

Surface state vs orbital Kondo resonance at Cr(001): Arguments for a surface state interpretation

M. Budke,* T. Allmers, and M. Donath

Physikalisches Institut, Westfälische Wilhelms-Universität, Wilhelm-Klemm-Strasse 10, 48149 Münster, Germany

M. Bode

Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, USA

(Received 24 March 2008; revised manuscript received 7 May 2008; published 26 June 2008)

We have performed a combined scanning tunneling spectroscopy, photoemission, and inverse photoemission study of the surface electronic structure of Cr(001). Our results show three surface-related features, one below, one above, and one right at the Fermi level E_F . While the surface-sensitive features below and above the Fermi level show characteristics of $d_{xz,yz}$ orbital symmetry, the feature right at E_F exhibits predominantly d_{z^2} -like orbital symmetry. Upon exposure to oxygen, its spectral weight continuously shifts into the unoccupied electronic states. These results are in conflict with the interpretation of this peak as orbital Kondo resonance but point toward a Shockley-type surface state.

DOI: [10.1103/PhysRevB.77.233409](https://doi.org/10.1103/PhysRevB.77.233409)

PACS number(s): 73.20.At, 68.37.Ef, 72.15.Qm, 79.60.Bm

The surface electronic structure of Cr(001) has been intensively investigated in recent years. One focus of interest was a surface-sensitive feature that appears close to the Fermi level E_F , first observed in a combined experimental and theoretical work by Klebanoff *et al.*¹⁻³ Using polarized light in their photoemission (PE) setup, they identified a d_{z^2} -like surface state at E_F . Comparing their data with the theoretical part of the work which predicted a d_{z^2} -like surface state 0.68 eV above E_F , they concluded that the observed feature was mainly unoccupied and their photoemission results showed this surface state truncated by the Fermi edge. Additionally, a second surface state was identified at a binding energy of about 0.7 eV, which was assigned to nearly degenerate spin-up and spin-down surface states with d_{xz} and d_{yz} orbital character. About ten years later, Stroscio *et al.*⁴ performed scanning tunneling spectroscopy (STS) on the Cr(001) surface. Since in STS the sample bias voltage, as referred to the tip potential, can be tuned to negative and positive voltage, this technique gives simultaneous access to occupied and empty electronic states below and above E_F , respectively. As a result, the measured signal is not any more truncated by the Fermi edge. Stroscio *et al.*⁴ were able to derive the precise energetic position for the feature at 0.05 eV below E_F , generally supporting Klebanoff's interpretation of a Shockley-type surface state with d_{z^2} orbital symmetry. According to band-structure calculations in the density-functional theory (DFT) scheme, such surface states are a general property of a bcc(001) surface.

Up to now, however, the surface electronic structure of Cr(001), as observed experimentally, cannot be described adequately by self-consistent DFT calculations, i.e., without accounting for electron correlation effects. In order to fit the calculated binding energy of the feature at E_F to the experimentally observed value within DFT, the surface magnetic moment was arbitrarily reduced down to a value, which is in contradiction to experimental results.¹ To overcome these inconsistencies, Kolesnychenko *et al.*^{5,6} proposed a completely different interpretation of the peak at E_F . Triggered by the observation of crosslike patterns in scanning tunneling microscopy (STM) images, they excluded a d_{z^2} -like orbital

symmetry for the feature at E_F and favored a $d_{xz,yz}$ -like character. Based on these findings, they came to the conclusion that the feature represents an orbital Kondo resonance⁷ formed by two degenerate $d_{xz,yz}$ surface states located about 1 eV below and above E_F . Similar to the conventional Kondo effect, where a local magnetic moment is screened by a spin-flip mechanism, which leads to a resonance in the density of states very close to the Fermi level, the orbital Kondo resonance is produced by the flip of the orbital moment of the $d_{xz,yz}$ surface states. In fact, in addition to the above mentioned occupied surface state observed by Klebanoff *et al.*,¹⁻³ an unoccupied surface state at an energy of 1.7 eV above E_F had been identified by inverse photoemission (IPE) before.⁸

The interpretation in terms of an orbital Kondo resonance was recently scrutinized by a temperature-dependent STS study.⁹ While not being able to bring about a decision which of the two models—the “surface state” or the “Kondo resonance” model—is correct, the obtained data allowed for putting constraints on the conditions under which the two models might be valid. Namely, if interpreted in terms of a surface state, a fit to the temperature-dependent spectral width results in an electron-phonon mass-enhancement factor being five to ten times larger than the Cr bulk value. Furthermore, it was observed that oxygen exposure of Cr(001) leads to a peak at ≈ 135 meV, which is energetically too far apart from the Fermi level to be interpreted in terms of a Kondo resonance. It could not be determined, however, whether the peak continuously shifts with increasing oxygen concentration or if the Cr-related peak intensity decreases while a new impurity-induced surface state arises.

In this Brief Report, we present results on the surface electronic structure of Cr(001), which were obtained by combining STS, PE, and IPE in one ultrahigh vacuum (UHV) system. Consequently, we were able to apply these methods to one and the same well-defined preparation of the Cr sample, thereby excluding any inconsistencies in our data, which are due to preparation-dependent effects. We show that our PE and IPE measurements consistently indicate a d_{z^2} -like orbital symmetry for the peak at E_F , while the occupied as well as the unoccupied surface state show $d_{xz,yz}$ behaviors. Additionally, upon exposure of the Cr(001) surface

to oxygen, we observed a shift of the spectral weight away from the Fermi level into the unoccupied part of the density of states. These two experiments are in conflict with the interpretation of this peak as orbital Kondo resonance and provide solid arguments for the Shockley-type surface-state model.

Our experimental setup is described in detail elsewhere.¹⁰ Briefly, it consists of a multichamber UHV system with base pressures below 3×10^{-11} mbar in each chamber. In addition to the already mentioned techniques, it is equipped with techniques for surface preparation and analysis such as argon-ion sputtering, Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED). While STS is performed in a separate chamber of the UHV system, PE and IPE are installed in the same chamber. Thereby, any sample transfer inside the vacuum system can be avoided when switching between PE and IPE. For excitation in PE, a standard helium gas discharge lamp is used, providing unpolarized photons with an energy of 21.2 eV. The emitted electrons are detected by an electron energy analyzer with a total-energy resolution of about 20 meV. For excitation in IPE, an electron beam is used. The electrons that impinge on the sample undergo radiative transitions into unoccupied states, thereby emitting photons which are detected at a fixed energy of 9.8 eV by Geiger-Müller counters located at angles of 70° and 35° with respect to the electron beam. This allows a qualitative analysis of the radiation pattern of the observed states.^{11,12} The main advantage of our IPE system is its variable energy resolution from 400 to 200 meV, which allows the precise determination of peak positions even close to the Fermi level.^{13,10}

The preparation procedure of the Cr(001) surface was identical to Ref. 9. The quality of the surface was carefully checked by AES, LEED, and STM. In agreement with Hänke *et al.*,⁹ the cleaning procedure resulted in a clean surface with terrace widths of several 100 nm. The results obtained from the clean Cr(001) crystal at room temperature are shown as filled black data points in Fig. 1. The top panel displays STS data, which exhibit a peak position right at E_F . The peak width amounts to about 300 meV, which reduces significantly upon cooling the sample (not shown here). PE and IPE results are shown in the middle and bottom panels, respectively. Besides the peak at the Fermi level, which is in both cases truncated by the Fermi edge, the PE results show a feature at -0.5 eV, while the IPE data reveal a broad structure at about 1.65 eV above E_F .

The spectrum below E_F is dominated by a feature at -0.5 eV that reacts very sensitively to surface contamination. In experiments performed on imperfectly prepared Cr sample, we found the peak at about -0.65 eV with lower intensity, which is comparable to the results of Klebanoff *et al.*¹⁻³ and also to recent results¹⁴ that identified a peak at -0.7 eV as bulk band transition. Upon further cleaning cycles, we found the peak to shift toward E_F and to strongly increase in intensity. When the clean sample is again exposed to 0.4 L oxygen, the peak is instantly quenched (open dots in Fig. 1) and a possibly bulklike contribution at -0.65 eV remains. The same behavior was seen in another recent photoemission study.¹⁵ Since it is quenched upon adsorption of 0.4 L oxygen, we assign the peak at -0.5 eV to a surface state.

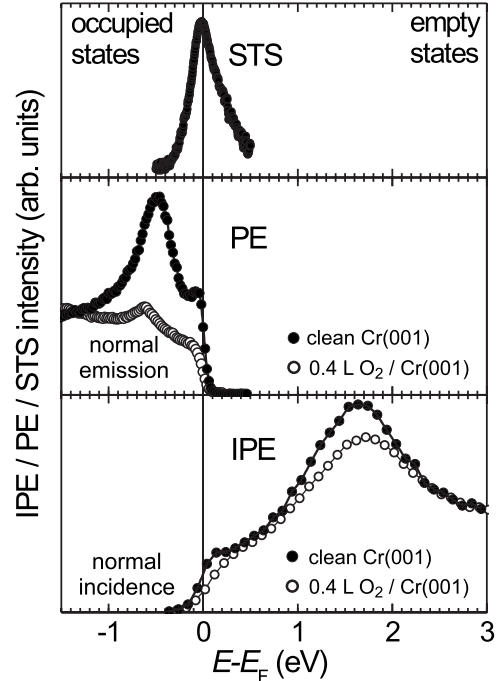


FIG. 1. Surface electronic structure of Cr(001) as measured by STS (top), PE (middle), and IPE (bottom panel) at $T=295$ K. All three methods identify a surface-sensitive feature at E_F on the clean surface (filled dots). The open dots show PE and IPE measurements for 0.4 L oxygen on Cr(001). ($1\text{L}=1.33 \times 10^{-6}$ mbar·s)

The peak at the Fermi level as seen by STS shows up, as expected, truncated by the Fermi edge in the PE spectrum. Its energetic position can be derived to $E_F \pm 0.05$ eV.

The bottom panel of Fig. 1 represents the IPE results. The spectrum is dominated by a broad structure at about 1.65 eV above E_F , which was found to react sensitively to surface contamination (open dots). However, the broad structure also contains bulklike contributions, which were also identified in an earlier IPE study.⁸ An additional peak close to E_F appears in the IPE spectrum as shoulder at about 0.13 eV. However, its true position is probably closer to E_F . This effect is due to the limited energy resolution of about 200 meV and was demonstrated by measurements of the Fermi-level crossing of a surface state on Cu(111).¹⁰ Note that the intensity at E_F is not only reduced upon adsorption of oxygen (open dots) but also slightly shifts in energy to about 0.35 eV (see Fig. 1). We will discuss this in a detailed adsorption experiment.

The experimental results presented so far guarantee that we observe the same surface-sensitive feature at E_F by three different techniques, i.e., STS, PE, and IPE, on a well-defined clean sample. To decide whether the observed state at E_F can be interpreted as orbital Kondo resonance or as Shockley-type surface state, we analyzed the orbital symmetry of the observed states. The interpretation as orbital Kondo resonance is based on the assumption that the state at E_F has the same symmetry as the surface states below and above E_F , namely, $d_{xz,yz}$. In contrast, according to DFT calculations,⁴ the Cr(001) Shockley-type surface state is expected to show a d_{z^2} -like orbital symmetry. In Fig. 2 we show PE and IPE results for different experimental geometries to get insight

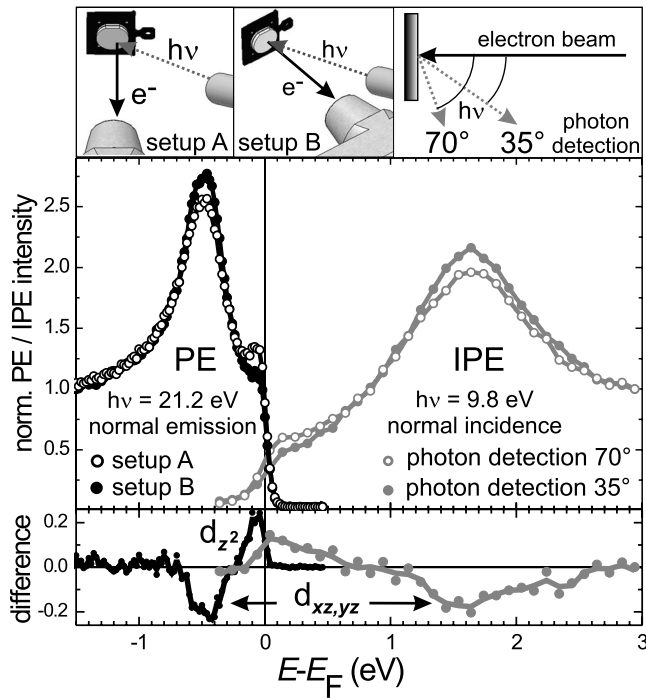


FIG. 2. PE and IPE spectra obtained at $T=295$ K in experimental geometries with different sensitivities to d_{z^2} -like (open dots) and $d_{xz,yz}$ -like (filled dots) orbital characters (see text for details). The same symmetry assignment was obtained at $T=160$ K (not shown).

into the orbital character of the electronic states. Note that the data were obtained from the same preparation of the Cr(001) surface.

IPE data for normal electron incidence are shown in Fig. 2 as open (filled) gray dots for a photon take-off angle of 70° (35°) with respect to the electron beam (see top panel of Fig. 2). The two data sets were taken simultaneously. The radiation pattern of a d_{z^2} -like state shows maximum intensity parallel and smallest intensity perpendicular to the crystal surface. Consequently, higher intensity is expected in the 70° counter than in the 35° counter for a d_{z^2} -like state. Exactly this behavior is observed in the IPE spectra. The surface state at 1.65 eV shows the opposite behavior, consistent with a $d_{xz,yz}$ -like orbital symmetry.

Our PE results support these findings. The open (filled) black dots were taken in the experimental setup A (B) (see top panel of Fig. 2). In both setups the electrons are detected in normal emission. However, setup B differs from setup A by—with respect to the surface normal—a smaller angle of light incidence. This was experimentally realized by rotating both the sample and the electron analyzer with respect to the photon source. Since light is always transversally polarized, setup A has a higher sensitivity for a d_{z^2} -like state than setup B, although we used unpolarized light for excitation. Our results reveal that the peak at E_F has significantly higher intensity if measured in setup A than in setup B, which indicates that the PE measurements confirm a d_{z^2} -like orbital symmetry for the state at E_F and are in agreement with our IPE results. The surface-related feature at -0.5 eV shows the opposite behavior, pointing to a $d_{xz,yz}$ -like orbital symmetry, in line with the results for the unoccupied surface state and

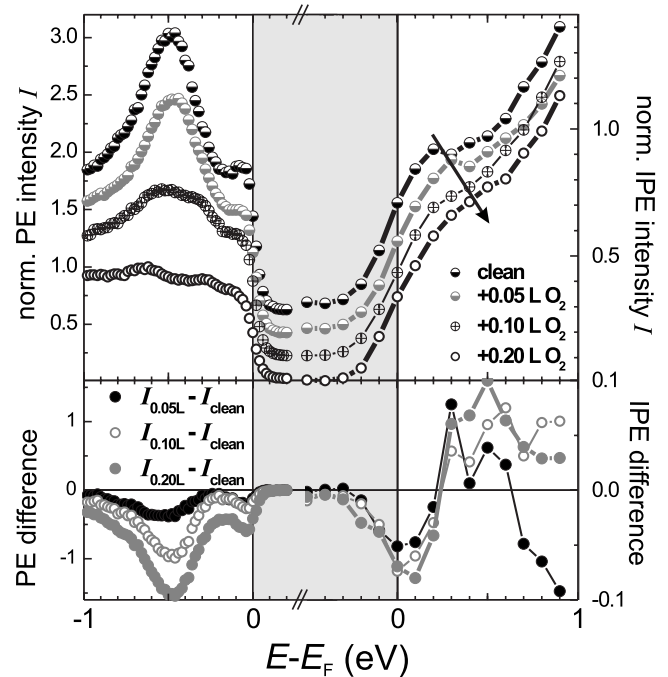


FIG. 3. PE (left) and IPE (right) spectra for Cr(001) upon oxygen adsorption at $T=295$ K. The data for different oxygen exposures are offset with respect to each other. The spectral changes induced by oxygen adsorption are displayed in the bottom panel as difference spectra.

the expectations from theory. Our PE and IPE measurements consistently exclude the state at E_F has the same $d_{xz,yz}$ -like orbital symmetry as the surface states below and above E_F . Instead, it is a surface state with d_{z^2} -like character. This is in conflict with an interpretation in terms of an orbital Kondo resonance.

In a second decisive experiment, we performed an adsorption experiment with oxygen, as proposed by Hänke *et al.*,⁹ starting from a clean Cr(001) surface. The results are shown in the top panel of Fig. 3. To get a better view of changes in the near Fermi-energy region, only an energy range of 1 eV around E_F is shown. For reasons of comparison, the PE spectra have been normalized to equal background intensity at -1.5 eV below E_F . The IPE results are not normalized as usual, i.e., to equal background intensity or to equal maximum intensity, but given with their real intensities relative to each other, i.e., normalized to equal charge absorbed from the sample. This careful analysis was necessary for a meaningful interpretation of the data as shown below.

The results for the clean Cr(001) surface are shown as half-filled black dots in the top panel of Fig. 3. When 0.05 L oxygen is dosed to the surface, the surface state at E_F is rapidly quenched in the PE spectrum. The IPE measurements, however, show an increased intensity at about 0.25 eV above E_F . This becomes obvious in the difference spectra shown in the bottom panel. While the PE difference is negative throughout the entire energy range, indicating a general intensity reduction upon oxygen exposure, the IPE difference becomes positive at about 0.3 eV due to a slight shift of the peak position in the IPE spectrum (see arrow in top panel). The shift of the spectral weight away from the Fermi level

continues as the oxygen dosage is increased to 0.1 L (crossed circles) and 0.2 L (open dots). Finally, the peak is observed at about 0.4 eV above E_F . Although it is difficult to derive the exact peak positions, the IPE measurements provide strong evidence of a continuous shift away from the Fermi level. This observation is inconsistent with an interpretation as orbital Kondo resonance but consistent with a Shockley-type surface state.

It remains the question about the mechanism, which lead to the crosslike patterns in the STM data centered around impurities, as observed by Kolesnychenko *et al.*⁵ These patterns were taken as evidence of an orbital Kondo resonance with $d_{xz,yz}$ symmetry. Theoretically, however, it has been shown that electronic states at the surface Brillouin-zone center, such as s - and d_{z^2} -like states, only lead to a constant tunneling current without contributing to the measured corrugation. This result was obtained by expanding the local density of states (LDOS) in symmetrized two-dimensional plane waves.¹⁶ The above-mentioned states represent the lowest-order term of the expansion. Only higher order terms, which may represent $d_{xz,yz}$ -like contributions, result in a lateral variation of the tunneling current. In the particular case of Cr(001), our PE and IPE results show that the electronic structure at E_F is dominated by a surface state with primarily d_{z^2} -like symmetry. We have to keep in mind, however, that

electronic states with pure atomic-like orbitals do not exist in solids. Instead, they always hybridize with other states of different orbital symmetries. We speculate that the Cr(001) surface state at the Fermi level possesses some admixture of $d_{xz,yz}$ symmetry, which gives rise to the observed features with corresponding symmetry in STM images.

In summary, our experiments show that the surface-sensitive feature at the Fermi level of Cr(001) exhibits predominantly d_{z^2} -like orbital symmetry and that its spectral weight continuously shifts into the unoccupied electronic states upon adsorption of oxygen. These results cannot be explained in terms of the orbital Kondo resonance model. Instead, they are in favor of a Shockley-type surface state with d_{z^2} orbital symmetry as general feature of bcc(001) surfaces. Future theoretical studies may shed light on still open questions such as the size of the surface magnetic moment or the extent of the electron-phonon coupling at Cr(001).

We are indebted to G. Rangelov for helpful discussions. This research was partly supported by the Deutsche Forschungsgemeinschaft (priority program SP1133) and the Office of Science, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. DE-AC02-06CH11357.

*Corresponding author: mbudke@uni-muenster.de

¹L. E. Klebanoff, S. W. Robey, G. Liu, and D. A. Shirley, Phys. Rev. B **30**, 1048 (1984).

²L. E. Klebanoff, S. W. Robey, G. Liu, and D. A. Shirley, Phys. Rev. B **31**, 6379 (1985).

³L. E. Klebanoff, R. H. Victora, L. M. Falicov, and D. A. Shirley, Phys. Rev. B **32**, 1997 (1985).

⁴J. A. Stroscio, D. T. Pierce, A. Davies, R. J. Celotta, and M. Weinert, Phys. Rev. Lett. **75**, 2960 (1995).

⁵O. Yu. Kolesnychenko, R. de Kort, M. I. Katsnelson, A. I. Lichtenstein, and H. van Kempen, Nature (London) **415**, 507 (2002).

⁶O. Yu. Kolesnychenko, G. M. M. Heijnen, A. K. Zhuravlev, R. de Kort, M. I. Katsnelson, A. I. Lichtenstein, and H. van Kempen, Phys. Rev. B **72**, 085456 (2005).

⁷A. K. Zhuravlev, V. Yu. Irkhin, M. I. Katsnelson, and A. I. Lichtenstein, Phys. Rev. Lett. **93**, 236403 (2004).

⁸L. K. Wilson and P. T. Andrews, Surf. Sci. **377-379**, 271 (1997).

⁹T. Hänke, M. Bode, S. Krause, L. Berbil-Bautista, and R. Wiesendanger, Phys. Rev. B **72**, 085453 (2005).

¹⁰M. Budke, T. Allmers, M. Donath, and G. Rangelov, Rev. Sci. Instrum. **78**, 113909 (2007).

¹¹M. Donath, M. Glöbl, B. Senfänger, and V. Dose, Solid State Commun. **60**, 237 (1986).

¹²Th. Fauster, R. Schneider, and H. Dürr, Phys. Rev. B **40**, 7981 (1989).

¹³M. Budke, V. Renken, H. Liebl, G. Rangelov, and M. Donath, Rev. Sci. Instrum. **78**, 083903 (2007).

¹⁴N. Nakajima, O. Morimoto, H. Kato, and Y. Sakisaka, Phys. Rev. B **67**, 041402(R) (2003).

¹⁵H. Nakajima, S. Pukird, W. Suraban, T. Saitoh, and A. Kakizaki, Surf. Rev. Lett. **9**, 861 (2002).

¹⁶S. Heinze, X. Nie, S. Blügel, and M. Weinert, Chem. Phys. Lett. **315**, 167 (1999).