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Partially occupied surface state at the Fermi level of La(0001)

A. V. Fedorov, A. Höhr, E. Weschke, and K. Starke
Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin-Dahlem, Germany

V. K. Adamchuk
Institute of Physics, St. Petersburg State University, St. Petersburg 198904, Russia

G. Kaindl
Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin-Dahlem, Germany
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A partially occupied surface state at the Fermi level of a well-ordered La(0001) film grown on W(110) is observed by photoemission and inverse photoemission, which provide direct pictures of the occupied and unoccupied part, respectively. The occupied part of the surface state gives rise to an intense direct recombination line in the $N_{4,5}O_{2,3}O_{2,3}$ Auger-electron spectrum. The surface state is found to be sensitive to O_2 adsorption and disordering of the surface induced by Ar-ion bombardment. The present results support a view that such surface states occur generally on close-packed surfaces of the rare-earth metals.

Electronic surface states on metal surfaces have been the subject of numerous experimental and theoretical studies since the first surface state had been observed for W(100).[1] The interest in surface states arises from the strong influence of the surface electronic structure on chemical and physical properties of metal surfaces. With this motivation, considerable efforts have been made in studying such states, e.g., in context with the reconstruction of the (001) surfaces of tungsten and molybdenum,[2] the surface magnetism of iron and nickel,[3,4] and in connection with chemisorption.[5] Recently, an occupied surface state was also observed by angle-resolved photoemission (PE) for Gd(0001) films grown epitaxially on a W(110) substrate,[6] shortly after the existence of such a state had been postulated theoretically.[7] It was originally thought that the existence of this surface state is related to the magnetism of the Gd(0001) surface, which is still quite controversial, with contradicting reports on magnetic surface reconstruction.[6–9] Subsequently, an analogous *d*-like occupied surface state was reported for Tb(0001) in angle-resolved[10] as well as high-resolution angle-integrated PE work.[11] Similar *d*-like surface states just below the Fermi level have also been observed for well-ordered epitaxially grown films of Ho(0001), Tm(0001), and Yb(111).[12] This suggests that *d*-like surface states at the $\bar{\Gamma}$ point of the surface Brillouin zone are a general property of close-packed surfaces of the heavy rare-earth (RE) metals. For the light RE metals, no clear evidence for the presence of a surface state exists up to now mainly due to the difficulty in preparing clean and well-ordered surfaces.

In the present study we report on the observation of a partially occupied surface state at the Fermi level of La(0001) grown epitaxially as a thin film on W(110). Photoemission and inverse photoemission (IPE) spectra, respectively, provide a direct picture of the occupied and empty part of the surface state. In addition, the occupied part of the surface state gives rise to a relatively intense direct-recombination line in the $N_{4,5}O_{2,3}O_{2,3}$ Auger-electron spectrum. Considering the rather similar bulk band structures of trivalent RE metals,[13] the present observations for La(0001) suggest that *d*-like surface states are a general property of close-packed RE metal surfaces. In this way, a new picture arises of the surface electronic structure of RE metals, rather different from what has been in the literature.[14]

The PE and IPE experiments were performed at the Freie Universität Berlin, while the Auger-electron spectroscopy (AES) work was performed at St. Petersburg State University. Angle-resolved PE spectra were taken with a hemispherical electron energy analyzer (VSW-ARIES) using photons from the TGM-1 beamline at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY). The total-system resolution was $\cong$180 meV [full width at half maximum (FWHM)]. The IPE spectrometer used is equipped with a toroidal-grating monochromator, a position-sensitive detector, and a Pierce-type electron gun.[15] The angle-resolved IPE spectra were recorded in the constant-initial-state mode with constant kinetic energy of the incoming electrons, recording photons in the energy range from 13.0 to 17.5 eV; the total-system resolution was $\cong$250 meV (FWHM). AES spectra were recorded in the dN/dE mode at a primary electron energy of 2 keV employing a 4-grid hemispherical analyzer with 0.3% relative resolution. The W(110) substrate was cleaned by the standard procedure;[16] $\cong$70-Å-thick La(0001) films were grown on this substrate at room temperature by vapor deposition of high-purity La metal at a rate of $\cong$1 Å/min evaporated thermally from a resistively heated Ta crucible. The film thickness was monitored by a quartz microbalance calibrated by AES, and the sample temperature was monitored by a movable AlCr/NiCr thermocouple. For film thicknesses exceeding $\cong$50 Å, AES signals from the W

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substrate could no longer be detected. The films grown under these conditions showed a diffuse low-energy electron diffraction (LEED) pattern that changed—upon annealing at 100 °C for a period of 5 min—to sharp LEED spots corresponding to a (0001) surface. When the annealing temperature exceeded 100 °C, La islands were formed. Well-ordered La(0001) films with sharp LEED spots could only be produced if the pressure in the experimental chamber stayed below 2×10^{-10} mbar during La evaporation. The surface-related nature of the spectral features from the surface state was confirmed by O_2 adsorption as well as by inducing surface disorder through bombardment with low-energy Ar ions. All spectra were taken with the sample at room temperature.

Figure 1 displays PE spectra (left panel) and IPE spectra (right panel) of La(0001); the spectra were recorded at normal emission and normal incidence of the electrons, respectively. The PE and IPE spectra each show two prominent spectral features, labeled A and B in the PE and A' and C in the IPE case. While peaks B and C at energies of $\cong 1.5$ eV below and above E_F, respectively, can be readily assigned to bulk features, peaks A and A' lie directly at E_F in the region of a wide gap in the bulk band structure along the ΓA direction.[13] Peaks A and A' are not exhibiting any dispersion when the electron momentum normal to the surface is changed by increasing the photon energy in the PE case [spectrum (b)] or the primary electron energy in the IPE case [spectrum (e)]. This is different from the bulk-band-structure peaks B and C, which clearly disperse with the electron momentum. In addition, peaks A and A' can be quenched by O_2 adsorption [see spectra (c) and (f), respectively].

These observations identify peaks A and A' as spectral features due to the occupied and empty part, respectively, of a surface state located directly at E_F. This surface state seems to be the analogue of the d-like surface state theoretically predicted for Gd(0001) (Ref. 7) and experimentally observed by PE for most of the heavy RE metals.[6,10–12] Here, we have first identified such a surface state for the (0001) face of the light RE metal La. From a study of the photon-energy dependence of the PE cross section of this state for photon energies up to 100 eV, a $4f$-related nature can be ruled out, while the data support a $5d$-like character. This surface state on La(0001) is therefore very likely a d-like state as expected from the similarities of the band structures of La and Gd metal.[13]

We also identify a surface-related feature at $\cong 116$ eV in the region of the $N_{4,5}O_{2,3}O_{2,3}$ Auger spectra of La(0001) shown in Fig. 2. Comparison of the spectrum recorded for clean La(0001) [see Fig. 2(a)] with the one reported previously for polycrystalline La metal[18] allows the straightforward assignment of the 65-eV peak to an $N_{4,5}O_{2,3}O_{2,3}$ Auger transition and of the 83-eV peak to an $N_{4,5}O_{2,3}V$ Auger transition. Peak D at an energy of 116 eV in spectrum (a), however, has not been observed previously in AES spectra of polycrystalline La metal.[17] The intensity of this peak is considerably reduced upon Ar-ion bombardment of the La(0001) surface [see Fig. 2(b)], whereas the intensities of the other spectral lines remain essentially unchanged. One could argue that such a

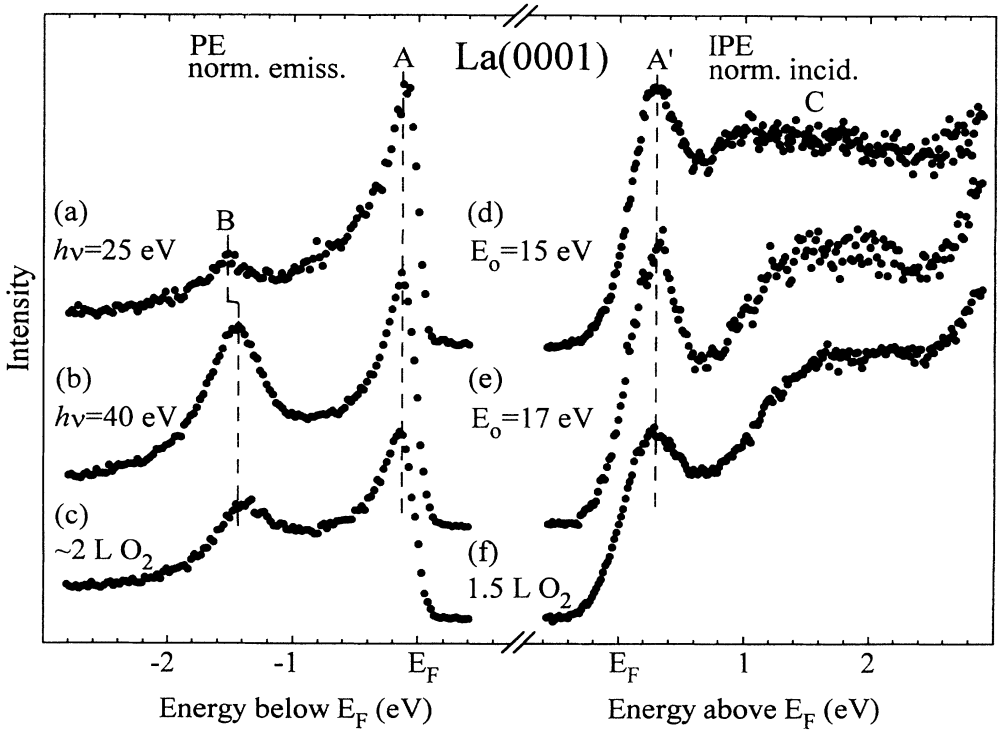

FIG. 1. Left panel: Photoemission spectra of La(0001) taken at $h\nu=25$ eV (a) and $h\nu=40$ eV (b) for a clean and well-ordered surface; (c) PE spectrum after adsorption of $\cong 2$ Langmuir (1 L $=10^{-6}$ Torr s) O_2 taken at $h\nu=40$ eV. The spectra are normalized to the same incident photon flux. Right panel: Inverse photoemission spectra taken at primary electron energy of $E_0=15$ eV (d) and $E_0=17$ eV (e) of a clean and well-ordered La(0001); (f) IPE spectrum taken at $E_0=17$ eV after adsorption of 1.5 L O_2.

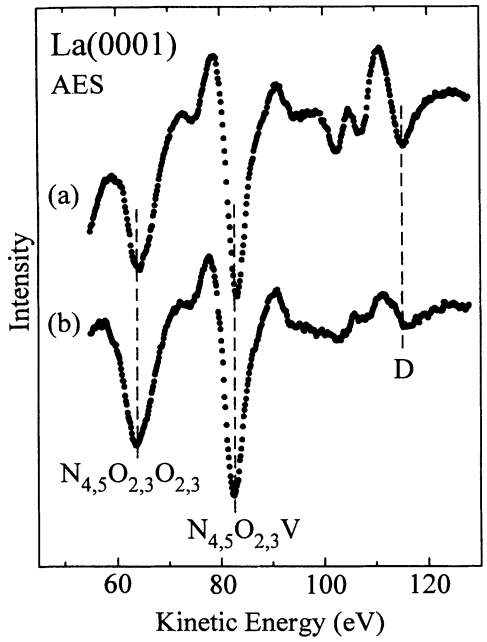

FIG. 2. Electron-excited Auger electron spectra (a) of a well-ordered La(0001) surface and (b) after Ar-ion bombardment (500 eV, for 1 min). The spectra are given in the derivative mode. Note the quenching of feature D upon Ar-ion bombardment.

behavior of peak D is caused by some kind of surface contamination, which is removed by the Ar-ion bombardment. However, there is no chemical element with an Auger transition at $\cong 116$ eV.[18] The disappearance of the LEED spots upon Ar-ion bombardment indicates that it causes some kind of disordering of the La surface. The simultaneous quenching of peak D hence shows that it is closely related to the crystallinity of the La(0001) surface.

To assign peak D, we consider a direct recombination process of the $4d$ core hole produced by electron bombardment of La(0001), similar to those discussed in connection with AES from rare-earth metals.[19] The energy (E_i) of the state from which the electron is emitted is then given by

$$E_i = E_{4d \rightarrow 4f} - 116 \text{ eV} , \quad (1)$$

where $E_{4d \rightarrow 4f}$ is the excitation energy of a $4d$ core electron to the $4f$ state. $E_{4d \rightarrow 4f}$ is known from photoelectron-yield measurements: The maxima in the giant resonance cross sections of the $5p$, $5s$, and $5d$ photoelectrons from LaB_6, e.g., are at $\cong 116.6$ eV (Ref. 20) leading to an initial-state energy of $E_i \cong 0.6$ eV, i.e., directly at E_F within the limits of error. We therefore assume that this state is the occupied part of the surface state of La(0001). Our assignment is strongly supported by the dependence of the intensity of the 116-eV peak on the degree of ordering of the La(0001) surface. These results represent an observation of a surface state via a direct recombination peak in the Auger spectrum. Feature D is also one of the very few surface-related spectral features observed up to now in AES spectra.[21]

In summary, a partially filled surface state directly at the Fermi level has been observed for a rare-earth metal, La(0001). It is d-like and shows up in the PE, IPE, and Auger spectra, in the latter case in the form of a direct-recombination line. In conjunction with occupied d-like surface states observed for the heavy RE metals Gd, Tb, Ho, Tm, and Yb, the present results suggest that such surface states constitute a general feature of close-packed surfaces of RE metals. In this way a new picture arises of the surface-electronic structure of RE metals that is quite different from what can be found in the literature, particularly in the review of Ref. 14. Most reports on surface-electronic properties of RE metals based on studies of polycrystalline or poorly ordered surfaces need extensive revision. This was recently demonstrated for the example of the surface core-level shift of Tb(0001) that changes by a factor of $\cong 2$ when the surface is well annealed.[11] More systematic work on the surface-electronic structure of the rare-earth metals is in progress in our laboratory.

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