

Origin of contrasting surface core-level shifts at the Be(10 $\bar{1}0$) and Mg(10 $\bar{1}0$) surfaces

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As expected, very similar oscillatory multilayer relaxations exist at the (10 $\bar{1}0$) surfaces of the isoelectronic Be and Mg. But surprisingly, these two systems exhibit drastically different behaviors in the surface core-level shift (SCLS). For Be, our density-functional theory calculations show that the SCLS persists down to the fifth layer, and depends strongly on lattice relaxation and final-state effect. In contrast, for Mg only the atoms in the first layer have a small and insensitive SCLS. The physical origin of the disparate features in the SCLS can be traced to the different bonding natures of the two elements in bulk form: strongly covalentlike for Be, and nearly free-electron-like for Mg.

X-ray photoemission spectroscopy (XPS) provides useful information about the chemical environment of surface atoms by measuring core-level binding energies. Recently, high-resolution XPS techniques have been developed and widely used in determining surface core-level shifts (SCLS) at various semiconductor and metal surfaces.¹ Moreover, recent *ab initio* calculations^{2,3} of SCLS including both initial- and final-state effects have reached the level of accuracy needed for direct quantitative comparison with experiments. These advances not only make measurement of SCLS an increasingly important and reliable means for surface analysis, but also offer new opportunities for revealing the fundamental interactions involved at surfaces.

The SCLS for beryllium surfaces have recently drawn much attention in connection with their interesting surface relaxations.⁴⁻¹⁰ In Be(0001)⁴ the top three interlayer spacings undergo large expansions, which cannot be observed in other simple metals. These anomalous lattice relaxations stimulated a XPS study⁵ where three large SCLS peaks originating from the expanded surface layers were successfully resolved. For Be(10 $\bar{1}0$) showing an oscillatory multilayer relaxation,⁹ several SCLS peaks from the deeper layers were predicted in a recent *ab initio* calculation and observed experimentally by XPS.¹⁰ As an isoelectronic system, Mg surfaces have been reported to show similar surface structures as the corresponding Be surfaces: i.e., the first interlayer spacing of Mg(0001) expands,¹¹ and Mg(10 $\bar{1}0$) shows an oscillatory multilayer relaxation.^{12,13} These similarities in lattice relaxation at the (10 $\bar{1}0$) surfaces of Be and Mg suggest that the corresponding SCLS might also exhibit similar behaviors.

In this letter, we present the results of *ab initio* calculations of the SCLS at the Be(10 $\bar{1}0$) and Mg(10 $\bar{1}0$) surfaces. Although both surfaces have similar oscillatory multilayer relaxations, their SCLS are quite different: The SCLS at

Be(10 $\bar{1}0$) persists down to the fifth layer; in contrast, Mg(10 $\bar{1}0$) reveals only one SCLS coming from the first-layer atoms. In addition, the final-state effect on the SCLS, which has an essential role in Be(10 $\bar{1}0$), is negligible for Mg(10 $\bar{1}0$). Our surface electronic analysis explains these contrasts by revealing that Be(10 $\bar{1}0$) and Mg(10 $\bar{1}0$) behave quite differently both in the charge redistribution at the surfaces and in the screening of surface core holes, the origin of which can further be traced to the known difference in bonding nature of bulk Be and Mg.

In our study, we employ the plane-wave-basis pseudopotential method within the local-density approximation.¹⁴ Nonlocal pseudopotentials are generated by the scheme of Troullier and Martins¹⁵ in the separable form of Kleinman and Bylander.¹⁶ We use the Ceperley-Alder exchange-correlation functional,¹⁷ as parametrized by Perdew and Zunger,¹⁸ and a plane-wave basis with a kinetic-energy cutoff of 20 Ry. Both Be(10 $\bar{1}0$) and Mg(10 $\bar{1}0$) surfaces are modeled by using periodic slab geometries consisting of 18 atomic layers and a vacuum spacing of about 11 Å. The \mathbf{k} -space integration is carried out with 96 points in the surface Brillouin zone. The SCLS is calculated using initial- and final-state theories. The initial-state SCLS is defined by the difference of the eigenvalues of a given core level at different sites. Here this shift is calculated from the expectation value of the self-consistent electrostatic potential on the 1s and 2p atomic orbital for Be and Mg, respectively. Generally the initial-state theory that neglects screening of the core hole has predicted unsatisfactorily the photoemission peaks.^{2,19} The final-state SCLS is given by the total-energy difference of the crystals containing a core hole at the different substitution sites, and is equal to the initial-state shift plus a correction due to screening of the core hole.^{2,3} In order to simulate the presence of a photon-induced core hole in the

TABLE I. Calculated multilayer relaxations for Be(10 $\bar{1}$ 0) and Mg(10 $\bar{1}$ 0) in comparison with experiments. The values are given by the change of the interlayer spacing (%) relative to the corresponding bulk interlayer spacing (Ref. 20). Here, the negative (positive) sign indicates a contraction (expansion) of the interlayer spacing relative to the bulk one.

| | Δd_{12} | Δd_{23} | Δd_{34} | Δd_{45} | Δd_{56} |
|------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Be(10 $\bar{1}$ 0) | | | | | |
| Present theory | -18.8 | +4.0 | -11.4 | +4.1 | -4.4 |
| Previous theory ^a | -20 | +4.4 | -13 | +3.8 | - |
| Experiment ^a | -25 | +5.0 | -11 | +2 | - |
| Mg(10 $\bar{1}$ 0) | | | | | |
| Present theory | -14.7 | +7.1 | -7.6 | +1.6 | -4.7 |
| Experiment ^b | -14.5 | +6.5 | -7.5 | +3.0 | -5.0 |

^aReference 9.

^bReference 13.

Be atom, we generate the atomic pseudopotentials with a screened $1s$ core hole from the excited atomic configuration of $1s^1 2s^2 2p^1$; similarly, for Mg we generate the atomic pseudopotentials with a screened $2p$ core hole from the excited atomic configuration of $2p^3 3s^2 3p^1$. For the final-state calculation we use a (2×2) unit cell to make negligible the interactions between the core holes in neighboring cells.

The surface relaxations are calculated by the changes in the interlayer spacing (d_{ij}) between layers i and j , relative to the bulk interlayer spacing. Our results for Be(10 $\bar{1}$ 0) and Mg(10 $\bar{1}$ 0) are compared with the previous theoretical and experimental results^{9,13} in Table I. For both surfaces we find the oscillatory multilayer relaxations down to the sixth layer. It is notable that the present theoretical values for the relaxations are in good agreement with the low-energy electron diffraction I - V analysis data (see Table I).

We calculate the SCLS at Be(10 $\bar{1}$ 0) and Mg(10 $\bar{1}$ 0) using initial- and final-state theories. Our results for both surfaces are given in Table II, in comparison with the previous theoretical and experimental results.¹⁰ For Be(10 $\bar{1}$ 0) our SCLS persists down to the fifth layer, and their values, if the numerical uncertainty of the SCLS calculations were taken into

account,²¹ agree well with the previous theoretical ones.¹⁰ Especially, our final-state SCLS for the first-, second-, and third-layer atoms are in excellent agreement with the experimental measurements.¹⁰ The final-state effect due to the screening of the core hole is reflected by the difference between the initial- and final-state SCLS, given by $\Delta S_1 = -0.55$, $\Delta S_2 = -0.16$, $\Delta S_3 = -0.13$, $\Delta S_4 = +0.01$, and $\Delta S_5 = -0.02$ eV. Therefore, the final-state effect is significant down to the third layer. For Mg(10 $\bar{1}$ 0) our initial-state theory finds only one SCLS for the first-layer atoms ($S_1 = +0.28$ eV). The shift for the second-layer atoms ($S_2 = +0.07$ eV) would be within the numerical uncertainty of the bulk core-level. Final-state theory gives $S_1 = +0.20$ and $S_2 = +0.06$ eV. Thus, the final-state effect exists only in the first-layer atoms with $\Delta S_1 = -0.08$ eV. We note that the range and magnitude of the final-state effect in Mg(10 $\bar{1}$ 0) are much smaller than those in Be(10 $\bar{1}$ 0).

To understand the different behaviors in the SCLS at Be(10 $\bar{1}$ 0) and Mg(10 $\bar{1}$ 0), we have analyzed the charge redistribution due to surface formation. Figures 1(a) and 1(b) show the one-dimensional (1D) charge density profiles for the bulk-truncated surface ($\rho_{\text{bulk-tr}}$, the dashed line) and the

TABLE II. Calculated initial-state and final-state SCLS (eV) at the relaxed Be(10 $\bar{1}$ 0) and Mg(10 $\bar{1}$ 0) surfaces, in comparison with previous theory and experiment. Initial-state SCLS for the bulk-truncated Be(10 $\bar{1}$ 0) and Mg(10 $\bar{1}$ 0) surfaces are also given in parentheses. Here, the negative (positive) sign indicates a lower (higher) binding energy shift.

| | S_1 | S_2 | S_3 | S_4 | S_5 |
|-------------------------|------------------|------------------|------------------|------------------|------------------|
| Be(10 $\bar{1}$ 0) | | | | | |
| Initial | +0.04 (+0.21) | -0.62 (-0.51) | -0.15 (-0.09) | -0.17 (-0.17) | -0.12 (-0.11) |
| Final | -0.51 | -0.78 | -0.28 | -0.16 | -0.14 |
| Initial ^a | 0.00 | -0.59 | -0.11 | -0.11 | +0.01 |
| Final ^a | -0.57 | -0.80 | -0.39 | -0.19 | -0.18 |
| Experiment ^a | -0.50 | -0.71 | -0.24 | | |
| Mg(10 $\bar{1}$ 0) | | | | | |
| Initial | +0.28 (+0.31) | +0.07 (+0.06) | +0.02 (+0.02) | 0.00 (0.00) | -0.03 (-0.02) |
| Final | +0.20 | +0.06 | +0.01 | | |

^aReference 10.

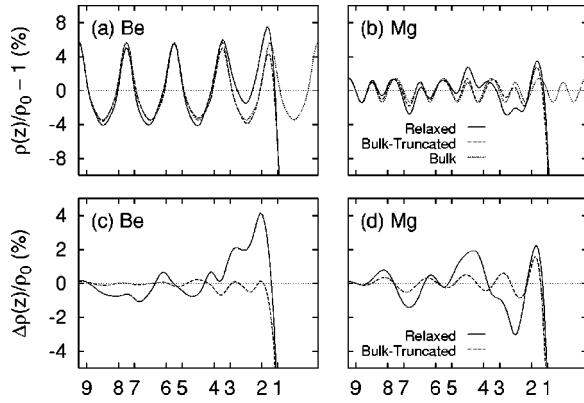


FIG. 1. One-dimensional charge density profiles for the bulk-truncated and relaxed Be($10\bar{1}0$) (a) and Mg($10\bar{1}0$) (b), and change of charge density, relative to the bulk crystal, at the bulk-truncated and relaxed Be($10\bar{1}0$) (c) and Mg($10\bar{1}0$) (d). For comparison, the bulk charge density is shown by the dotted line.

relaxed surface (ρ_{relax} , the solid line), obtained by averaging the charge density parallel to the surface. When compared to the bulk charge density shown by the dotted line in Figs. 1(a) and 1(b), we find quite different behaviors in charge redistribution between Be($10\bar{1}0$) and Mg($10\bar{1}0$) [see Figs. 1(c) and 1(d)]. First, unlike in Mg($10\bar{1}0$), where the electron density variation $\Delta\rho_{\text{bulk-tr}}$ is significant and follows the Friedel oscillations, these oscillations are faint in Be($10\bar{1}0$). Second, the charge response to lattice relaxations in Be($10\bar{1}0$) is “stiffer” than in Mg($10\bar{1}0$) where the difference between $\Delta\rho_{\text{bulk-tr}}$ and $\Delta\rho_{\text{relax}}$ is relatively very small. These results reflect the distinct characters of valence electrons in Be($10\bar{1}0$) and Mg($10\bar{1}0$) as *covalentlike* and *free-electronlike*, respectively, because (i) the Friedel oscillations at metal surfaces are typical for the free-electron-like system,^{12,22,23} and (ii) a large accumulation of electrons near the surface region during relaxation is a sign of the covalent-like system.²⁴ As evidenced in the bulk region in Fig. 2, Be has directional bonding (i.e., strong p_z bonding) along the $[0001]$ direction, while Mg has isotropic bonding.²⁵ As a result, we

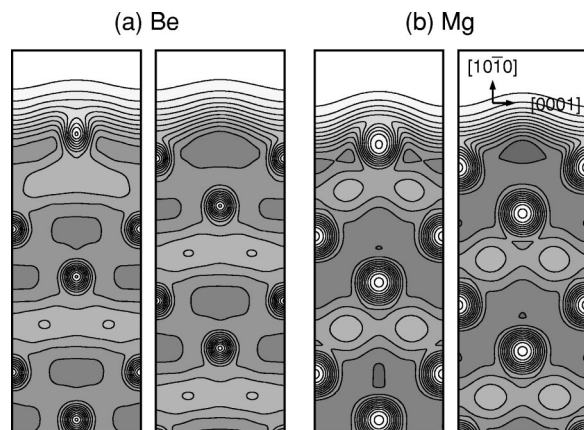


FIG. 2. Contour plots of the charge density for bulk-truncated Be($10\bar{1}0$) (a) and Mg($10\bar{1}0$) (b). The plots are drawn in two vertical planes containing the first-fourth and second-third layer atoms, respectively. Contour spacings are 10% of bulk density.

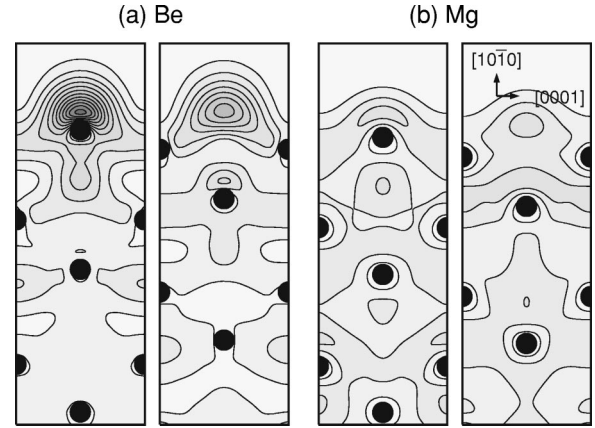


FIG. 3. Contour plots of the charge density of empty states right above the Fermi level for Be($10\bar{1}0$) (a) and Mg($10\bar{1}0$) (b). The energy window is taken such that the total charge is equal to one hole per 1×1 unit cell. The cuts are the same as in Fig. 2. Contour spacings are 2.5% of bulk density. The atomic positions are indicated by filled circles.

obtain the contrasting 1D charge density profiles along the $[10\bar{1}0]$ direction: In bulk Be, the density corrugation is significant by about 4.5% of the average bulk density $\rho_0 = 2.582 \times 10^{-1} e/\text{\AA}^3$ and a high density peak exists only in the short interlayer spacing [Fig. 1(a)], whereas in bulk Mg the density corrugation is small by about 1.5% of $\rho_0 = 9.345 \times 10^{-2} e/\text{\AA}^3$ and the two high density peaks are located in both the long and short interlayer spacings [Fig. 1(b)]. We expect that the SCLS in most cases well reflect the nature of chemical bondings at the surface. Therefore, for Be($10\bar{1}0$), whose covalent-like electrons are stiff to the screening of the surface formation, the SCLS persist down to the deeper layers. In contrast, for Mg($10\bar{1}0$), whose free-electron-like electrons screen very efficiently the surface formation, only one SCLS exists for the first-layer atoms.

The different behaviors of the final-state effect between Be($10\bar{1}0$) and Mg($10\bar{1}0$) can be explained by examining the charge density character of the screening electrons. As the core hole is assumed to be completely screened, an extra valence electron per core hole is added to the slab in order to maintain charge neutrality. In this completely static screening, the screening charge of the core hole consists mainly of the empty states of the $2p$ (for Be) and $3p$ (for Mg) orbitals.^{2,3,6} In Fig. 3, we plot the charge density of the empty states right above the Fermi level, which shows that the screening charge in Be($10\bar{1}0$) are mostly localized around the first-layer atom, whereas in Mg($10\bar{1}0$) it is well distributed around both surface and bulk regions. Hence, when a core hole is created, the final-state screening in Be($10\bar{1}0$) is significant in the surface layer atoms, but is minimal for Mg($10\bar{1}0$), consistent with our results for the final-state effect presented above.

From the comparison of the initial-state SCLS between the bulk-truncated and relaxed surfaces, we find that in Be($10\bar{1}0$) the lattice relaxation influences significantly the SCLS up to the top three layer atoms, whereas in Mg($10\bar{1}0$) the SCLS is hardly changed upon relaxation (see Table II).

This difference between Be(10 $\bar{1}0$) and Mg(10 $\bar{1}0$) is consistent with the difference in charge redistribution near the surface after relaxation, i.e., large charge accumulation in Be(10 $\bar{1}0$) and small charge variation in Mg(10 $\bar{1}0$) [see Fig. 1(c) and 1(d)]. It has been reported that the SCLS at Be(0001) changes little with relaxation.^{6,8} Therefore, the correlation between relaxation and SCLS in Be(0001) is much more similar to that in Mg(10 $\bar{1}0$) than Be(10 $\bar{1}0$). This is also consistent with the observation that at Be(0001) the valence electrons behave more free-electron-like.²⁶ In this sense, Be surfaces would maintain the different bonding characters with respect to the crystallographic orientation, i.e., covalentlike at the (10 $\bar{1}0$) surface and free-electron-like at the (0001) surface.²⁷ We believe that this is possibly due to the fact that in Be(10 $\bar{1}0$) the strong p_z bonding is kept parallel to the surface, while in Be(0001) it is broken by the surface formation.

In summary, our initial- and final-state theories predict large different behaviors in the surface core-level shifts at the

Be(10 $\bar{1}0$) and Mg(10 $\bar{1}0$) surfaces. This difference is caused by the different charge redistributions upon the surface formation and the different screening effect of the core hole. It is remarkable that the charge redistribution at the bulk-truncated surface, the charge response to lattice relaxations, and the charge density of the screening electrons all show disparate features between these two isoelectronic systems. These differences have been shown to result from the different bonding characteristics of bulk Be and Mg.

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²⁰The two different bulk interlayer spacings in Be(10 $\bar{1}0$) and Mg(10 $\bar{1}0$) are given as $d_{12}=d_{34}=d_{56}=0.651$ and 0.902 Å, and $d_{23}=d_{45}=1.302$ and 1.804 Å, respectively.

²¹The employed plane-wave-basis cutoff, \mathbf{k} points, and slab thickness yield well-converged results for the surface relaxations, hardly affecting the initial-state SCLS (within ± 0.02 eV). For the final-state SCLS an error of less than ± 0.05 eV is estimated from a large unit-cell calculation of (3×2) .

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²⁷Such different bonding characters between Be(10 $\bar{1}0$) and Be(0001) are consistent with the conclusion from the electron energy loss spectroscopy data of the surface phonon dispersions of both surfaces, i.e., the bonding at Be(10 $\bar{1}0$) is more complicated than the free-electron-like bonding at Be(0001). See J.B. Hannon, E.J. Mele, and E.W. Plummer, *Phys. Rev. B* **53**, 2090 (1996); Ph. Hofmann and E.W. Plummer, *Surf. Sci.* **377**, 330 (1997).