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Surface states at close-packed surfaces of simple metals

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Angle-resolved photoemission spectra from close-packed surfaces of thin epitaxial films of the earth-alkali metals Mg, Ca, and Sr on W(110) are reported. While normal emission spectra of Mg are dominated by huge emissions from a Shockley surface state, respective emissions are lacking for Ca and Sr. It is shown by means of LDA band-structure calculations that the band gap responsible for the surface state of Mg is Shockley inverted, while admixtures of *d* states to the valence bands lead in case of Ca and Sr to the formation of ordinary gaps that are not suited for Shockley surface states. Consequences of this finding for the surface related electron structure of noble metals, Zn and Al group elements and rare-earth metals are discussed.

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I. INTRODUCTION

Since the pioneering work of Tamm[1] and Shockley[2] surface-states have attracted considerable interest. Being restricted to the outermost atomic surface layers these states represent an almost ideal example for two-dimensional electron systems, and since both structure and chemical composition of surfaces can easily be modified a variety of interactions and confinement effects can be studied. On the other hand, leading, e.g., to metallization of semiconductor surfaces, surface states affect heavily the physical and chemical properties of interfaces and are, therefore, particularly of large importance for nanotechnology and catalysis.

Related to their distinct nature surface states are usually classified as Shockley or Tamm states. Shockley states are described on the basis of the bulk band structure simply by coupling exponentially damped solutions of the Schrödinger equation in the gap to solutions of negative energy in the vacuum region. Tamm states, on the other hand, are results of an explicit consideration of the real structure, i.e., the broken symmetry of the system. This classification is somehow artificial since both types of states describe the same phenomenon of a wave function that is localized at the surface and decays in the bulk.[3–5] Shockley states appear close to the high binding energy (BE) border of a gap and reveal a free-electron-like behavior parallel to the surface, while Tamm states are often found in the upper half of the gap and reveal large and often negative effective masses. For Shockley states the matching condition that the first derivative of the wave function must be continuous may only be fulfilled if the gap is so-called Shockley inverted, i.e., if the wave function of the valence-band states at the lower (high BE) border of the gap reveal a node at the atomic surface sites. Such a situation is only achieved if the Fourier expansion coefficient V_G of the potential that is responsible for the gap is negative. This is opposite to the case usually discussed in textbooks, where Bloch functions with an antinode at the atomic sites are energetically lowered under the influence of an attractive potential $V_G > 0$. The existence of Tamm states, on the other hand, is related to the reduced atomic coordination at the surface, that leads to band narrowing and formation of dangling bonds. Their theoretical description demands a much more sophisticated approach to the surface electron structure than in the case of the Shockley states and may be realized in the framework of slab, supercell, or layered Korringa-Kohn-Rostoker (layer-KKR) calculations.

Considering close-packed surfaces of simple metals, Shockley states have been found at the fcc (111) surfaces of the monovalent noble metals Cu,[6] Ag,[7,8] and Au,[9] at the hcp (0001) surfaces of the divalent metals Be,[10,11] Mg,[12] and Zn,[13] and at the fcc (111) surface of trivalent Al.[14] Additionally, Shockley states were encountered at the close-packed surfaces of Ni,[15] Pd,[16,17] and Pt,[18] that resemble in some sense the situation of the isostructural noble metals: In the light of a rigid-band picture the Fermi energy is simply lowered leaving the bulk band structure unaffected. Thus, the band gaps remain Shockley inverted, but the surface states shift towards the Fermi energy and the *d*-bands cross the Fermi level at certain points of the Brillouin zone.

On the other hand, neither at the fcc (111) surface of divalent ytterbium[19] nor at close-packed surfaces of trivalent rare-earth metals were Shockley states found. Instead Tamm states were observed[19–30] that reveal mainly d_{z^2} character and a dispersion with a large effective mass.[19,24,30] From these observations one may conclude that *s*-*p* metals reveal Shockley states, while large admixture of *d* character to the states above the Fermi energy lead to a quenching of the Shockley state. The validity of this hypothesis may be tested by studying the (111) surfaces of the divalent metals Ca and Sr: In contrast to the earth-alkali metals Be and Mg, that are followed in the Periodic Table by the *s*-*p* elements B and Al, Ca and Sr are followed by the transition elements Sc and Y and are, therefore, expected to reveal certain *d* admixtures to bonding like in Yb. The same argument holds in principle also for Ba metal, but this element does not crystallize in a close-packed structure and is, therefore, not considered here. In the present contribution we report on a comparative angle-resolved photoemission (PE) study of Mg(0001), Ca(111), and Sr(111) surfaces, accompanied by band-structure calculations for all monovalent, divalent, and trivalent metals mentioned above. Samples were prepared in form of epitaxial films on W(110) with variable thickness between

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5 to 100 Å that allow proper determination of the band gap position by monitoring the thickness dependent binding energy shifts of quantum well states. While the PE spectra of Mg(0001) were found to be dominated by an intense Shockley state with parabolic dispersion around the $\bar{\Gamma}$-point such a state is missing for Ca(111) and Sr(111) surfaces. This is in good agreement with the results of our band-structure calculations, that reveal Shockley inverted gaps for the noble metals, Be, Mg, and Al, while ordinary gaps are found for Ca, Sr, Yb, and the trivalent rare earths. In particular, the band-structure calculations reveal an almost pure *s*-character of the valence-band states at the high-energy border of the gaps of Be and Mg, while the low-energy border is formed by *p*-like states. In Ca and Sr, on the other hand, the upper border reveals predominantly *p* character and the lower border is formed by *s*-*d* hybrids.

II. EXPERIMENTAL DETAILS

Photoemission (PE) experiments were performed using a high-resolution angle-resolved hemispherical electron energy analyzer (SCIENTA 200) together with a monochromatized He-discharge lamp using photon energies of 21.2 eV (He I) and 40.8 eV (He II). The total system resolution was set to 30 meV and an angular resolution of 1° was chosen. Clean structurally ordered films of Mg, Ca, and Sr metal were grown at room temperature by thermal deposition of the respective metals from Mo crucibles onto a clean W(110) substrate. Hexagonal LEED patterns indicated in all cases the formation of well ordered close-packed surfaces. While in the case of Mg(0001) (a=3.21 Å) a small lattice mismatch with respect to W(110) (a=3.16 Å) allows at least along one axis hexagonal growth without large distortions, the nearest neighbor distances in Ca (3.95 Å) and Sr (4.30 Å) are much larger than those in W and no hints of commensurable overstructures are found. A similar situation has been reported for divalent Eu on W(110) that grows pseudomorphically in hexagonal close-packed structure with almost the same lattice constant as Ca.[31] The thickness of the films were calibrated by means of a microbalance and the observation of sharp quantum-well (QW) states in the PE spectra that indicated additionally a strict layer-by-layer growth mode. Oxygen and carbon contaminations were checked by monitoring respective regions in the valence-band PE spectra and were found to be negligible for Mg and less than 3% at the Ca and Sr surfaces. The pressure in the measuring chamber was in the upper 10^{-9} Pa range during the PE experiments and raised only shortly to 10^{-7} Pa during film preparation.

For comparison with the experimental results bulk band-structure calculations were performed in the framework of the local-density approximation (LDA) using the Hedin-Lunquist exchange-correlation potential[32] and the method of optimized linear combinations of atomic orbitals (LCAO) in its fully relativistic version using the FPLO code.[33]

III. RESULTS AND DISCUSSION

Figure 1(a) shows a series of PE spectra from Mg films of different thickness recorded in normal emission geometry and with 40.8 eV photon energy.[34] Varying the photon energy none of the observed peaks shows dispersion along the ΓA direction suggesting a two-dimensional character of the respective states. The spectra are dominated by a strong emission at about 1.6 eV that is almost unaffected from the film thickness and is attributed to the Shockley surface state. Additional peaks are found at both sides of the surface state that change their number and energy positions with thickness and are, therefore, identified as quantum well states or resonances of Mg bulk bands along the ΓA direction. Such states are formed by the confinement of the electrons in the Mg film perpendicular to the surface. Since the electron structure of the substrate along the bcc Γ-Σ-N direction is characterized by a broad energy gap between 6.3 eV and 3.4 eV binding energy,[35,36] the electron wave functions are reflected at these energies on both sides, the Mg/vacuum side and the Mg/W(110) interface and form quantum well states. As is obvious from Fig. 1(a), states exist also in the energy region between 3.4 eV and the Fermi level E_F. Here, partial reflections are caused by the symmetry differences between film and substrate and different lattice parameters. Respective states are called quantum well resonances. For simplicity, however, we will use the terminus QW for both types of states.

The QW states were analyzed in the framework of a simple phase accumulation model[34] treating the metal film as a quantum well perpendicular to the surface and estimating the phase shifts at the two interfaces in the light of a two-band approach.[4,37] The top panel of Fig. 1(c) shows results of a best fit of the model parameters to the experimental data that allowed a determination of the binding energies of the upper (1.23±0.09 eV) and lower border (1.79±0.09 eV) of the band gap in reasonable agreement with results of LDA band-structure calculations (1.30 and 1.69 eV, respectively) that predict correctly the center of gravity of the gap but underestimate the width by 44%.

The left-hand panel of Fig. 1(b) presents a corresponding series of PE spectra from Ca films of different thicknesses on W(110) taken again in normal emission geometry and with 40.8 eV photon energy. In contrast to the data of the Mg films the dominating emissions from the surface state are obviously missing, and the peaks at the low BE side of the gap reveal a much higher intensity than those at the high BE side pointing to different photoemission cross sections and probably different angular momentum character of the states. In order to emphasize the weak structures on the high BE side, the right-hand panel shows the same set of data amplified by a factor of 15. The data were analyzed within the same phase accumulation model as applied to the Mg films. The lower panel of Fig. 1(c) shows the respective results of a best fit to the data. From this fit the BE positions of the upper and lower edges of the band gap are determined to be 0.34±0.09 and 0.90±0.09 eV in fair agreement with our LDA results that predict values of 0.13 and 1.03 eV. Again, the center of gravity of the gap is correctly predicted by the theory but now the width is overestimated by a factor of 1.6. This different behavior with respect to Mg may be related to admixtures of *d*-states to bonding as will be discussed below. Our analysis confirms that there is no hint of an additional surface state emission within the gap. In order to understand

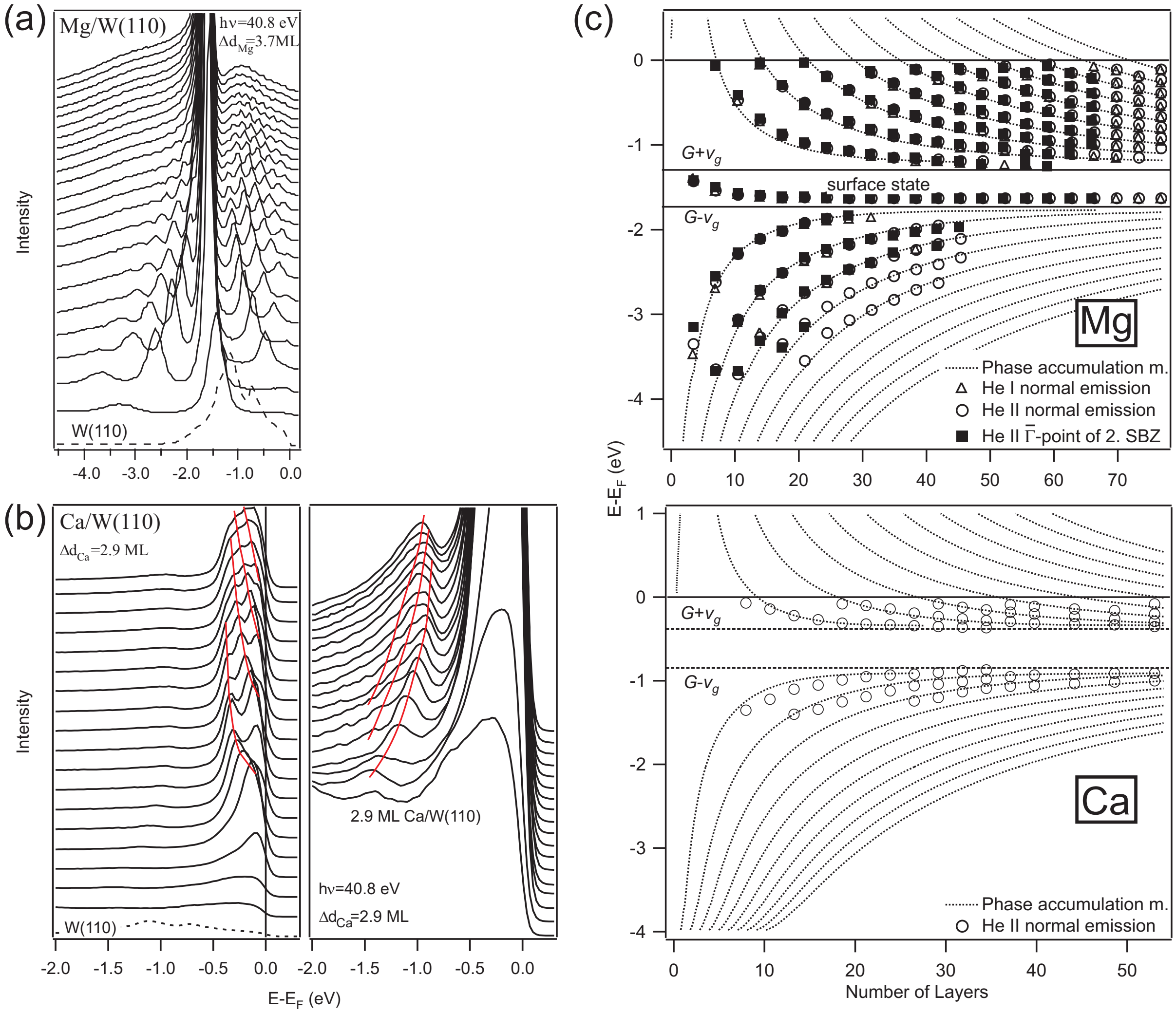


FIG. 1. (Color online) (a) Angle-resolved photoemission spectra of hcp Mg(0001)/W(110) taken for different coverage in normal emission geometry. (b) A corresponding set of data for fcc Ca(111)/W(110). Right-hand panel: same data as on the left-hand side, but amplified by a factor of 15 in order to emphasize the QW states at the low kinetic energy side of the gap. (c) Thickness dependence of the binding energy positions of the QW and surface states for Mg/W(110) and Ca/W(110), respectively. Theoretical predictions on the basis of the phase accumulation model (dotted lines) as compared to experimental observation (markers).

this surprising fact the results of the LDA calculations where analyzed in more detail.

The upper panel of Fig. 2 shows the calculated bulk band structure in $\bar{M}\,\bar{\Gamma}\bar{K}$ directions of Mg projected along the (0001) surface and analyzed with respect to the angular momentum character of the states. Contributions of different angular momentum characters are visualized by a color-scale ranging from light (100%) to dark (0%). As is obvious from this figure the occupied bands reveal predominantly *s* character as may be expected from the [Ne] $3s^2$ configuration of the free atoms. The lower borders of the narrow band gaps, however, reveals up to 100% *p* character leading to a Shockley inverted nature of the gaps. This gives rise to a Shockley state as reproduced by a layer KKR calculation that is included in Fig. 2 (taken from Ref. 34). *d* character is almost completely absent since the element following Mg in the periodic system is the *s*-*p* element Al. This situation changes dramatically in going to Ca and Sr that are followed in the periodic system by the transition elements Sc and Y, respectively. The lower panel of Fig. 2 shows the projected band structure of Ca decomposed into contributions of *s*, *p*, and *d* states. Caused by *d* contributions to bonding the band gaps are much broader than in Mg and similar to the one encountered for the divalent rare-earth metal Yb.[19] Below the gaps the electron structure is governed by *s*-*d* hybrids while at least around the $\bar{\Gamma}$ point the upper border of the gap reveals almost pure *p* character. Thus, in contrast to Mg the gap is not Shockley inverted, and respective surface states are not expected.

Figure 3 shows the photoemission spectra of 17 ML Sr film on W(110). Also in this case the surface state is missing and only QW states are observed, confirming the fact that a *d* admixture to the valence-band changes the symmetry of the band gap edges resulting in a normal band gap.

Based on this observation bulk band-structure calculations can be used to predict surface states on metal surfaces. Figure 4 shows part of the periodic table of the close-packed metals and their possible Shockley states, Table I summa-

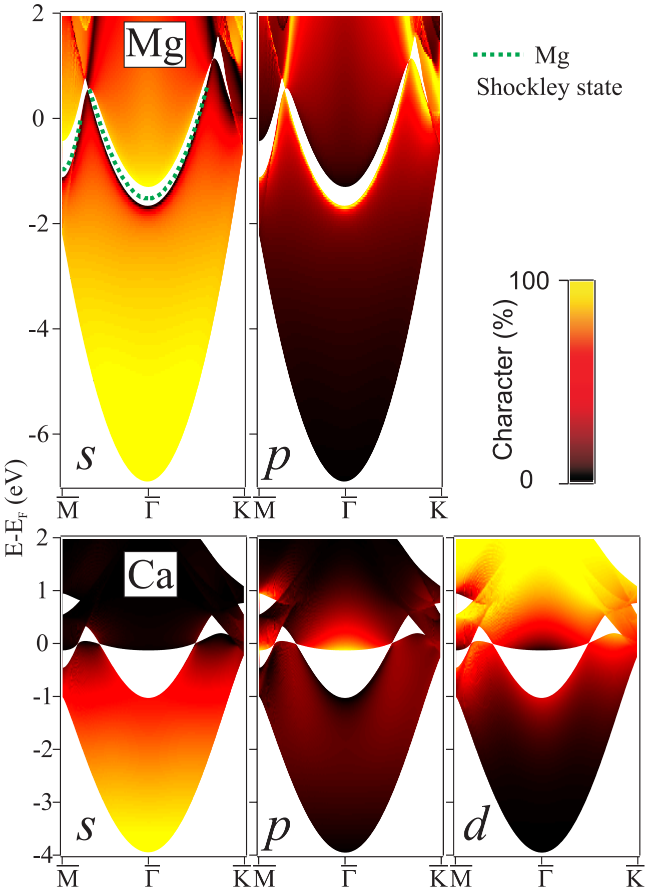


FIG. 2. (Color online) LDA band-structure calculations of Mg and Ca, respectively, projected along the direction of the hcp(0001) and fcc(111) surface normal, respectively, and decomposed with respect to the different angular momentum characters. The calculated dispersion of the Mg Shockley surface state was taken from Ref. 34.

rizes the positions of the experimentally observed Shockley states. In the latter the positions obtained at room temperature are given. Note that the Shockley state shifts depending on the temperature due to the change in the crystal lattice parameter.[38]

As visualized in Fig. 4, apart from the known cases, Shockley states are expected for the close-packed surfaces of Cd and Hg while the close-packed surfaces of all other divalent and trivalent metals including the rare earths (not shown) are characterized by normal gaps without Shockley states. For Cd(0001) our calculations reveal a Shockley inverted gap with a width of only 21 meV. Former slab calculations using the ideal hexagonal c/a ratio revealed that the width and symmetry of the Cd gap depend strongly on the geometry and the calculation details. Results suggested a normal band-gap and did not give evidence for a Shockley state in Cd.[40] Experiments, however, found a very small peak just at the position of a expected Shockley state[41] that may be interpreted as a surface state. Hg crystalizes in a rhombohedral lattice not adopting a close-packed surface. In our calculation for a supposed hcp lattice with $a=2.98$ Å (Ref. 42) and a c/a ratio like that of Cd ($c/a=1.89$) a Shockley inverted band gap with $\Gamma_4^-=-3.024$ eV and $\Gamma_3^+=-3.057$ eV was obtained resulting in a gap width of 33 meV that should contain a Shockley state. This finding is in reasonable agreement with photoemission data of very thin Hg films that find a two-dimensional nearly not (with $k_{\|}$) dispersing peak at -3.25 eV and QW states at both sides of the energy gap.[42] However, since the width and opening of Shockley inverted gaps depends strongly on the supposed lattice constant, clear

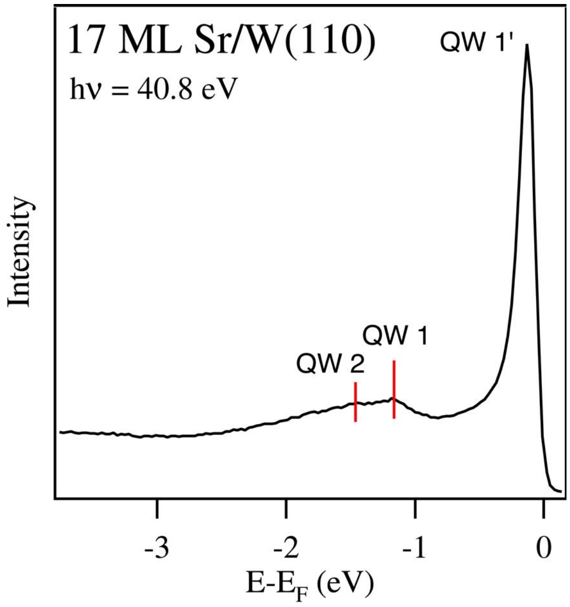
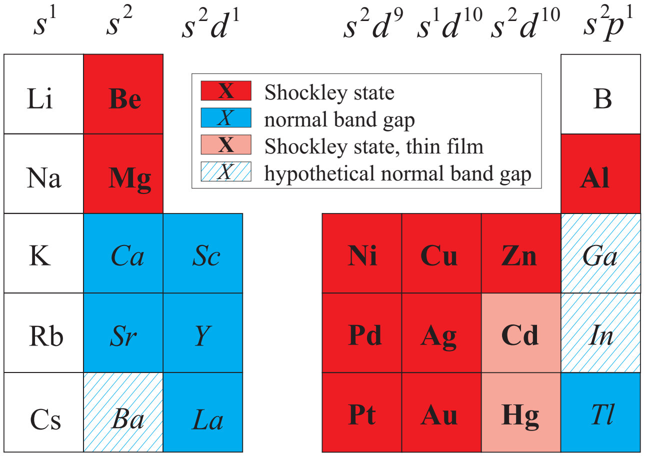


FIG. 3. (Color online) Angle-resolved PE spectrum of 17 ML Sr/W(110) taken in normal emission geometry. Bars denote the position of the two upmost QW states at the low-energy border of the band-gap.



s^1	s^2	s^2d^1	s^2d^9	s^1d^{10}	s^2d^{10}	s^2p^1
Li	**Be**					B
Na	**Mg**					**Al**
K	*Ca*	*Sc*	**Ni**	**Cu**	**Zn**	*Ga*
Rb	*Sr*	*Y*	**Pd**	**Ag**	**Cd**	*In*
Cs	*Ba*	*La*	**Pt**	**Au**	**Hg**	*Tl*

🟥 X Shockley state
🟦 *X* normal band gap
X Shockley state, thin film
▨ *X* hypothetical normal band gap

FIG. 4. (Color online) Schematic presentation of a part of the periodic system indicating those elements where Shockley states at close-packed surfaces are expected (bold letters) or not (italic letters) on the basis of our band-structure calculations at ambient pressure. Dark and light shaded patterns denote elements where presence or absence of Shockley states was confirmed by PE experiments. Cross-hatched patterns correspond to elements that do not crystallize in close-packed bulk structures. Maintaining the unit-cell volume hypothetical fcc structures of these elements do not reveal Shockley inverted gaps.

TABLE I. Energy positions (in eV) of the Shockley state relative to the Fermi level E_F measured at room temperature (Refs. 10, 11, 13–15, 17, 18, 34, 38, and 39).

Be	Mg	Al	Ni	Cu	Zn	Pd	Ag	Pt	Au
−2.80	−1.63	−4.56	−0.10	−0.39	−3.60	+1.30	−0.03	−0.19	−0.44

prediction of Shockley states in closed-packed Cd and Hg is not possible.

Among the IIIA-group elements of the periodic system only Al and Tl crystallize under normal conditions in close-packed structures. Boron is nonmetallic at ambient pressures but becomes metallic (and superconducting) at high pressure.[43] Calculations[44] predict a fcc phase above 360 GPa with a lattice constant of 2.32 Å. Our calculations for such a fcc (111) structure reveal a large Shockley inverted gap with $\Gamma_4^-=-5.6$ eV and $\Gamma_3^+=-16.8$ eV. Also fcc Al(111) should contain a Shockley state ($\Gamma_4^-=-4.451$ eV, $\Gamma_3^+=-4.563$ eV) that was experimentally confirmed.[14] α-gallium crystalizes in an orthorhombic lattice and undergoes a phase transition to a fcc structure with a lattice constant of 3.65 Å at approximately 120 GPa.[45] Under such conditions close-packed Ga surfaces reveal a Shockley inverted gap ($\Gamma_4^-=-7.045$ eV, $\Gamma_3^+=-5.814$ eV). Indium does not exist at ambient pressure in a close-packed structure. Calculations[46] predict a possible transition to fcc at extreme high pressures (800 GPa) related to a reduction of the unit cell volume to 30%. Under such a pressure also for close-packed In surfaces a Shockley inverted gap is expected. The main difference of the electronic properties of Al and those of the following group-IIIa elements is the increased localization of the s orbitals in the latter that leads to relatively weak s-p hybridization and is also responsible for the different chemical properties of alkaline earths and Zn-group elements. In Ga and In, increasing pressure leads to a increasing s-p mixing, that is the driving force for the phase transition towards a fcc structure.[46,47] At a certain pressure, the s-p mixing approaches the one of Al and a Shockley inverted gap is obtained instead of the normal gap expected for the same structure at ambient pressure. This is nicely reflected in Tl, the heaviest element among the group-IIIA elements: Tl crystallizes in hcp structure already at ambient pressure and reveals a normal band gap. Higher pressure again reduces the normal band gap converting it to a Shockley inverted gap at a reduced unit cell volume of $V/V_0=0.7$.

IV. CONCLUSIONS

In summary, we have shown that the electron structure of the close-packed Mg surface is dominated by a Shockley state, while respective states at the close-packed surfaces of Ca and Sr are quenched due to the d character of the electron states around the Fermi energy. The same mechanism is responsible for the lack of Shockley-states at the close-packed surfaces of divalent and trivalent rare-earth metals, while the precondition for these states, the presence of a Shockley inverted gap, was confirmed for the close-packed surfaces of the noble metals, Ni, Pd, Pt, Zn, and Al by means of LDA band-structure calculations. For Ga, In, and Tl only normal gaps are expected for the (hypothetic) fcc(111) surfaces. At high pressures, however, increased s-p mixing leads to a conversion into a Shockley inverted gap.

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