The electrostatic potential energy at a plane surface of a point ionic crystal. II. Numerical

results for an ion near the (100) KCl surface

The electrostatic potential energy at a plane surface of a point ionic crystal: II. Numerical results for an ion near the (100) KCl surface

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Abstract. A simple formula is derived for the calculation of the electrostatic potential of an ion near the (100) surface of a KCl crystal using a lattice sum method. The potential is found to be short ranged, tending to zero far from the surface. The potential is identical to that obtained from the solution of the Poisson equation. Although rapid convergence is achieved in the present method, it is still many times slower than the expression derived from the Poisson equation. At an adsorption site, the electrostatic potential was found to be 0.3 eV. To get the right result from a direct version of the lattice sum, and 10^4 terms must be taken.

1. Introduction

The electrostatic potential of a univalent ion in the vicinity of the surface of an ionic crystal and the binding energy of the adsorbed ion are important quantities in the study of surface stability (Smith 1982, 1986) and its dynamical transformation by way of surface diffusion, crystal growth and evaporation (Chernov and Bulakh 1981, Cheng *et al* 1986). On an unrelaxed surface, the binding energy of an ion is the electrostatic potential energy of the ion at a distance from the surface layer equal to the inter-ionic separation in the lattice (contact distance) and such positions, if directly above a surface ion, are known as the adsorption sites.

There are two equivalent methods of calculating the electrostatic potential. One can be defined in terms of the Poisson equation and the other by lattice summation. The electrostatic potential at a distance z above a one layer 2D array of KCl with infinite widths was calculated using the Poisson equation approach (Lennard-Jones and Dent 1928) and the potential above the (100) surface of an infinitely thick slab of KCl was then generalised in terms of a series summation whose terms are those contributed from the 2D array. This potential $\phi(r)$, as defined by (1), was found to be short ranged, i.e. it decays rapidly to zero over a short distance above the surface layer

$$\phi(r) = \frac{4}{a} \sum_{n_x, n_y}{}' \frac{(-1)^{(n_x^2 + n_y^2)/2} \exp[-2\pi(z/a)(n_x^2 + n_y^2)^{1/2}]}{(n_x^2 + n_y^2)^{1/2}\{1 + \exp[-\pi(n_x^2 + n_y^2)^{1/2}]\}} \cos 2\pi\left(\frac{n_x x}{a} + \frac{n_y y}{a} + \frac{n_x + n_y}{4}\right) \quad (1)$$

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where a is the unit cell dimension and the summation is only over odd layers of ions n_x and n_y along the x and y direction. Subsequently Hove (1955) has modified (1) to

$$\phi(r) = \frac{8}{r_0} \sum_{n_x, n_y}' \frac{\exp[-\pi z (n_x^2 + n_y^2)^{1/2}] \cos \pi n_x x \cos \pi n_y y}{(n_x^2 + n_y^2)^{1/2} \{1 + \exp[-\pi (n_x^2 + n_y^2)^{1/2}]\}} \tag{2}$$

where r_0 is the inter-ionic separation. The sum is now over odd values between 0 and infinity and the position coordinates (x, y, z) are scaled by r_0. Hove only considered the $(1, 1)$ term sufficient for calculating potential energies near the surface. The electrostatic potential energy of a univalent ion at its equilibrium adsorption site above a KCl crystal surface was found to be about 0.3 eV. However this approach failed to calculate the electrostatic potential energy of an ion near the polar (111) face of an NaCl type crystal because of special mathematical difficulties (Lennard-Jones and Dent 1928).

On the other hand, lattice summation methods are more often adopted to calculate the electrostatic potential energy of an ion inside and above the surface of an ionic crystal. Essentially the problem is to evaluate the expression

$$\phi(r) = \sum_j q_j / |r - r_j|. \tag{3}$$

The distance $|r - r_j|$ is the separation between the surface ion with position vector r and the lattice ion with charge q_j and position vector r_j. Direct summation of (2) for such a 2D (monolayer) array of ions requires 10^4 terms for good convergence (Schwalm 1982). However, fast convergence of the lattice sum can be achieved by means of an integral transform of $1/|r - r_j|$ in terms of, for example, the theta function (Hoskins *et al* 1977). This approach is also of mathematical interest as it turns out to be part of the studies of higher-dimensional analogues of the Riemann ζ function (Glasser and Zucker 1980). One of us has recently shown that the transformed expression for both surface and bulk potential contains two components. One is a quickly converging series in terms of the complementary error function. For a finite crystal whose unit cell dipole moment is zero, the second component is dependent on its size and shape. However this term seems computationally complicated (Smith 1983). For any crystal, whose unit cell chosen has a non-zero dipole moment and as a result contains polar faces, this second component is divergent. We have also a clearer exposition of this shape dependent or divergent term (Smith 1986).

In this study, we present a simple lattice sum electrostatic potential for a particular case of the (100) non-polar face of a NaCl type crystal. Numerical results, included from those derived in our earlier studies (Hoskin *et al* 1977, Smith 1983), are compared with those obtained from the Poisson equation solution approach.

2. Definition of the crystal lattice

We consider a cubic KCl lattice containing unit cells of dimension a. Their positions are specified by lattice vector $n = n_x a_1 + n_y a_2 + n_z a_3$ where the a_i are vectors along the principal axis of the unit cells with length equal to that of the unit cell. The lattice vectors of unit cells P_n originate from the centre of an arbitrarily chosen unit cell P_0 and terminate at the centre of the unit cell P_n. Each unit cell contains N point charges $q_i |e|$ where e is the electronic charge. The position vectors of these ions with respect to the centre of the unit cell are r_i. For the KCl type lattice, $N = 8$ and the position

of the cations are $(a/4, a/4, a/4)$, $(a/4, -a/4, -a/4)$, $(-a/4, -a/4, a/4)$, $(-a/4, a/4, -a/4)$ and those for the anions are $(-a/4, a/4, a/4)$, $(a/4, -a/4, a/4)$, $(a/4, a/4, -a/4)$, $(-a/4, -a/4, -a/4)$.

The net ionic charge and dipole moment P of a unit cell is zero so that

$$\sum_i q_i = 0 \tag{4}$$

and

$$P = \sum_i q_i r_i = 0. \tag{5}$$

Similarly the reciprocal lattice can be defined with unit cell vectors b_i in the direction of a_i but magnitude equal to the reciprocal of $|a_i|$.

3. Derivation of the surface electrostatic potential

We want to evaluate the electrostatic potential at a position r with respect to the centre of P_0:

$$\phi(r) = \sum_i^N \sum_{n_x=-N}^0 \sum_{n_y=-M}^M \sum_{n_z=-M}^M q_i/|r - r_j - n| \tag{6}$$

where M and $N \to \infty$.

In previous work we transformed $1/r$ into an integral in terms of the Jacobi theta function (Hoskin *et al* 1977) or complementary error function (Smith 1983) such that the resulting series can be evaluated with just a few terms to obtain good convergence.

In this study, we also make use of the transformation identities (7) and (8) as used in (Hoskins *et al* 1977, Smith 1983)

$$\frac{1}{x} = \frac{1}{\sqrt{\pi}} \int_0^\infty t^{-1/2} \exp(-tx^2) \, dt \tag{7}$$

and

$$\exp(-ty^2) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^\infty du \, \exp(-u^2/t + 2iuy). \tag{8}$$

We first transform the double sum over n_x and n_y, $F(r; n_z)$, with (7)

$$F(r; n_z) = \sum_{n_x=-M}^M \sum_{n_y=-M}^M 1/|r - r_j - n|$$

$$= \sum_{n_x=-M}^M \sum_{n_y=-M}^M \frac{1}{\sqrt{\pi}} \int_0^\infty t^{-1/2} \exp[-t(x-1)^2]$$

$$\times \exp[-t(y - m)^2] \exp[-t(z - n)^2] \, dt. \tag{9}$$

However, we will not split (9) into two terms in which one of them is the complementary error function as in Smith (1983). The integrand in (9) can be transformed using the

identity (8). Thus

$$F(\boldsymbol{r}; n_z) = \pi^{-3/2} \sum_{n_x=-M}^{M} \sum_{n_y=-M}^{M} \int_0^\infty t^{-3/2} \exp[-t(x-n_x)^2]$$

$$\times \int_{R^2} \mathrm{d}^2 u \exp(-u^2/t) \exp[2iu(n_x-x)] \exp[2iu(n_y-y)] \tag{10}$$

where R^2 is the real space. Factorising $\exp(-u^2/t)$ from the integral over $\boldsymbol{u}$ into that over t and we will demonstrate that I_t, the integral over t,

$$I_t = \int_0^\infty t^{-3/2} \exp[-(u^2/t + t(z-n_z)^2)] \, \mathrm{d}t$$

can be evaluated exactly by the change of variable $s = -|\boldsymbol{u}|/t + \sqrt{t}|z-n_z|$. Completing the square for the integrand and substituting for s we obtain

$$I_t = \exp(-2|\boldsymbol{u}||z-n_z|) \int_0^\infty t^{-3/2} \exp[-(\sqrt{t}|z-n_z| - |\boldsymbol{u}|/\sqrt{t})^2] \, \mathrm{d}t$$

$$= \sqrt{\pi} \exp(-2|\boldsymbol{u}||z-n_z|)/|\boldsymbol{u}|.$$

Therefore

$$F(r, n_z) = \frac{1}{\pi} \sum_{n_x=-M}^{M} \sum_{n_y=-M}^{M}$$

$$\times \int_{R^2} \mathrm{d}^2 u \exp[2iu_z(n_x-x)] \exp[2iu_y(n_y-y)] \exp(2|\boldsymbol{u}||z-n_z|)$$

$$= \frac{1}{\pi} \int_{R^2} \mathrm{d}^2 u \frac{\exp(-2|\boldsymbol{u}||z-n_z|)}{|\boldsymbol{u}|} \exp(-2iu_x x) \exp(-2iu_y y)$$

$$\times \sum_{n_x=-M}^{M} \exp(-2imu_x) \sum_{n_y=-M}^{M} \exp(-2inu_y). \tag{11}$$

The sums over n_x and n_y are now finite geometric series, e.g.

$$\sum_{n_y=-M}^{M} \exp(-2in_y u_y) = \frac{\sin(2M+1)u_y}{\sin u_y}. \tag{12}$$

Equation (11) thus becomes

$$F(r, n_z) = \frac{1}{\pi} \int_{R^2} \mathrm{d}^2 u \frac{\exp(-2|\boldsymbol{u}||z-n_z|)}{|\boldsymbol{u}|} \exp(-2iu_x x) \exp(-2iu_y y)$$

$$\times \frac{\sin(2M+1)u_y}{\sin u_y} \frac{\sin(2M+1)u_x}{\sin u_x}. \tag{13}$$

We note that (7) has transformed the x and y component of the space variable $|\boldsymbol{r}-\boldsymbol{n}|$ into $\boldsymbol{u}$ space which should likewise consist of an integer variable and a real variable

$$\boldsymbol{u} = \pi\boldsymbol{k} + \boldsymbol{v} \qquad \boldsymbol{k} = (k_x, k_y). \tag{14}$$

We can thus consider the $\boldsymbol{u}$ space as the reciprocal space with lattice composed of unit cells T_k whose position is specified by reciprocal lattice vector $\pi\boldsymbol{k}$ and dimension π such that $\boldsymbol{v} \in T_0 = [-\pi/2a, \pi/2a]^2$, the reference unit cell in $\boldsymbol{u}$ space.

The integral in (13) can be split into a sum over k of integral over T_0:

$$F(r, n_z) = \frac{1}{\pi} \sum_k \int_{T_0} \mathrm{d}^2 u \frac{\exp(-2|u||z - n_z|)}{|u|} \exp(-2\mathrm{i}u_x x) \exp(-2\mathrm{i}u_y y)$$

$$\times \frac{\sin(2M+1)u_x}{\sin u_x} \frac{\sin(2M+1)u_y}{\sin u_y}. \tag{15}$$

The sum over k can be further split into the $k = 0$ term, $F_2(r, n_z)$, and the rest, $F_1(r, n_z)$. Then

$$F_2(r, n_z) = \frac{1}{\pi} \int_{T_0} \mathrm{d}^2 u \frac{\exp(-2|u||z - n_z|)}{|u|} \exp(-2\mathrm{i}u_x x) \exp(-2\mathrm{i}u_y y)$$

$$\times \frac{\sin(2m+1)u_x}{\sin u_x} \frac{\sin(2n+1)u_y}{\sin u_y}. \tag{16}$$

The contribution of F_1 to the surface electrostatic potential can be reduced to a simple expression. Thus the product from the sum of the two geometric series, with the aid of (13), becomes

$$\frac{\sin(2M+1)u_x}{\sin u_x} \frac{\sin(2M+1)u_y}{\sin u_y} = \frac{\sin(2M+1)v_x}{\sin v_x} \frac{\sin(2M+1)v_y}{\sin v_y}. \tag{17}$$

Given that the rest of the integrand is smooth, at large N and $k \neq 0$, the product becomes $\pi^2 \delta(v) + \mathrm{O}(1/N) = \pi^2 \delta(\pi k - u) + \mathrm{O}(1/N)$. Upon integrating over T_0 (Smith 1983), F_1 is converted into a simple formula

$$F_1(r, n_z) = \sum_{k \neq 0} \frac{\exp(-2\pi|k||z - n_z|)}{|k|} \exp(-2\mathrm{i}\pi k_x x) \exp(-2\mathrm{i}\pi k_y y). \tag{18}$$

Now we evaluate the sum over n_z in F_1:

$$\sum_{n_z = -\infty}^{0} F_1(r, n_z) = \sum_{n_z = -\infty}^{0} \sum_{k \neq 0}^{\infty} \frac{\exp(-2\pi|k||z - n_z|)}{|k|} \exp(-2\mathrm{i}\pi k_x x) \exp(-2\mathrm{i}\pi k_y y). \tag{19}$$

The sum over n_z is a semi-infinite geometric series with, when $z > 0$, a common factor $-\exp(-2\pi|k|)$ (Smith 1983). This sum is of the same form as that found in Lennard-Jones and Dent (1928). In this case, however, the sum is over successive layers of lattice unit cells which contain two ion layers:

$$\sum_{n_z = -\infty}^{0} F_1(r, n_z) = \sum_{\substack{k_x = -\infty \\ (k_x, k_y) \neq (0,0)}}^{\infty} \sum_{k_y = -\infty}^{\infty} \frac{\exp(-2\pi|k||z - n_z|)}{|k|[1 - \exp(-2\pi|k|)]} \cos[2\pi(k_x x + k_y y)]. \tag{20}$$

We shall now demonstrate that, upon summing over the charges (j) in a unit cell, by virtue of the charge neutrality and zero dipole moment within a unit cell and the symmetry of the arrangement of ions in an NaCl type lattice the net contribution to the electrostatic potential from F_2 ($k = 0$ term) is zero. When the charge-dependent part is factorised, x_j is replaced by $x - x_j$ for convenience of presentation. The replacement, for a given (x, y, z), results in just a shift of (the arbitrary chosen) origin

$$\sum_j q_i \sum_{n_z = -\infty}^{0} F_2 = \frac{1}{\pi} \sum_{n_z = -\infty}^{0} \int_{T_0} \mathrm{d}^2 u \frac{1}{|u|[1 - \exp(-2|u|)]} \frac{\sin(2M+1)u_x}{\sin u_x} \frac{\sin(2M+1)u_y}{\sin u_y}$$

$$\times \exp(-2|u|z) \exp(-2\mathrm{i}u_x x) \exp(-2\mathrm{i}u_y y) \sum_{j=1}^{N} q_j$$

$$\times \exp[-2(|u|z_j - \mathrm{i}u_y y_j - \mathrm{i}u_x x_j)]. \tag{21}$$

Since we are considering the term in which $k = 0$ and v small ($v \in T_0$), near $u = 0$, we can expand the exponential factors in the sum over j in (21) to quadratic terms in u:

$$\sum_{j=1}^{N} q_j \exp[-2(|u|z_j - iu_y y_j - iu_x x_j)]$$

$$\simeq \sum_{j=1}^{N} q_j(1 - 2|u|z_j + 2u^2 z_j^2)(1 - 2iu_y y_j - 2u_y^2 y_j^2)(1 - 2iu_x x_j - 2u_x^2 x_j^2)$$

$$= \sum_{j=1}^{N} q_j(1 - 2|u|z_j - 2iu_y y_j - 2iu_x x_j + S_1 + S_2 + O(u^3)) \tag{22}$$

where

$$S_1 = 2u^2 z_j^2 - 2u_y^2 y_j^2 - 2u_x^2 x_j^2$$

and

$$S_2 = 4iz_j y_j |u| u_y + 4ix_j z_j |u| u_x + 4ix_j y_j u_x u_y.$$

The first term in (21) vanishes because of the charge neutrality of the unit cell. The next three terms containing x_1, y_1 and z_1 (S_1) also become zero because of the zero dipole moment condition (5). S_2 contains terms which are odd functions of x in $T_0 \in [-\pi/2, \pi/2]^2$ and therefore they vanish upon integration over T_0. The remaining term in the sum over j is

$$\sum_{j=1}^{N} q_j(z_j^2 - \tfrac{1}{2}y_j^2 - \tfrac{1}{2}x_j^2). \tag{23}$$

In the NaCl type lattice, $x_j^2 = y_j^2 = z_j^2 = a^2/16$. These remaining terms are zero as well. The higher-order terms left out are $O(1/M)$ and so vanish in the limit $M \to \infty$. Thus the contribution to the surface electrostatic potential from $F_2(r, n_z)$ need not be considered further. Hence

$$\phi(r) = \sum_{j=1}^{N} q_j \sum_{\substack{k_x = -\infty \\ (k_x, k_y) \neq 0}}^{\infty} \sum_{k_y = -\infty}^{\infty} \frac{1}{|k|} \frac{\exp(-2\pi|k|(z - z_j))}{1 - \exp(-2\pi|k|)}$$

$$\times \cos\{2\pi[k_x(x - x_j) + k_y(y - y_j)]\} \tag{24}$$

for $z - z_j > 0$, i.e. above this surface. In both (1) and (24), the form of the sum over the x and y directions and the z direction reflects the symmetry of the surface.

The error of taking a finite number of terms (small k) for the numerical evaluation of (24) can be estimated as follows. Let us suppose we have summed over k vectors with $|(k_x, k_y)| \leq K$. Then we have left out a contribution whose modulus obeys

$$\left| \sum_{j=1}^{N} q_j \sum_{k > K}^{\infty} \frac{1}{|k|} \frac{\exp[-2\pi|k|(z - z_j)]}{1 - \exp(-2\pi|k|)} \cos\{2\pi[k_x(x - x_j) + k_y(y - y_j)]\} \right|$$

$$\leq \frac{8|q_j|}{1 - \exp(-2\pi)} \sum_{|k| > K} \frac{1}{|k|} \exp[-2\pi|k|(z - z_j^*)]$$

where z_j^* is the largest z_j or those at the surface layer. The sum over k can be replaced by an integral

$$\frac{16\pi|q_j|}{1 - \exp(-2\pi)} \int_K^{\infty} dk \exp[-2\pi(z - z_j^*)k] = \frac{8\exp[-2\pi(z - z_j^*)K]}{[1 - \exp(-2\pi)](z - z_j^*)}. \tag{25}$$

Evidently, the error given in (25) of summing over a small range of k space decreases exponentially with the distance away from the surface layer. Suppose $z - z_j^* = \frac{1}{8}$, a position close to the surface layer, the error in taking only $|k| < K$ is $\sim 64 \exp(-\pi K/4)$. For $K = 10$ (adding up 400 terms) the error is less than $64 \exp(-5\pi/2) \sim 2.4 \times 10^{-2}$. However a similar error of 1.24×10^{-2} is achieved at a further distance, say $z - z_j^* = \frac{1}{4}$, away from the surface with $K = 5$ or approximately 100 terms.

4. Numerical results and discussion

The electrostatic potential of a univalent ion at a perpendicular distance z above a KCl surface with unit cell dimension $a = 630$ pm is obtained from both the lattice sum method (24) and from the solution of Poisson's equation (1). Scaling factors appropriate for (1) and (24) and for (2) were needed to convert the potentials to eV. The lattice sum expression (24) was evaluated over a circular shell of $K \leq 5$. The limits for evaluating (1) were both taken from -5 to 5. The choice of limits from -3 to 3 results in a 0.2% smaller potential. From Hove's approximation expression, (2) over -1 to 1 (i.e. nearest-neighbouring ions along lateral directions), this unconvergent potential is 6% less.

Fast convergence is achieved in both summation formulae (1) and (24) but the expression from the Poisson equation (1) requires considerably fewer terms for good convergence. Equation (1), however, was re-transformed back into lattice space and was summed only over odd layers of ions which, unlike the even layers, does not consist of a zero cosine factor as a result of the cubic geometry of the NaCl unit cell and the positioning of the cations and anions (and thus charge neutrality) within (equation (2.05) of Lennard-Jones and Dent (1928)).

On the other hand, more terms are needed for the lattice sum expression (24) which involves the sum over charges. However it is evaluated over unit cells in a two-dimensional reciprocal space over a similar range of summation compared to (1). The actual space covered is smaller. For a given z_j, i.e. ions within the same layer, and for all positions (x, y, z), the contribution to the potential from terms with one or both k_y and k_z even were found to be equal. For a (100) NaCl surface, the charge neutrality condition among these four ions in a unit cell will make the sum of these terms zero and will thus mean that only both odd k_x and k_y are needed to be summed. The summing of (24) over only odd k_x and k_y terms reduces the number of terms by between 50%, if summed over a smaller radius, to 75%, if summed over a larger radius but with more terms. Although the result over odd (k_x, k_y) only does not differ from the full sum, its speed convergence is still many times slower than (1).

The electrostatic potential obtained by both methods are identical. This is expected since both the lattice sum and the Poisson equation are based on the same idea of linear superposition of the various contributions to the potential and they are equivalent methods. The identical behaviour of the potential expressions (1) and (24) obtained from two theoretically equivalent methods is most encouraging since it verifies the correctness of our calculation and there is no other means available for such checking. At an adsorption site, the electrostatic potential energy was found to be about 0.3 eV. This value is in agreement with direct summation (Chernov and Bulakh 1981).

The potential, plotted in figure 1 as a function of z/a, is short ranged as we would expect from the cancellation of the approximately equal contributions due to the opposite charges nearby. The shape of the potential gradually flattens to zero for all
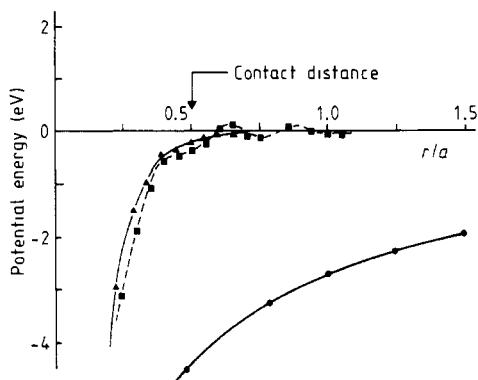
Figure 1. Electrostatic potential energy of an ion near the surface of an NaCl type crystal. $a = 630$ pm. ▲, this work; ■, Smith (1983); ●, pair Coulomb potential.

z when x and/or $y \to 0$ at which complete cancellation of interaction due to the symmetry of the NaCl lattice occurs

The electrostatic potential energy at a distance above a 2D or one layer KCl ion array, which was evaluated from (1) without the sum over n_z using the same limit of summation as in the 3D semi-infinite case was found to be 1% larger. The difference is smaller than to those obtained from the unconverged 3D potential summed with fewer terms over n_x and n_y or along the x and y directions. In the derivation of the potential for the 3D half-space sum (24) and the solution of the Poisson equation (1), the contribution to the potential from the underlying ionic arrays is represented as the sum of a geometric series over n_z with a negative common factor less than 1 or $(-\exp(-2\pi|\mathbf{k}|))$. The exponential decay of the subsequent terms in the series suggests that only the leading term(s) are significant. This is expected physically as the contribution to the potential from the next layer of ions underneath, which is of opposite charge to the corresponding ones above, always reduce the total. The small difference between the potential due to a 2D array and a 3D array (of semi-infinite depth) and the small number of terms needed for the evaluation of both (1) and (24) which are the results of a transformation of the respective potential functions into new expressions and, in the case of (24), reciprocal lattice space, has demonstrated their computational convenience over the direct summation.

We could not calculate the surface electrostatic potential using formulae developed from one of our previous studies (Hoskins *et al* 1977) because the asymptotic expansion term remains divergent. Calculation of the electrostatic potential using the transformation developed in Smith (1983) was more computationally elaborate. The electrostatic potential is similar to that obtained using either (1) or (24) except that it has a few fluctuations near the surface. The electrostatic potential energy at an adsorption site was found by us to be 0.47 eV, much higher than those calculated in (1) and (24) and others.

5. Conclusion

The derivation of a simple formula like (1) for calculating the electrostatic potential at a (100) surface of a KCl type crystal is possible as a result of its especially simple

lattice structure. In such a formula, only terms with both components of the reciprocal lattice vector odd are needed. This formula gives lattice sums which converge rather more quickly than the one derived here. Our formula (24) applies to any surface of a crystal made of whole unit cells with zero charge and net dipole moment per unit cell. Under these circumstances no terms which depend on the shape of the piece of crystal appear, in agreement with our earlier prediction (Smith 1983) on macroscopic shape-dependent potentials.

While the lattice sum derived here converges rather slower than that in (1), it is very general and can be applied to problems where the Poisson equation approach gives the wrong answer. A typical example is the potential near the (111) surface of KCl (Lennard-Jones and Dent 1928), where special mathematical difficulties arise because the unit cell dipole moment has a non-zero component normal to the surface. These are easily handled in our approach. They give rise to a diverging macroscopic shape-dependent potential (Smith 1986). Our method also shows how to handle this divergence by imposing an excessive layer of charge on the surface with surface charge density exactly that needed to act as a sink (or source) for the flux of the dipole moment per unit cell through the surface. Only with such an excess surface charge can such a surface be physically stabilised.

Experimentally a KCl crystal with {111} faces can be grown from a supersaturated solution containing Pb^{2+} ions. The added impurity ions presumably fulfil the energetic requirements, in addition to its similar size to K^+. As crystal growth progresses, these impurity ions are incorporated into the crystal in trace amounts with uniform spatial distribution (Cheng 1982). The gradual depletion of the added impurity ions in the solution phase can eventually result in crystals with both {100} and {111} faces.

For other real NaCl type crystals the surface binding energy and, because of the same form of the lattice sum expression for calculating bulk potential, the bulk energy at a lattice site are inversely proportional to a and therefore the contribution of electrostatic potentials to the ΔH of adsorption, solution or evaporation of these crystals behaves in the same manner.

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