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Calculation of the lattice structure on stepped surfaces of Ar and NaCl

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Calculations of surface distortions for high-Miller-index stepped surfaces are presented for Ar and NaCl. Negligibly small surface relaxation is found for the Ar surfaces. In the case of NaCl, surface buckling and surface atom displacements on the order of (5–10)% of the atomic step height are obtained. Polarization effects account for the much larger surface distortions in NaCl.

I. INTRODUCTION

Surfaces of crystals characterized by high Miller indices consist of terraces of low-index planes separated by steps often one atom in height.[1–5] The ordered stepped surfaces display varying degrees of thermal stability. Studies of chemisorption of hydrogen, oxygen, carbon monoxide,[6] and various hydrocarbons[7,8] on stepped platinum surfaces indicate that these atomic steps play a key role in enhancing surface chemical reactions. When a surface is cleaved, one expects relaxation of the surface atoms to new equilibrium positions slightly different from the bulk-equilibrium structure. A knowledge of the actual positions of atoms in a stepped surface may be useful in the understanding of the catalytic properties of stepped surfaces. Up to now, most of the work on stepped surfaces has been experimental. In this work, we try to answer theoretically this simple question: Where do the atoms on a stepped surface actually sit?

We present calculations of surface-atom displacements for Ar, a noble-gas solid, and NaCl, an alkali halide. The equilibrium structure of a stepped surface is determined by minimizing the surface energy of a step as a function of surface-atom positions. We chose Ar and NaCl because both have closed-shell electronic configurations so that only pair potentials enter into surface-energy calculations, and the forms of these potentials are relatively well known.

II. CALCULATION FOR Ar

For this calculation, we have chosen the stepped surface corresponding to cubic Miller indices (1 0 11) of the face-centered-cubic structure, as shown in Fig. 1(a). The surface is infinite along the $\hat{y}$ direction. The pair potential u_{ij} needed in cohesive energy computations is the Lennard-Jones potential:

$$u_{ij} = 4\epsilon[-(\sigma/r_{ij})^6 + (\sigma/r_{ij})^{12}], \tag{1}$$

where r_{ij} is the distance between atoms i and j; ϵ and σ are the rare-gas force constants: $\epsilon = 1.67\times10^{-14}$ erg and $\sigma = R_0/1.11$ for Ar,[9] R_0 being the nearest-neighbor distance. We define U_i, the ith atom's contribution to the cohesive energy to be the summation of pair potentials over all j atoms that interact with atom i,

$$U_i = \frac{1}{2}\sum_j u_{ij}\,. \tag{2}$$

It is clear that U_i takes different values depending on the position of the atom i. When i is at or near the surface, values of U_i may vary from atom to atom; where i is deep within the bulk, U_i takes on the bulk value U, irrespective of the atom index i. The stepped surface energy is defined in the following manner: (i) Pick out the set of surface atoms which define the smallest repetitive unit for the stepped surface in question; in the particular case of (1 0 11), the set consists of atoms numbered 1–12 in Fig. 1(a). (ii) Take every atom m that has (x, y, z) coordinates within the bounds defined by the repetitive unit ($-\hat{z}$ is the direction into the bulk), compute the difference $(U_m - U)$. (iii) The summation $\sum_m (U_m - U)$ is the surface energy per repetitive unit of the step, or simply, the step surface energy S. The quantity S is computed by direct lattice sums; it can also be defined as the surface energy per two-dimensional unit cell. Since the Lennard-Jones pair potential is rather short range, the bulk value U converges to its exact value to a very good approximation when the sum is carried out only up to the set of ten nearest neighbors. In evaluating S, only the atoms that are within the tenth-nearest-neighbor shell of a surface atom are allowed to contribute to the difference $U_m - U$.

The calculated value S for the (1 0 11) single step [Fig. 1(a)] is 64.2650×10^{-14} erg, which corresponds to 5.159×10^{-3} eV/Å^2 [area measured parallel to the (1 0 11) plane]. If this energy is assigned to the surface atoms exclusively, and in a uniform fashion, it corresponds to 5.3554×10^{-14} erg per surface atom, which is to be compared with the bulk cohesive energy of -13.8593×10^{-14}

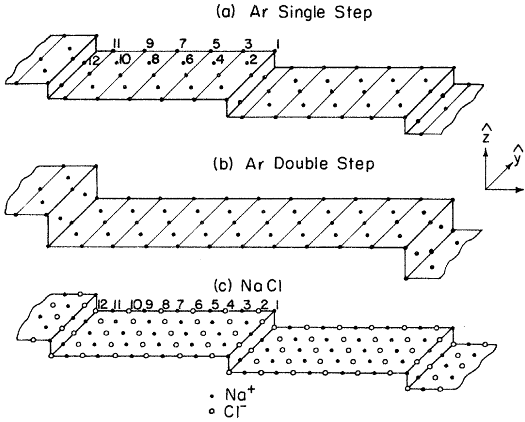

FIG. 1. Crystal surfaces corresponding to cubic Miller indices (1 0 11) for (a) an Ar single step; (b) an Ar double step; and (c) a NaCl single step.

erg per atom. The above value can also be compared with the surface energy 5.6283×10^{-14} erg per atom or 4.990×10^{-3} eV/Å^2 corresponding to a perfect (0 0 1) surface. The step configuration which is consistent with the same Miller indices (1 0 11) but with double atomic step height [Fig. 1(b)] gives $S=131.1568\times10^{-14}$ erg. This configuration has the same number of surface atoms as the single step [Fig. 1(a)]; it yields a surface energy of 5.4649×10^{-14} erg per surface atom or 5.264×10^{-3} eV/Å^2. Since this is a larger value than the one quoted for a single step, we predict the formation of step of monatomic height to be energetically more favorable than the formation of higher steps. This, unfortunately, is not a general result but arises directly from the short-range character of the pair potential. One can, in fact, arrive at this result if one only counts the number of nearest-neighbor bonds broken in different step configurations.

Hitherto, the atoms have not been allowed to relax. We expect, in general, very little relaxation in solids with Lennard-Jones pair interactions. An r^{-12} repulsive potential resembles very much a completely "vertical" hard core. An exactly impenetrable core means no relaxation whatsoever, since even in the bulk the atoms are located core to core. If we include only nearest-neighbor interactions and a Lennard-Jones potential, we obtain very small relaxation parameters. These are quoted in Table I as $\vec\delta_x$ and $\vec\delta_z$, which are the displacements along the x and z axes in units of a step height $(\frac{1}{2}a)$, where a is the cubic lattice constant. The results in Table I indicate atom displacements on the order of 2% of the step height directing outward from the surface. We reemphasize that these results in Table I derive from calculations including only nearest-neighbor interactions. Using the same approximation in the calculation for the (0 0 1) surface, an outward displacement of magnitude $0.02(\frac{1}{2}a)$ is predicted for the surface atoms. However, by taking account of interactions of pairs up through the set of tenth nearest neighbor for the (0 0 1) surface, one arrives at an inward contraction of $0.01(\frac{1}{2}a)$ for the surface. The change of sign in the displacement of surface atoms when neighbors further apart are included is accounted for by the following: The attractive part of the Lennard-Jones potential is of longer range than the repulsive part, when only nearest-neighbor interactions are included, the effect of the attractive part is underestimated, thus resulting in an outward displacement for the surface atoms; when the attractive potential is properly taken into account by summing over more neighbors, an inward displacement for the surface atoms is obtained. One therefore expects $\vec\delta_x$, $\vec\delta_z$ in Table I also to change sign if one were to include pairs up to the tenth nearest neighbor in the calculations for (1 0 11). The magnitude of these displacements are, however, still on the order of 1% of the step height, and therefore negligible.

In summary, for a Lennard-Jones solid, as expected from general considerations, one finds fairly large surface energies, as compared with bulk binding energies, but rather small in an absolute scale. One also finds negligibly small surface relaxation, consistent with the close-packed structure and the nearly impenetrable core properties of the repulsive force.

III. CALCULATION FOR NaCl

The appropriate ion-ion pair potential needed for the computation of surface energies is

$$u_{ij}=R(|\vec{r}_{ij}|)+\frac{q_i q_j}{|\vec{r}_{ij}|}+\frac{q_i(\vec{p}_j\cdot\vec{r}_{ij})}{|\vec{r}_{ji}|^3}+\frac{q_j(\vec{p}_i\cdot\vec{r}_{ji})}{|\vec{r}_{ji}|^3}-\vec{p}_i\cdot\left(\frac{3(\vec{p}_j\cdot\vec{r}_{ij})\vec{r}_{ij}}{|\vec{r}_{ij}|^5}-\frac{\vec{p}_j}{|\vec{r}_{ij}|^3}\right), \tag{3}$$

where $\vec{r}_{ij}$ is the displacement vector directed from ion j to i, q_i, q_j are the respective ionic charges, and $\vec{p}_i$, $\vec{p}_j$ the induced electric dipoles on ions i and j. The quantity $R(|\vec{r}_{ij}|)$ is the short-range re-

TABLE I. Displacement of surface atoms in an Ar (1 0 11) surface in units of a step height $\frac{1}{2}a$.

Atom label [see Fig. 1(a)]	$\vec\delta_x$	$\vec\delta_z$
1	+0.01	+0.02
2–11	0	+0.02
12	+0.00 (3)	+0.00 (3)

pulsive potential which we assume to be nonzero only for nearest-neighbor pairs; the second term is the long-range Coulomb potential. These two terms would have been all that is required in a computation of bulk cohesive energy. With the presence of a surface, the atoms near the surface experience a net electric field due to the rest of the ionic medium; the electric field polarizes the electrons in these surface atoms, giving rise to induced dipole moments on them. The last three terms of Eq. (3) are the polarization energy due to the presence of surface-induced dipoles. We show that these polarization terms are important in causing relatively large surface distortions by calculating as a function of surface-atom displacements (a) the surface energy of the (0 0 1) surface and (b) the step surface energy of the (1 0 11) surface. There exists in the literature many theoretical results on surface energy for (0 0 1) alkali halides based on various methods and models,[10–13] but none to our knowledge for a high-Miller-index step. The calculation for the (0 0 1) surface is included here to make the discussion on the calculation for (1 0 11) stepped surface more transparent, and also to provide a reference for comparison with the results of the stepped surface.

The smallest surface repetitive unit for a (0 0 1) surface is simply two nearest-neighbor ions, one Na^+ and one Cl^-; S, the surface energy per repetitive unit, as defined in the section for Ar, is computed by doing the proper lattice sums for every term in Eq. (3), allowing the Na^+ ion to distort by $\vec{\delta}_+$ and the Cl^- ion by $\vec{\delta}_-$. The symmetry of the (0 0 1) surface, with no superstructure, restricts the displacement to the direction normal to the surface. The inverse twelfth-power form[14] is used for the repulsive first term $R(|\vec{r}_{ij}|)$ in Eq. (3). The Coulomb term $(q_i q_j/|\vec{r}_{ij}|)$ is long range; however, the summation over two-dimensional Höjendahl squares[15] and 18 layers is more than adequate to reproduce the exactly calculated bulk cohesive energy[9]

$$-178.6\ \mathrm{kcal/mole} = -1.269\times10^{-11}\,\mathrm{erg/(ion\ pair)}.$$

All three terms for polarization energy in the pair potential involve the dipoles P_+ for Na^+ and P_- for Cl^-; they are obtained in the following manner:
(i) We compute the net Coulomb field $\vec{E}_{Ci}$ on ion i arising from the rest of the ionic medium, i.e.,

$$\vec{E}_{Ci}=\sum_j \frac{q_j}{|\vec{r}_{ij}|}\,\vec{r}_{ij}\ . \tag{4}$$

By virtue of symmetry, all the vectors—electric fields, dipole moments, and ion displacements—are normal to (0 0 1) surface. We use the convention (+) sign for the outward normal and (–) sign for the normal pointing inwards, into the crystal. Our computation for $\vec{E}_{Ci}$ shows that its value for an ion in the second layer has dropped to 1% of that for a surface ion. Therefore, only the ions on the surface are assumed to have nonzero dipoles.

(ii) In addition to the Coulomb field E_{Ci}, a surface ion experiences a dipole field $\vec{E}_{Di}$ due to all the induced surface dipoles:

$$\vec{E}_{Di}=\sum_j\left(\frac{3(\vec{P}_j\cdot\vec{r}_{ij})\vec{r}_{ij}}{|\vec{r}_{ij}|^5}-\frac{\vec{P}_j}{|\vec{r}_{ij}|^3}\right)\ . \tag{5}$$

Here P_j takes on the value P_+ or P_- depending on whether j is a surface Na^+ or Cl^- ion. The symmetry of a (0 0 1) surface renders the first term in Eq. (5) zero when summed over all surface j's. Therefore, E_{Di} is again parallel to the surface normal.

(iii) With α_+ and α_- as the electron polarizability of Na^+ and Cl^-, respectively, the dipole moments are obtained by solving the coupled implicit equations

$$\begin{aligned}\vec{P}_+ &= \alpha_+(\vec{E}_{C+}+\vec{E}_{D+})\ ,\\ \vec{P}_- &= \alpha_-(\vec{E}_{C-}+\vec{E}_{D-})\ ,\end{aligned} \tag{6}$$

with $\vec{E}_C$ and $\vec{E}_D$ as given in Eqs. (4) and (5), respectively. Using the values $\alpha_+ = 0.312\times10^{-24}\ \mathrm{cm}^{-3}$ and $\alpha_- = 3.06\times10^{-24}\ \mathrm{cm}^{-3}$,[9] we obtain for the perfect undistorted (0 0 1) surface, $P_+ = -0.8640\times10^{-19}$ esu cm and $P_- = 4.2723\times10^{-19}$ esu cm.

The polarization-energy terms of the pair potential has no bulk counterpart, the summation over pairs contribute entirely to S, the surface energy. To sum this part of u_{ij} correctly, one should attach a factor of $\frac{1}{2}$ when both ions of the pair are on the surface and a factor of unity when one ion is on the surface and the other is in the bulk. The surface energy is computed as a function of $\vec{\delta}_+$ and $\vec{\delta}_-$. The surface energy per ion pair is found to drop to a minimum of 4.7918×10^{-14} erg at $\vec{\delta}_+ = -0.064\ (\frac{1}{2}a)$, $\vec{\delta}_- = +0.060(\frac{1}{2}a)$. For reference, the surface energy of the perfect lattice is 17.787×10^{-14} erg/(surface-ion pair), and the bulk cohesive energy is -1.269×10^{-11} erg/(ion pair).

The equilibrium configuration for a NaCl (0 0 1) surface is therefore found to be a buckled surface, with all the Cl^- ions displaced outward and the Na^+ ions displaced inward, resulting in a dipole layer at the surface. The polarization energy is entirely responsible for this buckling. Were the polarization effect absent, the whole surface will relax inward slightly [actual computation shows less than 0.01 $(\frac{1}{2}a)$], which is essentially similar to the result obtained for Ar. With the polarization properly included, the driving forces on Na^+ are the Coulomb and polarization pulling it into the crystal with the repulsive force pushing it out; whereas in Cl$^-$, given the dipole layer at the surface, the Coulomb and the dipole-dipole part of the polarization [fifth term in Eq. (3)] are still the inward force, but the charge-dipole part of the polarization [third and fourth term in Eq. (3)] teams up with the repulsive force to push it out. A detailed understanding of how each of these driving forces works to yield the resultant $\vec{\delta}_+$, $\vec{\delta}_-$ is paramount in understanding the results of the calculation for the NaCl (1 0 11) stepped surface.

The NaCl (1 0 11) surface is shown in Fig. 1(c). The smallest repetitive surface unit is two adjacent parallel rows of 12 ions each; one such row, shown in the figure, has atoms labeled 1–12. Two adjacent rows are needed because Na$^+$ and Cl$^-$ on the corresponding (same label) lattice site on the step displace differently. Minimization of the step surface energy S as a function of the displacement of surface ions yields the desired equilibrium ionic positions of the stepped surface. In principle, this is the same problem as we have solved for the (0 0 1) surface. In practice, however, it is not feasible here to perform an exact calculation as was done for (0 0 1) for the following reasons: (a) Whereas for a (0 0 1) surface only two inequivalent displacement vectors appear—one for Na$^+$ and one for Cl$^-$—for a (1 0 11) surface the number of inequivalent displacement vectors has increased to 24; (ii) due to surface symmetry, the direction of the displacement vectors is completely determined for the (0 0 1) surface, but only restricted to the x-z plane in the (1 0 11). The variational parameters, taking into account only surface ions, increase therefore by a factor of 24. The exact calculation becomes extremely difficult if not impossible. We propose therefore an approximate procedure to bypass the difficulty. The approximations are carefully made, based on the physical insight we have gained in our exact calculation for (0 0 1). The reliability of this approximate procedure is also checked by applying it to the (0 0 1) case and obtaining from it results comparable with those from the exact calculation.

The exact calculation for (0 0 1) indicates that on a Na$^+$, the repulsive force is the only outward driving force that counterbalances all the other inward driving forces: Coulomb and polarization. If we allow only the Na$^+$ displacement to vary while the Cl$^-$ are kept fixed at their sites, we may examine the repulsive contribution U_{rep} and the Coulomb plus polarization contribution U_{att} to the surface energy S. In this case, $U_{\text{att}}(\vec{\delta}_+, \vec{\delta}_- = \text{constant})$ as a function of $\vec{\delta}_+$ turns out to have an essentially constant positive slope in the relevant range of $\vec{\delta}_+$, whereas $U_{\text{rep}}(\vec{\delta}_+, \vec{\delta}_- = \text{constant})$ as a function of $\vec{\delta}_+$ has a negative but quickly varying slope in the relevant range of $\vec{\delta}_+$. Locating the value of $\vec{\delta}_+$ such that

$$\frac{\partial U_{\text{rep}}(\vec{\delta}_+, \vec{\delta}_- = 0)}{\partial \vec{\delta}_+} = - \left. \frac{\partial U_{\text{att}}(\vec{\delta}_+, \vec{\delta}_- = 0)}{\partial \vec{\delta}_+} \right|_{\vec{\delta}_+ = 0} \tag{7}$$

yields the value $\vec{\delta}_+ = -0.07$ $(\frac{1}{2}a)$, remarkably close to the exact result $\vec{\delta}_+ = -0.064$ $(\frac{1}{2}a)$. Therefore, this approximate method of equating slopes of the attractive and repulsive surface energy works well in giving correct Na$^+$ displacement. A similar approach should not work at all for Cl$^-$ since the inward driving forces for Cl$^-$ are the dipole-dipole and Coulomb interaction, the outward driving forces are the hard-core repulsive and the charge-dipole interaction. It turns out that U_{in} and U_{out} have essentially the same slope over a wide range of $\vec{\delta}_-$, which render the balancing of slopes a useless tool to calculate $\vec{\delta}_-$. One would have to locate the actual minimum of the surface energy $U_{\text{in}} + U_{\text{out}}$ to get an accurate $\vec{\delta}_-$.

The procedure for calculating the (1 0 11) stepped surface structure is the following:

(i) Assume all the ions at their perfect-lattice sites.

(a) Compute the Coulomb field E_{Ci} on each surface ion; the largest field is on the corner site labeled 1 in Fig. 1(c). Again to within 2% error, the Coulomb field may be assumed to be zero on all except the 24 surface ions.

(b) Calculate the induced dipoles on the 24 surface ions. Without the benefit of symmetry, Eq. (5) for the dipole field needs to be applied in full and Eq. (6) becomes a set of 24 coupled implicit vector equations. The dipoles are obtained by numerical iterations.

(c) Knowing the dipole moments on all the surface sites, the pair potential u_{ij} in Eq. (3) is summed correctly over pairs to obtain the step surface energy S for the perfect undistorted step.

(ii) Keeping all the surface Cl$^-$ and all but one of the surface Na$^+$ at the perfect lattice sites, we

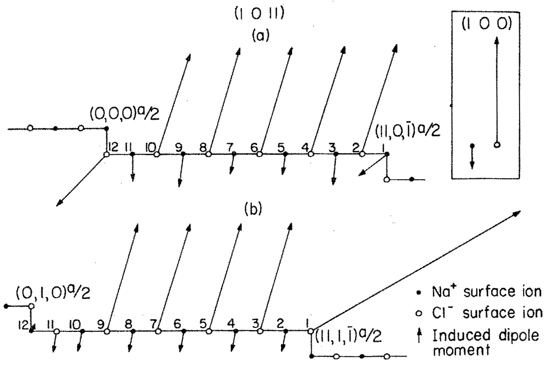

FIG. 2. Induced electric dipoles on the unrelaxed NaCl surfaces: (1 0 11) and (0 0 1).

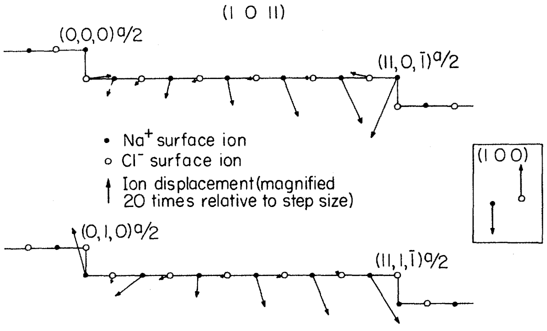

FIG. 3. Displacement of the surface ions in the NaCl surfaces: (1 0 11) and (0 0 1).

allow the Na$^+$ surface ion on site i to displace by $|\vec{\delta}_{+i}| = 0.01(\frac{1}{2}a)$ in different directions defined by θ_+, $\theta = 0°$ being along the inward normal and $\theta = 180°$ along the outward normal of a (0 0 1) surface, θ increases in the counterclockwise direction. Repeat procedures i(a), i(b) for each $\vec{\delta}_+$ and compute the attractive contribution U_{att} to the step surface energy. With the full 360° range at θ_+, the gradient

$$\left.\frac{\partial U_{\text{att}}}{\partial \vec{\delta}_{+i}}\right|_{\{\delta_{+j}\},\{\delta_{-j}\}}$$

is obtained for the Na$^+$ surface ion on each site i.

(iii) Compute the repulsive contribution U_{rep} to the step surface energy as a function of $\vec{\delta}_{+i}$, with the direction of $\vec{\delta}_{+i}$ defined by the direction of the gradient

$$\left.\frac{\partial U_{\text{att}}}{\partial \vec{\delta}_{+i}}\right|_{\{\delta_{+j}\},\{\delta_{-j}\}} .$$

Equilibrium $\vec{\delta}_{+i}$ is obtained by equating the gradient of U_{att} with the gradient of U_{rep}, as carried out for the (0 0 1) surface in Eq. (7).

(iv) Procedures (ii) and (iii) are carried out for each Na$^+$ surface ion on the sites 1–12. In this fashion, the displacements of the Na$^+$ surface ions on every site are calculated.

(v) To obtain the displacements for Cl$^-$ surface ions, we first allowed *all the* Na$^+$ *surface ions* to relax to their equilibrium positions determined in (iv). Now, Cl$^-$ surface ions are displaced, one site at a time. The displacement $\vec{\delta}_{-i}$ is varied both in direction and in magnitude; for each variation, procedures i(a)–i(c) are applied to obtain the step surface energy S. The $\vec{\delta}_{-i}$ for which S is a minimum is the desired result. No approximation is involved at this stage of computation.

Computational procedures (i)–(v) are conceptually clear, physically sound but, computationalwise, rather painstaking. The results are displayed in Figs. 2 and 3 and tabulated in Tables II and III. Figure 2 shows the induced dipoles on the unrelaxed (i.e., every surface ion sitting at the perfect lattice site) stepped surface. The stepped surface is defined by the two adjacent rows of 12 ions each. The insert shows the dipole moments on an unrelaxed (0 0 1) surface, which serves as a reference. Results of Figure 2 are tabulated in Table II. The surface-ion displacements are shown in Fig. 3 and tabulated in Table III. A dipole layer is again formed on the terrace of the stepped surface. The displacements at the corner sites (1 and 12) result in a shrinking of the step height by about 10%. Whereas the Na$^+$ displace essentially inward, the Cl$^-$ on the terrace displace almost parallel to the terrace; therefore,

TABLE II. Induced electric dipoles on the unrelaxed NaCl surfaces: (1 0 11) and (0 0 1).

	Dipole moments on Na$^+$		Dipole moments on Cl$^-$	
Site label [See Fig. 1(c)]	Magnitude $\|P_+\|$ (esu cm) (10^{-19})	Direction θ_+ (deg)	Magnitude $\|P_-\|$ (esu cm) (10^{-19})	Direction θ_- (deg)
1	1.3808	319	9.5469	127
2	0.7514	350	4.4826	163
3	0.7610	351	4.4433	163
4	0.7646	349	4.4295	162
5	0.7658	350	4.4172	163
6	0.7657	350	4.4067	162
7	0.7676	350	4.4094	163
8	0.7661	350	4.3706	163
9	0.7615	349	4.0616	161
10	0.7624	348	4.0616	161
11	0.9867	0	5.8336	186
12	0.2316	172	2.8402	316

For (001), $|P_+| = -0.8640\times10^{-19}$ esu cm, $\theta_+ = 0°$;
$|P_-| = 4.2723\times10^{-19}$ esu cm, $\theta_- = 180°$.

TABLE III. Displacement of surface ions in the NaCl surfaces: (1 0 11) and (0 0 1) in units of the step height $\frac{1}{2}a$,

Site label [See Fig. 1(c)]	Displacement of Na^+ Magitude $\vert\delta_+\vert$	Direction θ_+ (deg)	Displacement of Cl^- Magnitude $\vert\delta_-\vert$	Direction θ_- (deg)
1	0.114	337	0.00	
2	0.100	31	0.03	~255
3	0.088	25	<0.01	
4	0.076	21	0.01	~265
5	0.071	20	0.01	~265
6	0.058	15	0.01	~265
7	0.048	9	0.01	~265
8	0.038	354	0.01	~305
9	0.032	349	0.02	~285
10	0.060	311	0.02	~315
11	0.031	347	0.01	~355
12	0.084	195	0.05	~95

For (001) surface $|\delta_+| = 0.064$, $\theta_+ = 0°$;
$|\delta_-| = 0.060$, $\theta_- = 180°$.

the geometry of the displacements differ strikingly from that of the induced dipoles shown in Fig. 2 (the dipole interaction accounts for this). This calculation is not self-consistent in the sense that the surface ions are not allowed to move *all* together in the process of calculation. The procedure of allowing Na^+ to displace first and then letting the Cl^- to displace in the field of the distorted Na^+ tends to overweigh the displacements on the Na^+. However, one would expect the relative displacement $(\vec{\delta}_{+i} - \vec{\delta}_{-i})$ thus obtained to be not too different from the fully self-consistent result.

IV. CONCLUSION

To investigate the actual positions of atoms on a stepped surface, we deliberately use the two systems—the noble gas solid and an alkali halide—which are simple. They have no polarizable conduction electrons. For the truly simple case Ar, the result is also not very surprising. The surface atoms in the stepped structure essentially remain in the perfect-lattice-site positions. Polarization of electrons must be present to produce any appreciable distortion of the surface. The alkali halides indeed have no conduction electrons, but the ions themselves are polarizable. This polarization effect accounts for the much larger displacements [(5–10%) of the step height]. It also accounts for the buckling on the stepped surface.

Low-energy-electron-diffraction (LEED) data on low-Miller-index surfaces for both an inert gas solid[16] and an alkali halide[17] are available. Laramore and Switendick[17] in their analysis of the LEED intensity profiles for LiF (1 0 0) surface suggested that the top Li^+ and F^- sublayers are separated by about 0.25 Å in a direction normal to the surface. In terms of interlayer spacing $(\frac{1}{2}a)$, 0.25 Å corresponds to 0.124 $(\frac{1}{2}a)$ in LiF, coinciding with our calculated displacements of $-0.064(\frac{1}{2}a)$ for Na^+ and +0.06 for Cl^- in the NaCl (0 0 1) surface. This comparison between LiF and NaCl should of course be only an order-of-magnitude one since the numerical ionic displacements in our calculation are dependent on the electronic polarizabilities on the different ions and the form of repulsive pair potential used; furthermore, the result for LiF from LEED-intensity analysis is only approximate.

From these calculations of two specific examples one gains a feeling as to how atoms in other materials may displace. For example, on a metal-stepped surface where the conduction electrons are polarizable, we would expect surface distortions on the same order of magnitude as those obtained for NaCl: with the atoms on the terrace moving inward by perhaps 5% and the step height shrunk by (5–10%). This is a first theoretical calculation on the stepped surface. A similarly detailed calculation on a transition-metal surface would be required for investigating the catalytic properties of stepped surfaces. Such a calculation is, of course, orders of magnitude more complex than the ones reported here, and would require extensive studies of the effects caused by the itinerant conduction electrons as well as the more localized unfilled *d* shells.

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