**First-Principles Calculations of Surface Energy and Electronic Structure
of LiF, NaCl and MgO (100) Surfaces**

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First-principles calculations of surface energy and electronic structure of LiF, NaCl and MgO (100) surfaces

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Surface energy and electronic structure of LiF, NaCl and MgO (100) surfaces were calculated using the self-consistent-field Discrete Variational (DV) embedded cluster method in the local density approximation (LDA). Clusters of 100-164 atoms embedded in the semi-infinite host lattices were used to achieve the desired convergence. The (100) surface energies of 0.75J/m^2 , 0.47J/m^2 and 1.53J/m^2 calculated for LiF, NaCl, and MgO, respectively, were compared with experimental data and other theoretical values. The surface atoms of LiF and NaCl were found to maintain their bulk ionic characters. The effective charges of MgO surface atoms were found to differ from the bulk atoms. The surface charge density contours were plotted and their corrugation amplitudes were compared with the He-atom diffraction results. The surface partial density of states were compared with optical, photoemission, and electron energy loss spectroscopic results.

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I. INTRODUCTION

The surface structures of the (100) faces of the rocksalt-structure compounds, LiF, NaCl and MgO, have been the subject of numerous theoretical and experimental investigations. The interest of these surfaces is motivated by the theoretical predictions of differential relaxation of the cation and anion sublattice of the surface atomic plane due to their different ionic polarizabilities.[1] The magnitude of the surface differential relaxation in the plane normal direction, or rumple, calculated by the various shell models[2-5] has been the subject of debates for many years. However, there is a general consensus that the anion sublattice moves away from the bulk relative to the cation sublattice if rumpling exists. Subsequently, the static relaxation of the (100) surface of these three compounds was studied by many experimental investigators using low energy electron diffraction (LEED)[6-9] and He-atom scattering techniques[10-17] to check the theoretical predictions. Information about the surface geometry, in the LEED experiments, is obtained from fitting the experimental LEED intensity profiles with the theoretical intensity profiles calculated from shell models[6-9] or from a non self-consistent augmented plane wave (APW) method.[18] In the He-atom scattering experiment, surface geometry and surface bonding information are derived from fitting the measured diffraction beam intensities to the surface corrugation function, which is a replica of the surface valence electron density contours[19], obtained from the hard corrugation surface model.[20-22] According to the LEED and He-atom scattering results, the (100) surfaces of LiF and NaCl are relative flat with no or very small rumpling. On the other hand, the (100) surface of MgO has larger relaxation but the nature of the cation and anion sublattice displacement is uncertain. Results obtained from LEED experiments suggest that the oxygen sublattice on the surface plane moves away from the bulk. But with this geometry of the MgO (100) surface, the total corrugation amplitude obtained from the He-atom

scattering experiment should be larger than that derived from an unrelaxed surface. Instead, the experimental value is about half of the expected value. This discrepancy is still unresolved.

The surface energies of the (100) faces of LiF, NaCl and MgO were calculated as early as 1912 by Born and Stern[23] and subsequently by many investigators [24–28] using empirical methods. First-principles methods have been used, recently, to calculate the surface energy of MgO. Causa *et al.*[29] calculated the (100) surface energy using a self-consistent *ab initio* Hartree-Fock method, without electron correlation, on a slab of MgO and obtained a value of 1.43 J/m² which is only half of that obtained by Gibson *et al.*[30] using the Harris-Foulkas functional method in the local density approximation (LDA) on a free cluster of 27000 atoms. The theoretically calculated surface energies are within a factor of two of the experimental values.[31–34]

Recently, we have extended the self-consistent-field Discrete Variational (DV) embedded cluster method in the LDA to calculate electronic structure and energetics of different α -Al₂O₃ surfaces.[35] In the present study, we have calculated the electronic structure, surface energies and the surface charge density contours of the (100) surfaces of LiF, NaCl and MgO. We have investigated the surface relaxation of these compounds by comparing the calculated surface charge density contours of relaxed and unrelaxed surfaces with the total corrugation amplitudes obtained from He-atom scattering experiments.

The second section of the paper gives a brief description of our method. The third section presents the calculated surface energies and comparisons with experimental measurements and other theoretical values. The effective surface charges and surface charge density contours are presented. The corrugation amplitudes found in the surface charge density contours are compared with experimental He atom diffraction results. The calculated layer by layer surface partial density of states are compared

with optical, photoemission, and electron energy loss spectroscopic results and other band structure calculations. The final section gives our conclusions.

II. THEORETICAL APPROACH

A. Crystal, surface structure and clusters chosen

LiF, NaCl and MgO have the same crystal structure with four molecules in the cubic unit cell.[36] Each cation has six nearest neighbor anions in an octahedral coordination, and vice versa. The (100) surface is characterised by a reduction of the ligand coordination of both cations and anions from six to five: four in the surface plane and one in the plane below.

The (100) surface structure used in the present calculations are assumed to be the unrelaxed ideal bulk termination. A top view of a portion of the (100) surface is shown in Fig. 1. For clarity, only the atoms on the surface layer are shown. Embedded in the semi-infinite surface host lattices, clusters of 100-atoms were found to be large enough to achieve the desired convergence in the surface energy and electronic structure for LiF and NaCl. But a larger cluster of 164-atoms was required for the MgO surfaces. The 100-atoms cluster is made up of top four layers atoms within the dotted square shown in Fig. 1. The MgO cluster consists of the top four layers atoms within the dashed square shown in Fig. 1. The *seed* atoms, which are in the top three atomic layers and within the surface unit mesh area surrounded by the solid lines in Fig. 1, are completely coordinated by the rest of the cluster atoms within the dotted/dashed squares in Fig. 1. The charge densities of *seed* atoms are used to construct the self-consistent two-dimensional periodic surface charge density and potential. The charge densities of the atoms in the remaining infinite number of layers underneath are found to be bulk-like and thus are fixed at the charge densities from the self-consistent bulk calculations. The atoms outside the clusters were treated as *host* atoms, which are the

atoms in the top four layers but outside the dotted/dashed squares in Fig. 1 and all of the atoms underneath the top four layers. Host atoms enter into the formation of the total charge density and potential, but they are not part of the cluster variational space. More details about the choices of the embedded clusters, *seed* and *host* atoms can be found in the previous publication.[37]

B. Formalism for the Semi-infinite Surfaces

A complete discussion of the formalism for the semi-infinite surfaces and applications to the sapphire (0001) and (1 $\bar{1}$ 02) surfaces have been published.[35]. Therefore, only a brief review of the formalism will be given here.

The ground state electronic structure of clusters was obtained using the self-consistent DV method. At the beginning of the self-consistent iteration, charge densities for appropriate cations and anions, which are taken from the bulk calculations, are summed to form the total charge density for the semi-infinite crystal. Coulomb, exchange and correlation potentials are evaluated from the total surface charge density. A simple pseudopotential is added to atomic sites of the host to represent the Pauli principle exclusion of cluster electrons from the host core region. Here the host is everything not explicitly contained in the variational cluster. Cluster wavefunctions and energy eigenvalues are next found by the variational solution of the local density Schrödinger equation, using a basis set constructed from numerical atomic-like wavefunctions. The cluster eigenstates are populated according to Fermi-Dirac statistics to obtain the cluster charge density. The cluster charge density is decomposed according to a scheme similar to the Mulliken population analysis to determine the effective atomic configurations which are then spherically averaged. The iteration loop is closed by summing *seed atom* charge densities to produce a new surface charge density estimate and the iteration is continued until the orbital populations are converged to

$10^{-4}e$ in the present calculations. This procedure is called the self-consistent-charge approximation to the potential. The embedding potential for the ionic host lattice is obtained by the Ewald summation of the long-range Coulomb terms, plus a direct summation over 200-500 nearby atoms of residual Coulomb potentials and charge densities obtained by self-consistent iterations.

The total energy is calculated in the spin-restricted LDA as[38].

$$E_t(\rho) = \sum_i \epsilon_i n_i + \int \rho \left(-\frac{1}{2} V_e - V_{xc} + E_{xc} \right) d^3r + \frac{1}{2} \sum' \frac{Z_\mu Z_\nu}{R_{\mu\nu}} \quad (1)$$

where i labels single-particle functions with eigenvalue ϵ_i and occupation n_i , ρ is total charge density, V_e the Coulomb potential due to the electrons, V_{xc} the exchange-correlation potential and E_{xc} is the corresponding energy density per electron. The above total energy can be expressed in terms of the energy density as

$$E_t(\rho) = \int e(\vec{r}) d^3r + \frac{1}{2} \sum' \frac{Z_\mu Z_\nu}{R_{\mu\nu}} \quad (2)$$

by rewriting the first term in Eq.(1) as

$$\sum_i \epsilon_i n_i = \int \left(\sum_i \epsilon_i n_i |\Psi_i|^2 \right) d^3r \quad (3)$$

where Ψ_i is the normalized wavefunction. The essential assumption of our embedded cluster method is that the energy density of a crystal over a *finite* volume (e.g. unit cell) can be well approximated by using the eigenvalues and wavefunctions of the embedded clusters of *finite* sizes. Previous calculations on sapphire surfaces[35] and the present work supported this assumption. This provides us an efficient way to calculate the total energies associated with *finite* volumes such as the cohesive energy and the surface energy. The total energies calculated in this fashion are of order of 10^5 eV/atom, and it is very difficult and expensive to obtain enough precision for direct comparison of energy differences. However, it is possible to extract a much more precise binding energy with respect to some reference system energy over the same

volume with the same sampling grid with the atoms in the same position but now assumed to be non-interacting. In addition, a high precision adaptive integration scheme[39] was developed and used in the volume integration of the energy density. In this way, cohesive energy values are obtained to better than 5 meV/atom.

III. RESULTS AND DISCUSSION

A. Surface energy

The surface energy of a solid is one of its most fundamental properties. There is still a dearth of experimental values for the surface energy, because many difficulties are associated with measuring it. In the theoretical calculations, the total energy $E(\Omega)$ over a given volume Ω is calculated using a procedure described in the previous section. For surface calculations, the basal area of the volume Ω was chosen to be the surface unit mesh, and its height was chosen from the bottom of the third atomic layer below the surface, where charge and energy have already converged to the bulk value, up to infinite distance above the surface. The surface energy E_s is calculated as $E_s = E(\Omega) - E(bulk)$. $E(bulk)$ is the total energy calculated over the volume of several unit cells which contain the same number of nuclei and electrons as in the volume Ω .

Listed in Table I are calculated and measured surface energies for LiF, NaCl and MgO (100) surfaces. From Table I, we see that the calculated surface energy values obtained from different empirical methods vary by a factor of two for LiF and NaCl, and about 24% for MgO. Our calculated surface energies are 120%, 50%, 28% larger than the average experimental values for LiF, NaCl, and MgO (100), respectively. These discrepancies include both experimental and theoretical errors. The overestimation in our present first-principle theoretical calculations may arise from the unoptimized surface structure and the LDA approximation. It is known that

the surface energies are difficult to measure and depend sensitively on the measuring techniques and the sample quality. From Table I, we see that the value obtained by Gibson *et al.*[30] using the LDA Harris-Foulkes functional on a free cluster of 27000 atoms is larger by a factor of two than the value obtained by Causa *et al.*[29] using the self-consistent *ab initio* Hartee-Fock method without correlation on a three layers thick slab. Our calculated MgO (100) surface energy is much smaller than the value obtained by Gibson *et al.* but a little larger than the value of Causa *et al.*

B. Surface charge density

The Mulliken atomic configurations of atoms in the top two surface layers of the LiF and NaCl (100) surfaces are found to differ by $10^{-3}e$ from the corresponding bulk values. The atoms in the third layer are bulk-like. The Mulliken atomic configuration from the bulk calculations are Li $2s^{0.005}2p^{0.008}$ and F $2s^{2.000}2p^{5.987}$ for LiF, and Na $3s^{0.035}3p^{0.015}3d^{0.004}$ and Cl $3s^{1.990}3p^{5.956}$ for NaCl. However, for MgO (100) the Mulliken atomic configurations of atoms in the top two layers show some deviations from the bulk as listed in Table II. There is $0.05e$ charge transfer from the second layer into the surface layer. The enhancement of the effective charges of the surface Mg and O atoms relative to the bulk as shown in Table II was also suggested by Martin and Bilz through fitting data from empirical models with experiments.[5] The atoms in the third layer are bulk-like in terms of their effective atomic configurations.

Shown in Figs. 2-4 are the (100) surface electron density contours on the (010) cutting planes for LiF, NaCl, and MgO, respectively. The contour diagrams shown are typical of the highly ionic materials. For LiF and NaCl, we see no noticeable changes in the shapes of the charge density in the bonding regions for atoms at the top three surface layers. This indicates that the surface atoms maintain their bulk ionic bonding nature. For MgO, we notice some changes of density contours in the

top two surface layers.

The LiF, NaCl, and MgO (100) surfaces have been investigated with He atom diffraction.[12-17] The coherent elastic scattering intensities were used to reconstruct the surface corrugation function of the simple sinusoidal forms.[11, 14-17] The total corrugation amplitudes were found[11] to be 0.61Å for LiF, ~ 0.68 Å for NaCl. Values of 0.36Å[14, 17], 0.46 ± 0.02 Å[15], and 0.47 ± 0.02 Å[16] were reported for MgO. It was shown that the repulsive part of the He-surface interaction is given by an almost linear, surface-independent function of the surface electron density at the He site.[19] Using the linear relationship of Ejsberg-Nørskov[19], the classical turning points of the He atoms occur on charge density contours at $2.7 \times 10^{-5} e/a_0^3$ and $8.5 \times 10^{-5} e/a_0^3$ for 20 meV and 64 meV He energies. The total corrugation amplitudes of the 7-th contour line with a value of $6.4 \times 10^{-5} e/a_0^3$, as shown in Figs. 2-4, are 1.168 a.u. (0.62Å), 1.089 a.u. (0.58Å), and 1.485 a.u. (0.79Å) for LiF, NaCl, and MgO, respectively. The 0.62Å value for LiF agrees well with the 0.61Å value deduced from the experiment. The 0.58Å value for NaCl is smaller than ~ 0.68 Å from the experiment. This discrepancy may arise from the sinusoidal form of a hard wall potential used in deducing the amplitude from the experimental scattering intensity. The contours for NaCl, as shown in Fig. 3, are much different from the sinusoidal form. In summary, the experimental He-atom diffraction results on LiF and NaCl (100) agree well with the present calculations without introducing the surface rumple. The MgO amplitude of 1.485 a.u. (0.79Å) at the unrelaxed geometry is much larger than 0.36-0.47Å deduced from the experiments. Recent low-energy electron diffraction (LEED) experiments found $1 \pm 2\%$ relaxation and $5 \pm 2.5\%$ rumple on the MgO (100) surface.[9] To see the effect of surface rumple or relaxation on the amplitude, we have performed a series of calculations of the surface charge density contours at the different surface atomic geometries. We found that the differential relaxation, or rumpling, of the surface

Mg and O atoms has a major effect on the amplitudes of the surface charge density contours while the uniform relaxation of surface Mg and O atoms has little effect. We found that the rumplings with O atoms moving up into the vacuum relative to the Mg atoms, as suggested by all empirical model calculations, result in larger amplitudes than the unrelaxed geometry. For example, the 1% rumpling ($\Delta=0.02\text{\AA}$) gives an amplitude of 1.644 a.u. ($0.87\text{\AA}$). On the other hand, a 5% rumpling ($\Delta=-0.11\text{\AA}$) with Mg atoms moving up into the vacuum relative to the O atoms results in a smaller amplitude of 0.945 a.u. ($0.50\text{\AA}$) in better agreement with the H-atom diffraction data. More experimental and theoretical work is needed to resolve the surface atomic geometry of the MgO (100) surface.

C. Surface density of states

Shown in Figs. 5-7 are layer by layer anion and cation partial density of states (PDOS) for the top three surface atomic layers of the (100) surface of LiF, NaCl, and MgO, respectively. The PDOS are normalized to one molecular formula unit per unit mesh area and convoluted by a Lorentzian function of 0.5 eV full width at half maximum height. The zero of energy for all curves is the vacuum level, which is defined as the potential value far above the surface.

The shape of the Li and the F PDOS from the second and third surface atomic layers shown at the top of Fig. 5 have already converged to the bulk PDOS. The lower valence band (F $2s$) at -27 eV has 1.0 eV width, the upper valence band (F $2p$) around -9 eV has 3.0 eV width, and their separation is 15.8 eV. These values compared well with the corresponding 0.9 eV, 3.0 eV, and 15.7 eV values found from the self-consistent local density bulk band structure calculations of Zunger and Freeman.[40] The 10.9 eV energy gap was obtained between the occupied valence band and unoccupied conduction band shown in Fig. 5. It is larger than the 9.8 eV gap

calculated by Zunger and Freeman[40] but smaller than the 14.2 eV gap derived from thermorefectance experiments.[41] Due to the localized nature of the cluster orbitals, the energy gaps from the LD embedded cluster method are generally found to be larger than those obtained from the band structure calculations. The errors in the calculated LD energy gap are known to come from the self-interaction errors in the LDA.[42, 43]

Comparing the F 2*p* band of the surface layer with those from the layers underneath, we see that its width is 0.5 eV narrower and the main peak shifts 0.3 eV upward. This upward relative shift may explain the 3.5 eV total width of the F 2*p* band found in recent photoemission experiments on LiF (100),[44] which is larger than the 3.0 eV obtained by the LDA bulk calculations.[40]

The shape of the Na and the Cl PDOS from the second and third surface atomic layers, shown at the top of Fig. 6, converges to the bulk PDOS. The 2.3 eV width of the upper valence band (Cl 3*p*) around -6.5 eV compares well with the 2.0 eV value obtained from the self-consistent LDA bulk band structure calculations[45] and the experimental photoemission value of 3.0 ± 0.3 eV.[46] The 7.8 eV energy gap found in Fig. 6 is larger than the 5.5 eV gap from the LDA band structure calculations[45] and smaller than the experimental gap of 9.0 eV.[47] A gap of 9.5 eV was found[43] when the self-interaction correction was included in the LDA calculations. Comparing the Cl 3*p* band of the surface layer with those from the layers underneath, we see that its width is 0.3 eV narrower and the main peak shifts less than 0.1 eV.

The shape of the Mg and the O PDOS from the third surface atomic layers, shown at the top of Fig. 7, converges to the bulk PDOS. The 3.6 eV width of the upper valence band (O 2*p*) around -12.5 eV is narrower than the LDA band structure values of 4.8 eV[48, 49] and 5.5 eV[50]. The experimental values are 5-6 eV[51] and 6.5 eV[52] from x-ray photoelectron spectroscopy (XPS), and 4.8 ± 0.3 eV[53] from

ultraviolet photoelectron spectroscopy (UPS). Unlike the LiF and NaCl but similar to our α - Al_2O_3 results[37,35], the 9.4 eV energy gap found in Fig. 7 is about twice the LDA band structure values of 4.5 eV[48,49] and 4.2 eV[50], and is 1.6 eV larger than the experimental gap of 7.8 eV.[54] This implies that the self-interaction errors in our LDA embedded cluster methods have different magnitudes for oxides and halides.

From Fig. 7, we see that the PDOS of the top two surface layers differs from the bulk-like PDOS of the third layer. The main peak of the occupied O 2*p* valence band from the top surface layer was found to be 2 eV above the bulk valence band maximum. Electron transitions from these surface states into the unoccupied conduction band can explain the ~ 6 eV energy loss feature observed on the MgO (100) surfaces.[55] Tsukada, Adachi and Satoko[56] have used a free cluster of $(\text{MgO}_5)^{8-}$ to model the MgO (100) surfaces. They assigned the ~ 6 eV energy loss feature to transitions from valence states into an unoccupied surface state ($11a_1$) at 2 eV below the lowest conduction states. This unoccupied surface state is absent in our embedded cluster calculations.

IV. CONCLUSIONS

As shown in our previous work on sapphire surfaces, the first-principles discrete variational embedded cluster method can provide surface energy, surface charge density and surface density of states in reasonable agreement with experiments. By comparing the corrugation amplitudes of the surface charge density contours calculated at different surface geometry with the data obtained from He-atom diffraction experiments, information about the surface rumpling can be obtained. Based on this comparison, LiF and NaCl (100) surfaces show no more than 1% rumple, the MgO (100) surface may have a 5% rumple with surface Mg atoms moving up into the vacuum relative to the O atoms.

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TABLES

TABLE I. Comparison of theoretical and experimental surface energies (J/m²) for LiF, NaCl and MgO (100) surfaces.

Method	LiF	NaCl	MgO
<i>First-principles method</i>			
Present work	0.75	0.47	1.53
Gibson <i>et al.</i> ^a			2.64
Causa <i>et al.</i> ^b			1.43
<i>Empirical method</i>			
Born, Stern ^c	0.42	0.15	1.44
Glauberma ^d	0.36	0.13	1.23
Lennard-Jones, Taylor ^e		0.10	1.36
Shuttleworth ^f	0.19	0.16	
Van Zeggeren, Benson ^f	0.17	0.19	
Tasker, Duffy ^g			1.16
<i>Experimental</i>			
Gilman ^h	0.34		1.20
Kusnetsov, Teterin ⁱ		0.30	
Benson <i>et al.</i> ^j		0.28	
Hutchinson, Manchester ^j		0.37	

^a Harris-Foulkes functional cluster method.[30]

^b *Ab initio* Hartree-Fock slab method.[29]

^c Simplest atomistic theory.[23]

^d Same as Bron and Stern, but allows surface contractions.[25]

- ^e Using somewhat different potential energy equations.[24]
^f Using the complete Born-Mayer potential equation.[26, 27]
^g Static lattice shell model.[28]
^h Using cleavage method.[31]
ⁱ Using impact cleavage method.[32]
^j Using heat of solution method.[33, 34]

TABLE II. The Mulliken orbital populations and charges for the top 3 atomic layers of the MgO (100) surface and for the bulk MgO.

Layer height (a.u.)	Atom Type	Orbital Population (e)	Charge (e)
0.00	Mg	$3s^{0.02}3p^{0.01}3d^{0.02}$	1.95
	O	$2s^{2.00}2p^{6.00}$	-2.00
			-0.05
-3.98	Mg	$3s^{0.04}3p^{0.03}3d^{0.02}$	1.92
	O	$2s^{2.00}2p^{5.87}$	-1.87
			0.05
-7.96	Mg	$3s^{0.03}3p^{0.02}3d^{0.01}$	1.94
	O	$2s^{2.00}2p^{5.94}$	-1.94
			0.00
Bulk	Mg	$3s^{0.03}3p^{0.02}3d^{0.01}$	1.94
	O	$2s^{2.00}2p^{5.94}$	-1.94

FIGURES

FIG. 1. The top view of the surface atomic layer of a (100) surface. The unit mesh area is the square enclosed by the solid lines. The dotted square is the lateral boundary of the 100-atoms embedded clusters for LiF and NaCl (100). The larger dashed square is for MgO (100).

FIG. 2. LiF (100) surface charge density contours on the (010) cutting plane. The minimum and maximum contours are $10^{-6}e/a_0^3$ and $0.1e/a_0^3$, and successive contours differ by a factor of two.

FIG. 3. NaCl (100) surface charge density contours on the (010) cutting plane. Same conventions as Fig. 2.

FIG. 4. MgO (100) surface charge density contours on the (010) cutting plane. Same conventions as Fig. 2.

FIG. 5. Li $2s2p$ (dashed curve) and F $2s2p$ (solid curve) partial density of states of the top three atomic layers in the LiF (100) surface. Curves are shifted upwards for a clear view. The vertical dashed line separates the occupied states in the left-hand side from the unoccupied states in the right hand side. The zero of energy scale for all curves is the vacuum level.

FIG. 6. Na $3s3p3d$ (dashed curve) and Cl $3s3p$ (solid curve) partial density of states of the top three atomic layers in the (100) NaCl surface. Same conventions as Fig. 5.

FIG. 7. Mg $3s3p3d$ (dashed curve) and O $2s2p$ (solid curve) partial density of states of the top three atomic layers in the MgO (100) surface. Same conventions as Fig. 5.

Fig. 1 /J. GUO

Fig. 2 /J. GUO

Fig. 3 /J. GUO

Fig. 4 /J. GUO

Fig. 5/J. GUO

Fig. 6/J. GUO

Fig. 7/J. GUO