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Madelung effects at crystal surfaces: Implications for photoemission

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An equation originally derived by Lennard-Jones and Dent for the estimation of Madelung potentials is utilized to study the properties of these potentials within the bulk and at the surfaces of crystals. It is clear from the equation that potentials at atomic sites only one lattice constant distant from the surface are, in general, indistinguishable from those in the bulk. The equation indicates also that Madelung sums in real space can be so organized as to make them more tractable computationally than they are usually considered to be. Madelung potentials for atomic sites at and near surfaces are obtained for NaCl(100), NaCl(110), CsCl(110), zinc blende (110), wurtzite (11$\bar{2}$0), and rutile (001).

I. INTRODUCTION

Crystal-field effects on potentials in the vicinity of crystal surfaces[1,2] were studied not long after the publication of Madelung's original investigations[3] for bulk. In a classic paper, Lennard-Jones and Dent[2] considered the electrostatic potential outside the surface of an ionic crystal.[4] Contrary to expectation, the potential was shown to be of shorter range than that due to van der Waals forces. There have been investigations of the difference between the Madelung potential at a surface and that of the bulk: Herzfeld[1] treated ionization effects at the surface of AgBr; more recently, Levine and Mark[5] have asked whether this difference should cause surface atoms of semiconductors or insulators to have core- or valence-electron energy levels lying in their band gaps; and Slater,[6] Parry,[7] and others have calculated the Madelung potential as a function of depth below a surface. The fact that surface-bulk differences are of concern in the electron photoemission study of solids is hardly surprising, but until recently surface-atom chemical shifts have been notable by their failure to appear in the spectra. With the advent of angle-dependent photoemission techniques and with the ability now to choose photon energy so as to minimize the escape depth of the photoejected electrons, spectral lines associated with surface atoms are beginning to be observed.[8,9]

The purpose of this paper is to extend our understanding of surface Madelung effects and to present computed results heretofore unavailable for certain surfaces of CsCl, wurtzite, zinc-blende, and rutile structures. These are especially interesting in that surfaces of metal oxides which have the wurtzite, rutile, and corundum[6] structures are employed as catalysts,[10] and photoemission studies have recently been made of the zinc-blende surfaces of GaAs(110) and GaSb(110) by Eastman and co-workers.[8]

In Sec. II we derive a key equation[2] of Lennard-Jones and Dent (henceforth denoted LJD) by a method differing from theirs. Some implications of this equation for surface Madelung effects and for the calculation of bulk Madelung potentials appear not to have been recognized. From the LJD equation, which describes the potential due to an infinite planar slab of charges, it may be seen that the potential reaches its asymptotic value in a very short distance normal to the slab if the slab has no net charge. As a consequence, atoms within the crystal at a distance only one lattice constant from the surface have Madelung potentials which are indistinguishable from those of atoms well within the bulk. Further, a bulk or surface Madelung potential calculation reduces to sums involving but a few slabs and, as will be seen, accurate results may be obtained without the need to sum far out in real space in the slabs. This means that Madelung sums in real space can be accurately evaluated by small-scale computation with present-day computers and, in simpler cases, even with programmable hand calculators. As an aid in understanding the short-range character of the potential due to a slab, the longer-range potential due to a column of charges is considered in Sec. III. The result for the column is, of course, also pertinent to stepped surfaces. Real-space sums for a number of crystal surfaces are given in Sec. IV. Results are limited to cases in which the surface plane of ions, in addition to having no net charge, would be a mirror plane if it were in the crystal interior. This is often, though not always, the case for principal cleavage planes; certain other cleavages will be considered in a subsequent paper. Although the Madelung sums have been calculated in real space, the LJD equation involves a sum over two-dimensional reciprocal-lattice vectors and, providing one is not evaluating the potential for a point within the slab, the sum may be limited to just a few vectors. It is thus a simple hand calculation once the reciprocal-lattice vectors have been determined. Lacking the in-slab result, one cannot calculate the absolute Madelung term; one can, however, easily calculate the variation in the potential as one moves away from a surface and, given a value for the potential in the bulk, one can obtain the absolute value of the potential at or near the surface. In Sec. V this scheme is employed and its results are compared with those of Sec. IV.

A number of things are neglected in this paper. Surface potential effects associated with surface reconstruction, with surface-bulk differences in the oxidation states of atoms, or with charge transfer between the surface and the bulk have not been considered. Also, the effective potential of a charged ion in the vicinity of a surface or of the final-state hole left behind by a photoelectron involves significant polarization terms.[11] Some of these matters will be dealt with in subsequent papers.

II. THE LENNARD-JONES–DENT EQUATION

In this section we show that the potential outside an array of charges distributed periodically within a planar slab decays exponentially to a constant and, if there is no net charge in the slab, the constant is equal to $2\pi\sigma_\perp$, where $\sigma_\perp$ is the dipole moment perpendicular to the plane per unit area of the slab. The decay terms vary as e^{-Gz}, where G is the magnitude of a two-dimensional reciprocal-lattice vector appropriate to the slab, and z is the perpendicular distance of the sampling point from the plane. Inasmuch as the smallest nonzero $\vec{G}$'s are of the order of $2\pi/a_0$, with a_0 a lattice constant and $e^{-2\pi}=0.0019$, it is clear that decay to the asymptotic value of $2\pi\sigma_\perp$ is very rapid.

Such a result follows from the general expression for the potential due to an infinite planar distribution of charges. Let

$$\phi(\vec{r}) \equiv \phi(\vec{\rho}, z) = \sum_i \frac{q_i}{|\vec{r}-\vec{r}_i|}\,, \tag{1}$$

where q_i is the quantity of ith charge, $\vec{r}_i$ gives its location, and $\vec{r}$ locates the point at which the potential is being sampled, with $(\vec{\rho}, z)$ being the cylindrical coordinates of that position. If the charges lie close to a plane and if they are periodic in position in the slab, the potential can be written

$$\phi(\vec{\rho}, z) = \sum_{\vec{G}} e^{i\vec{G}\cdot\vec{\rho}}\phi_{\vec{G}}(z)\,, \tag{2}$$

where the $\vec{G}$'s are the reciprocal-lattice vectors of the two-dimensional array and where

$$\phi_{\vec{G}}(z) = \frac{1}{A}\int d\vec{\rho}\, e^{-i\vec{G}\cdot\vec{\rho}}\phi(\vec{\rho}, z)\,, \tag{3a}$$

with A the planar area.

One may write

$$\vec{r}_i = \vec{R}_j + \vec{\delta}_k\,,$$

where $\vec{R}_j$ locates the jth unit cell and $\vec{\delta}_k$ gives the position of the kth charge within the cell. Restricting the slab to be one unit cell thick, $\vec{R}_j$ must be parallel to the slab but $\vec{\delta}_k$ may have components parallel and perpendicular to it, i.e.,

$$\vec{\delta}_k = \vec{\delta}_k^{\parallel} + \vec{\delta}_k^{\perp}\,.$$

Letting

$$\vec{\rho}\,' \equiv \vec{\rho} - \vec{R}_j - \vec{\delta}_k^{\parallel}\,,$$

it follows that

$$\phi_{\vec{G}}(z) = \frac{1}{A}\int d\vec{\rho}\, e^{-i\vec{G}\cdot\vec{\rho}} \sum_{j,k} \frac{q_k}{|\vec{r}-\vec{R}_j-\vec{\delta}_k|} = \frac{1}{A}\sum_{j,k} q_k e^{-i\vec{G}\cdot(\vec{R}_j+\vec{\delta}_k^{\parallel})}\int d\vec{\rho}\,' e^{-i\vec{G}\cdot\vec{\rho}\,'}\frac{1}{|\vec{\rho}\,'+\vec{z}-\vec{\delta}_k^{\perp}|}\,. \tag{3b}$$

Now,

$$\sum_j e^{i\vec{G}\cdot\vec{R}_j} = N\,,$$

the number of unit cells. The angular part of the integral is $2\pi J_0(\vec{G}\cdot\vec{\rho}\,')$ and

$$2\pi\int_0^\infty \rho' d\rho' J(\vec{G}\cdot\vec{\rho}\,')\frac{1}{[\vec{\rho}\,'^2+(z-\delta_k^\perp)^2]^{1/2}} = \frac{2\pi}{G}e^{-G(z-\delta_k^\perp)}\,.$$

Thus,

$$\phi(\vec{\rho}, z) = 2\pi\frac{N}{A}\sum_{\vec{G}} q(\vec{G})e^{i\vec{G}\cdot\vec{\rho}}e^{-Gz}\,, \tag{4a}$$

where $q(\vec{G})$ is a "structure factor"

$$q(\vec{G}) \equiv \frac{1}{G}\sum_k q_k e^{i\vec{G}\cdot\vec{\delta}_k^{\parallel}}e^{G\delta_k^\perp}\,. \tag{4b}$$

Equations (4) are the LJD equation.[12,13] For specialized cases the equivalent of this equation has appeared earlier in the literature in the work of Madelung[3] and of Born and Stern.[1] One notes that as z becomes large only the $\vec{G}\to 0$ term survives. For example, consider the unit cell to have a pair of charges, $+q$ and $-q$, with their dipole moment μ perpendicular to the plane. Setting $\delta^{\parallel}=0$ and $\delta^{\perp}=\pm\delta/2$, Eq. (4b) becomes

$$q(\vec{G}) = 2q\sinh(G\delta/2)/G$$
$$= \lim_{G\to 0} q\delta = \mu\,;$$

and far outside the plane

$$\phi(\vec{\rho}, z\to\infty) \to 2\pi N\mu/A \equiv 2\pi\sigma_\perp\,, \tag{5}$$

where, as before, $\sigma_\perp$ is the dipole density. It is worth noting that the contribution of a dipole layer to the work function is twice this, i.e., $4\pi\sigma_\perp$, since the potential is $+2\pi\sigma_\perp$ on one side of the dipole layer and $-2\pi\sigma_\perp$ on the other.

One may show that Eq. (5) is generally valid beginning by expanding the exponential of Eq. (3b)

$$e^{i\vec{G}\cdot\vec{R}_j} = 1 + i\vec{G}\cdot\vec{R}_j + \cdots .$$

In the limit $\vec{G}\rightarrow 0$, only the first term remains. Direct integration yields

$$\phi_{\vec{G}\rightarrow 0}(z) = \frac{2\pi N}{A}\int \rho' d\rho' \sum_k \frac{q_k}{[\rho'^2 + (z - \delta_k^\perp)^2]^{1/2}}$$

and, with no net slab charge, i.e.,

$$\sum_k q_k = 0 ,$$

we obtain

$$\phi_{\vec{G}\rightarrow 0}(z) = \frac{2\pi N}{A}\sum_k q_k \delta_k^\perp$$

as stated before.

In summary then, if there are normal dipoles in the slab $\phi \rightarrow 2\pi\sigma_\perp$, if there is net charge $\phi = \pm\infty$, and if neither is present, $\phi \rightarrow 0$. Further, the scale length for approach towards the asymptotic value is quite short, $\sim a$, a unit lattice vector in the slab.

A bulk Madelung sum thus reduces to a sum involving but a few slabs. Although Eq. (1), the real-space summation for any given slab, converges slowly, the calculation becomes quite compact by use of the following scheme. Do the sums for the slabs of interest and for a "distant" one, whose z corresponds to 5 to 10 slab thicknesses. All the sums converge at the same rate once the distance out along the slabs ρ is much larger than z; i.e., the difference between the finite and infinite sum is the same for all. Thus, with the asymptotic result for the "distant" slab, all the finite sums can be corrected. Typically, it is sufficient to extend the sums to about $100a_0$ along the slabs.

This approach may be viewed as a modern version of Madelung's original scheme[3] for calculation of bulk potentials. He divided the crystal into slabs and used the equivalent of Eq. (4), which he obtained for certain special cases, to calculate contributions from slabs other than that in which the sampling site lay. He divided that slab into strips and, in much the same way, calculated contributions from strips other than the one holding the sampling site. Finally, he summed this last strip analytically, something not readily done for many crystals of interest.

When the surface plane of atoms is a mirror plane in the bulk crystal and has a net charge of zero, a case to be further considered in Sec. IV, the Madelung potential at a surface atom is simply

$$\phi_s = \tfrac{1}{2}\phi_B + \tfrac{1}{2}\phi(\rho, 0) . \tag{6}$$

Here ϕ_B is the bulk Madelung term and $\phi(0)$ is the Madelung sum over the surface plane. Because the first term includes only $\frac{1}{2}\phi(0)$, the second term is needed. The rapid falloff with z of the contributions from slabs, $\phi(z)$, leads one to expect that $\phi(0)$ makes by far the largest contribution to ϕ_B, and thus that

$$\phi_s \sim \phi_B .$$

Indeed, it will be seen in Sec. IV that ϕ_s is typically only about ten percent less than ϕ_B.

A more general expression than Eq. (6), applicable whether or not there is mirror symmetry, is of course

$$\phi_s = \phi_B - \sum \phi(\rho, z) , \tag{7}$$

where the sum is over the slabs not existing on one side of the surface. Provided that $\sigma_\perp = 0$ for the slabs, only a few terms contribute. What is more, the sum does not involve $\phi(\rho, 0)$, the surface slab itself. In this case, Eq. (4) may be used as will be done in Sec. V.

III. ASYMPTOTIC BEHAVIOR AND CONVERGENCE CONSIDERATIONS

The potential due to a single dipole varies as $1/z^2$, and Eq. (5) for a sheet of dipoles shows that the potential at large z is constant. It is enlightening and useful to examine the intermediate case of the potential due to a column of charges. LJD have derived the result and it may be obtained following the preceding section. It is

$$\phi(z) = \frac{N}{L}\sum_{\vec{G}}\sum_k q_k e^{-i\vec{G}\cdot\vec{\delta}_k^{\parallel}} K_0(G(z - \delta_k^\perp)) , \tag{8}$$

where K_0 is a modified Bessel function, $\vec{G}$ is a two-dimensional reciprocal-lattice vector, and N/L is the inverse length of a unit cell in the column. In the limit of large z and again assuming no net charge in a unit cell

$$\phi(z \rightarrow \infty) \rightarrow \frac{N}{L}\frac{\mu}{z}, \tag{9}$$

where

$$\mu \equiv \sum_k q_k \delta_k^\perp . \tag{10}$$

Note that $\delta_k^\perp$ is parallel to z. We see that the potential due to the column of charges falls off asymptotically as $1/z$, a behavior intermediate between that of a single dipole and that of the planar sample. As a result, the spatial dependence of the potential at distances of the order of a from an edge or step on a crystalline surface can be quite different from that associated with a neat plane of cleavage.

The natural convergence of a planar or column sum in real space depends on the symmetry of the charge distribution in a unit cell. The potential at one site, due to the LMth moment of the charge distribution at the other, is the well-known spherical term[14]

$$\phi = \frac{8\pi(-1)^L}{2L+1}\,[(2L)!\,]^{-1/2}\,\frac{\mu_m^L Y_L^M(\hat{R})}{R^{L+1}}\,, \tag{11}$$

where μ_M^L is the Lth moment of the charge distribution and Y_L^M is a spherical harmonic of the direction R to the distribution. For moderate to large R values, the number of cells encompassed in a lattice sum varies as R^2 for a slab and as $\hat{R}$ for a column. With these weighting factors for Eq. (11), we see that the sum converges poorly for a slab if the unit cell has a dipole moment, but rapidly for slabs having higher moments or for columns with dipoles and higher moments. Clearly, for ease of computation it is advantageous to choose the unit cell so as to avoid low-order moments and this can often be done.

IV. RESULTS: REAL-SPACE SUMMATIONS

If the calculation is carried through a sufficiently large number of slabs, one can obtain not only the Madelung potential as a function of distance from the surface but also the bulk potential, ϕ_B, which may be compared with values available in the literature. Table I shows results of calculations of potentials at surfaces of several crystals as well as the Madelung energies of the bulk. The surface-site Madelung potentials are given with respect to ϕ_B and their signs correspond to the potential for a positive test charge. Electron binding-energy shifts have the same sign. The Madelung energies for the bulk are derived from the standard relation

$$E_B = \tfrac{1}{2}\sum_i q_i \phi_B^i\,,$$

where the sum is over the atoms making up a "molecule." This energy is often reported[15,16] with a common valence factor divided out; here, we indicate values taken for the charges. For 50/50 compounds such as NaCl, ϕ_B is equal in magnitude but opposite in sign at the two sites, and E_B has the same magnitude. For crystals such as TiO_2, in which the anion and cation are at ϕ_B of *different* magnitudes, the standard relation between ϕ_B^i and E_B is more complex. Parry's calculations[7] for NaCl surfaces and estimates of Levine and Mark[5] for several ϕ_s are included in Table I. The new estimates are in excellent agreement with Parry's results; they are generally in poorer agreement with those of Levine and Mark and the disagreement is most marked for GaAs, a case for which they made a semiquantitative estimate.

In all cases the Madelung potential at an atomic site in the surface layer is smaller in absolute magnitude than the potential in the bulk. Thus, in the surface, electrons at cation sites are more deeply bound and those at anions less bound than in bulk if all other factors, such as site charge, are the same. The shifts are seen to oscillate as one moves away from the surface towards the crystal interior and the bulk value is rapidly attained. These oscillations are associated with the fact that adjacent planes of atoms are not identical: i.e., just under a given atom there will tend to be one of opposite charge. Surface and bulk potentials differ by roughly ten percent.

For ionic charges of the order of one, the calculated shifts are clearly significant in relation to photoemission observations. For GaAs at the (110) surface, Eastman and co-workers have reported[8] that the Ga 3d core-level displays electron binding increased ~0.3 eV and the As 3d binding decreased ~0.3 eV from values of binding energies in the bulk. They attributed the shifts primarily to increased charge transfer between Ga and As at surface sites. However, the directions of the shifts observed are consistent with reduced Madelung potentials at the surface and, from the results given in Table I, they are consistent with $q \sim 0.38$. A molecular orbital estimate[17] by Coulson and coworkers is $q = 0.46$, and Picus *et al.* inferred a value of 0.43 from infrared vibrational studies.[18] Pauling provides a scheme for estimation of ionic charging based on electronegativity differences[19]; this yields a charge of 0.04 for a diatomic GaAs molecule and, when one multiplies this by 4 to account naively for tetrahedral bonding, one obtains a q of 0.16. Other versions[20,21] of the Pauling scheme yield $q = 0.20$ or $q = 0.28$. With Phillips's description[22] of bond ionicity in semiconductors one obtains $q \sim 0.24$. For other compounds, it should be noted, the Pauling and Phillips descriptions are in disaccord.[23] Finally Harrison's polarity factor[24] implies a value $q = 0.87$. It is clear that the difference between bulk and surface Madelung potentials can account entirely for the observed shifts. This difference is increased if what has been published about surface reconstruction is taken into account. There are, of course, phenomena other than those mentioned above which contribute to surface-bulk core-level shifts. Notably, there may be differences in final-state screening. However, in first approximation, these will produce common shifts at the different atomic sites rather than opposite shifts such as were ob-

TABLE I. Madelung potentials at atomic sites in and near unreconstructed surfaces of several crystals relative to the potentials in the crystal interior. In the leftmost column are listed the crystals with assigned site charges designated, the unit-cell dimensions, and the relevant crystal faces; the second column gives the distances from the crystal face listed to the position of the atomic site, in terms of a; in the next three columns are listed the surface-bulk Madelung potential differences in eV, $\phi_s - \phi_B$, as obtained with the calculational method described in Sec. III of this work and as calculated by others. Signs of the potentials correspond to a unit positive charge; thus for the 1:1 crystals the upper signs refer to negatively charged and the lower to positively charged sites. Electron binding-energy shifts correspond, for the individual sites, in sign and magnitude to the values given. Also given are the computed bulk Madelung energies E_B, in eV, and the corresponding Madelung constants[a] A_a.

Crystal	Distance of site from face	$\phi_s - \phi_B$ (eV)			E_B (eV)	A_a
		This work	Parry[b]	Levine and Mark[c]		
$Na^+Cl^-(100)$	0	∓ 0.337	∓ 0.33	∓ 0.35	-8.923_5	3.495
$a = 5.64$ Å	$a/2$		± 0.01			
	a		0			
$Na^+Cl^-(110)$	0	∓ 1.06	∓ 1.06	1.25		
	$(1/\sqrt{2})a$		± 0.16			
	$\sqrt{2}a$		∓ 0.01			
	$(3/\sqrt{2})a$		± 0.01			
	$(4/\sqrt{2})a$		0			
$Cs^+Cl^-(110)$	0	∓ 0.46		∓ 0.71	-7.129	2.035
$a = 4.11$ Å	$(1/\sqrt{2})a$	± 0.03				
	$\sqrt{2}a$	0				
$Ga^{q+}As^{q-}(110)$	0	$\mp 0.87q$		~ 1.45	$-q^2 9.636$	3.783
zinc blende	$(1/2\sqrt{2})a$	$\pm 0.10q$				
$a = 5.653$ Å	$(1/\sqrt{2})a$	$\mp 0.01q$				
$Zn^{2+}O^{2-}(11\bar{2}0)$	0	$\mp 1.92_5$			-47.828	2.698
wurtzite	$(1/2)a$	$\pm 0.18_5$				
$a = 3.2495$ Å	a	∓ 0.01				
$c/a = 1.602$	$(3/2)a$	0				
$z = 0.375$						
$Zn^{2+}S^{2-}(11\bar{2}0)$	0	$\mp 1.63_5$			-40.342	2.677
wurtzite	$(1/2)a$	± 0.16				
$a = 3.8225$ Å	a	∓ 0.01				
$c/a = 1.6378$	$(3/2)a$	0				
$z = 0.371$						
$Ti^{4+}O_2^{2-}(001)$		Ti O				
rutile	0	$+5.47_5$ -3.56			-141.26	11.260
	$(1/2)c$	-1.16 $+0.44$				
$a = 4.5929$ Å	c	$+0.13$ -0.05				
$c/a = 0.6443$	$(3/2)c$	-0.02 $+0.00_5$				
$x = 0.3056$	$2c$	0 0				

[a] For its definition see, e.g. Refs. 15 and 16.

[b] Reference 7.

[c] Reference 5.

served in GaAs and GaSb by Eastman *et al.*

$TiO_2(001)$ is the one case treated here for which the bulk Madelung terms differ at the two sites. While photoemission studies have been made on this surface,[25,26] there is the question as to whether the surfaces actually studied were sufficiently free of facets of other cleavage planes. TiO_2 cleaves principally on the (110) plane, which includes charged atomic layers. A charged surface layer is energetically unfavorable; the (110) surface layer is almost undoubtedly Ti rich and has Ti ions in a state of oxidation different from that in the bulk. These questions will be addressed in a later paper.

V. SURFACE SUMS: RECIPROCAL SPACE

As has already been discussed, Eq. (7), i.e.,

$$\phi_s = \phi_B - \sum \phi(z) ,$$

is particularly convenient for calculation of surface Madelung potentials, provided that ϕ_B, the bulk potential, is known. Evaluation of $\phi(z)$, where $z=0$, is readily made with Eq. (4) and several examples are given in Table II. Contributions from individual reciprocal-lattice vectors to $\sum\phi(z)$ are indicated for the surface layer (the same set of $\vec{G}$'s is used for the estimates of the interior layers). For comparison with experiment, accuracy better than a few hundredths of an eV is not needed, and it is seen that for the cases at hand, this accuracy can be obtained with only two $\vec{G}$'s of Eq. (4). This is easily done by hand calculation. Unfortunately, as Madelung recognized, ϕ_B is not as readily obtained, since it involves $\phi(z=0)$ for which Eq. (4) converges poorly. In such a case it is better to revert to the real-space sums of the preceding section.

VI. CONCLUSION

It has been shown that the Lennard-Jones–Dent equation indicates useful and convenient ways to calculate surface and bulk Madelung potentials. If a crystal is divided into slabs composed of unit cells of high symmetry, one finds that the individual slab sums are readily calculated and that the significant contributions to the potential at a given site are made by just a few adjacent slabs. The rapidity of approach of the potential to an asymptotic value implies that the potential at sites removed only one lattice constant from the surface is, in general, indistinguishable from the bulk potential. This has important consequences for such experiments as electron photoemission, a technique which, though probing only a small depth of crystal, thus probes "bulk" as well as surface properties. For surfaces corresponding to planes of mirror symmetry in the bulk which were considered here, surface site potentials are typically ten percent smaller than those in the bulk. This result must be considered in the interpretation of photoemission measurements on ionic and covalent materials, as can be seen from Tables I and II. Further, in comparisons of energy levels in isolated molecules with levels in the same molecules when adsorbed at sites lying just outside a surface plane, effects of similar magnitude are expected. Whereas the sum term in Eq. (7) takes into account the missing slabs for the bulk surface Made-

TABLE II. Madelung potentials at anion sites in and near surfaces of several crystals relative to the potentials in the crystal interior. These differences have been calculated on the basis of the Eqs. (7) and (4) given in the text. Contributions made by the individual reciprocal-lattice vectors to the full Madelung potential differences are listed in column 4. The two leftmost columns correspond to those in Table I; the next column gives the reciprocal-lattice vectors, in units of $2\pi/a$, pertaining to column 4; the rightmost three columns list the final Madelung anion-site surface-bulk and near-surface-bulk differences as obtained from summing column 4, from the method of Sec. III, and from the results of Parry.[a]

Crystal	Distance of site from face	$\vec{G}$ $(2\pi/a)$	$-\sum\phi(p,z)\vec{G}$ (anion, eV)[a]	$\phi_s-\phi_B$(anion, eV)		
				$-\sum\phi(p,z)$	This work Table I	Parry[b]
Na^+Cl^-(100)	0	(1,1)	−0.3358			
$a=5.64$ Å		(1,3)	−0.0013			
				−0.3371	−0.3373	−0.33
	$(1/2)a$			+0.0027		+0.01
	a			−0.0013		0
Na^+Cl^-(110)	0	(0,1)	−1.4131			
		$(\sqrt{2},1)$	+0.3635			
		$(2\sqrt{2},1)$	−0.0123			
		(next 4$\vec{G}$'s)	−0.0010			
				−1.0629	−1.0629	−1.06
	$(1/\sqrt{2})a$			+0.161	+0.161	+0.16
	$(\sqrt{2})a$			−0.017	−0.00	−0.01
	$(3/\sqrt{2})a$			+0.002		+0.01
Cs^+Cl^-(110)						
$a=4.11$ Å	0	$(\sqrt{2},0)$	−0.5806			
		(0,1)	0.1180			
		$(2\sqrt{2},1)$	0.0052			
		$(\sqrt{2},2)$	−0.0008			
				−0.4582	−0.46	

[a] The sum includes all planes and all symmetry-equivalent $\vec{G}$'s.

[b] Reference 7.

lung difference, this term represents the only slabs present for the adsorbed molecule. Thus, the elucidation of information about the chemical state of adsorbed species and of atoms at surface sites requires consideration of the Madelung effects. Beyond this, the existence of these effects provides unique avenues for obtaining chemical information from spectroscopic data.

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$$V=\frac{2\pi N}{A}\sum_{\vec{G}\neq 0}\frac{\mu^2}{G}e^{-Gz}\cos(\vec{\rho}\cdot\vec{G}),$$

where V is the interaction energy of a dipole with a planar array of like dipoles. Since $V=E_{z}\mu=-(\partial\phi/dz)\mu$, where E is the electric field, their result may be obtained from Eq. (4).

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