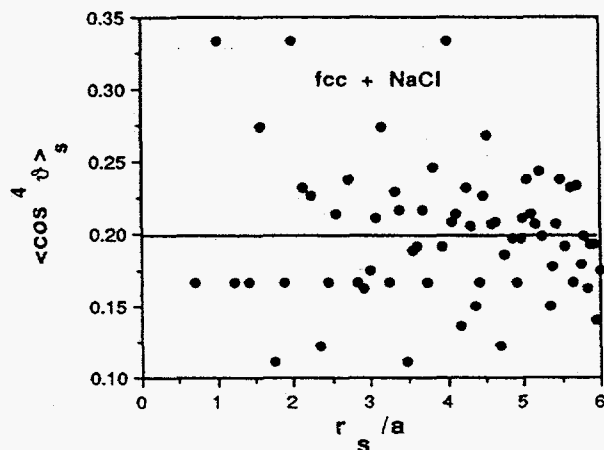


Fig. 9. Shell-by-shell values of $\langle \cos^4 \theta \rangle_s$ defined in Eq. (6), governing the absolute-convergence property of Eq. (8).

4. Free Surfaces

The above convergence analysis shows that, from a Coulomb point of view, the rocksalt structure should be viewed as an sc Bravais lattice with an octopolar basis rather than an fcc Bravais lattice with a dipolar basis. This raises the question as to whether free surfaces should not also be made up of octopolar building blocks. [8]

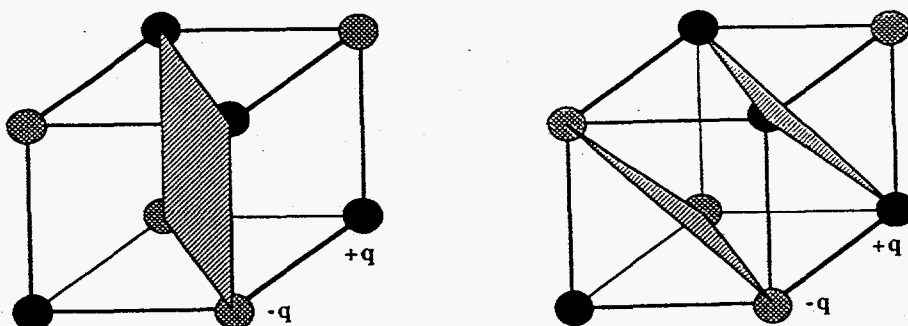


Fig. 10. Creation of atomically flat (a) (110) and (b) (111) surfaces in (fcc) rocksalt requires the breaking up of the octopoles.

Table 2. Relaxed energies (in mJ/m^2) of octopolar and flat surfaces of NaCl [5] and MgO [10] using the "type-2" potentials of Catlow et al. [11] and Catlow et al. [12], respectively. The NaCl results for the (100) and flat (110) surfaces are slightly higher than those given by Tasker [13] due to his use of the shell model, by contrast with the present results. The energies and structures determined via direct r^{-1} lattice summation and by means of Ewald's method agree quantitatively. [5,10]

surface	NaCl		MgO	
	fcc+dip.	sc+oct.	fcc+dip.	sc+oct.
(100)	223	223	1224	1224
(110)	456	366	2490	1993
(111) "+" term.	∞	539	∞	2879
(111) "-" term.	∞	546	∞	2899

As illustrated in Fig. 10 for the (110) and (111) surfaces in the rocksalt structure, creation of atomically flat surfaces generally requires a breaking up of the octopoles (except for the special case of the (100) surface). Table 2, giving the relaxed zero-temperature energies of the three principal surfaces in NaCl and MgO for both the atomically flat (fcc) surface and its octopolar (sc) reconstruction, illustrates that the breaking of up octopoles, indeed, increases the surface energy substantially.

The effect of octopolar reconstruction is particularly pronounced for the charged (111) surfaces whose *fcc* energy is infinite (see Fig. 11). This divergence is well-known to arise from the long-range dipole moment in the $|A^+C^-B^+A^-C^+B^-|$ stacking of (111) NaCl planes created when attaching NaCl *dipoles* to the |ABCl stacking of *fcc* (111) planes.

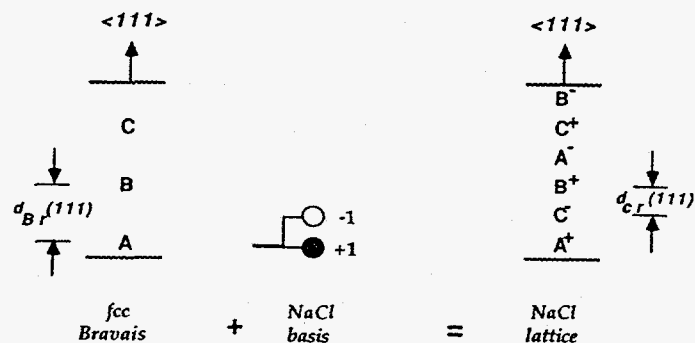


Fig. 11. Creation of the polar structure of the (111) surface in rocksalt by attachment of $\langle 111 \rangle$ -oriented NaCl basis molecules to an |ABCl.. stack of (111) planes in the fcc Bravais lattice. In accordance with the flat-plate capacitor problem, the energy of the slab diverges for infinitely separated, oppositely charged surfaces.

By contrast, the $|B^{-1/4}A^{+3/4}C^{-}B^{+}A^{-}C^{+}B^{-3/4}A^{+1/4}|$ stacking obtained when attaching $(NaCl)_4$ octopoles to the $|ABC|$ stacking of sc (111) planes (see Fig. 12) does not generate a dipole moment, although the two outermost (111) planes thus generated are still charged, however with only 1/4 and 3/4, respectively, of the charge of perfect-crystal (111) planes. The two oppositely charged octopolar "ground-state" structures with slightly different energies thus predicted therefore involve the top *three* lattice planes. However, the energies of both surfaces are finite and typically about two and a half times as large as that of the (100) surface (see Table 2); i.e., there is a reasonable chance that the surface appears in the crystal shape at elevated temperatures [14].

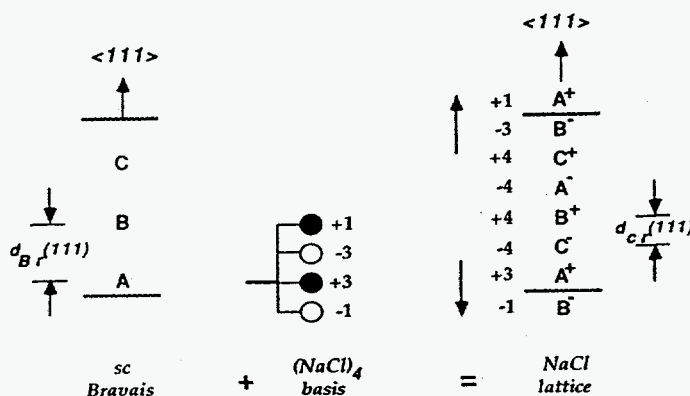


Fig. 12. Creation of the octopolar "ground-state" structure of the (111) surface in rocksalt by attachment of $\langle 111 \rangle$ -oriented octopolar molecules (see Fig. 10) to an $|ABC|$ stack of (111) planes in the sc Bravais lattice. The (either positively or negatively charged) outermost planes contain only 1/4 of the ions of a regular, fully occupied ideal-crystal (111) plane. The next plane towards the bulk is 3/4 filled and oppositely charged while, finally, the third plane from the surface is completely filled. This octopolar reconstruction involving the top three surface planes eliminates the long-range dipole moment of the flat but polar (fcc-based) surface in Fig. 11.

According to Table 2, in NaCl the cation-terminated (1/4 occupied) surface is favored slightly over the anion-terminated (1/4 occupied) surface whereas in MgO the anion-terminated surface has the lower energy. This difference arises from an intricate balance between the Coulomb and short-range-repulsive contributions to the total (111)-surface energy, indicating possibly a strong materials dependence of the structure of charged surfaces, by contrast with the structure of neutral surfaces. It also indicates that the structure and energy of charged surfaces are not dominated by Coulombic effects but, instead, by the short-range repulsion between the ions, i.e., by size effects. Unfortunately, no experimental verification of this octopolar reconstruction of either

the (110) or the (111) surface is to date available from experiments nor has the net charge of the terminating (111) plane been determined.

We finally mention that the predicted octopolar "ground-state" structures of *all* surfaces in (sc) rocksalt may be viewed as faceted (100) surfaces. For the (110) surface, this faceting has the appearance of the missing-row structure in Fig. 10(a); for the (111) surface, the partially charged - yet dipole-moment free - structure in Figs. 10(b) and 12 is obtained.

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