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Surface electronic structure of Y(0001): A consistent picture

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The photoelectron spectrum of the (0001) surface of single-crystalline yttrium bulk samples is rich in structure from the surface state near the Fermi energy to a series of spectral features between 2 and 10 eV binding energies. Many of them appear on other rare-earth surfaces, e.g., Gd, Ho, Pr, and Er, as well. However, it is an unsolved puzzle that none of the observed features, except for the surface state at the Fermi energy, can be found in data from clean rare-earth thin films. While some of the additional features in the results from single-crystal surfaces were already attributed to impurities such as chlorine, oxygen, and hydrogen, the peak at −9.6 eV remains a source of speculation for more than 20 years now. In this Rapid Communication, we provide a consistent picture of the surface electronic structure of Y(0001), which explains all differences between the data obtained from single-crystal surfaces and thin films. We show that the peak at −9.6 eV, which was previously assigned to a well-ordered clean surface, is in fact due to the formation of ordered carbon compounds originating from impurities in the bulk material.

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Photoemission studies of (0001) surfaces of single-crystalline rare-earth bulk samples (Refs. 1 and 2, and references therein) show a variety of spectral features between 2 and 10 eV binding energies. Some of these peaks could already be attributed to impurities that naturally occur in rare-earth single crystals despite applying the best refinement techniques.[2–4] Typical impurities found are oxygen, chlorine, and hydrogen, leading to peaks at about −6, −7, and −4 eV, respectively.[5–8]

Additionally, on nominally clean single-crystal surfaces of Sc, Pr, Y, Gd, Tb, Ho, and Er, an intense spectral feature is found at binding energies of 9–10 eV. This peak was first observed on Gd(0001) (Ref. 9) and later studied on Y(0001) to exclude an admixture of emission from $4f$-derived bands.[10] A remarkable attribute of this peak is its suggested dependence on the degree of surface crystallographic order, which led to the acronym "SODS" (surface-order-dependent state) in the literature.[2] However, in the past 20 years, the origin of this peak remained a source of speculation. It was supposed that the peak is an intrinsic feature of the surface electronic structure of Y(0001) caused by a many body effect involving an unoccupied surface state.[10] However, it remains a mystery why the SODS was never observed on rare-earth thin films. In fact, clean thin films of Y(0001) or Gd(0001) only show a surface state at about 0.2 eV below the Fermi energy, a bulk state at about −2 eV (Refs. 5 and 8), and the Gd $4f$ emission at −8.5 eV. If one recognizes that the surface state in the single-crystal data of Y(0001) (Ref. 10) shows up at significantly higher binding energy, namely, at −0.4 eV, one can even say that there is hardly any similarity between single-crystal and thin-film photoemission data obtained from Y(0001). Still, no experiment could prove so far that the SODS originates from contaminations on the surface. In addition, one has to keep in mind that thin films of Y and Gd are usually grown on W(110) or Mo(110), substrates with considerably different lattice constants than the overlayers. This leads to defects and/or dislocation lines arising from the strain caused by the lattice mismatch, which might be the reason for the SODS not to show up in the thin-film data.

Our contribution to this long-lasting discrepancy is to give a consistent picture of the surface electronic structure of Y(0001), the surface of a single-crystalline bulk sample, that solves the remaining inconsistencies with the thin-film data. We show that photoemission data obtained from a Y(0001) single crystal perfectly matches the thin-film data if the sample is held at a temperature of 1100 K during the measurement. Further, we provide evidence that the SODS is in fact due to the formation of carbon compounds at elevated temperatures, e.g., upon annealing. These carbon compounds are caused by the presence of carbon and oxygen impurities in the bulk material. This results in a stable 1×1 structure on the yttrium surface and pretends an excellent crystallographic order, although the surface is contaminated.

The experiments were performed in a multichamber ultrahigh-vacuum (UHV) system that is described in detail elsewhere.[11] Briefly, it consists of several UHV chambers with a base pressure of less than 3×10^{-11} mbar equipped with a variety of techniques including low-energy electron diffraction, Auger electron spectroscopy (AES), and ultraviolet photoelectron spectroscopy (UPS). The Y(0001) single crystal was grown by Ames National Laboratory and was cleaned for more than 50 h under UHV conditions. The cleaning process consisted of repeated sputter-annealing cycles with Ar ion sputtering at 1 keV for 10 min and subsequent annealing at 1100 K for 30 min. Annealing temperatures lower than 1000 K did not result in a depletion of Cl impurities in the near surface region. Beside Cl, other impurities such as O and C were identified by AES. At the end of the cleaning process, all impurities were reduced down to the detection limit of our AES system. However, it should be noted that such AES results were obtained only for sample temperatures still well above room temperature.

UPS data of a nominally clean Y(0001) single crystal at room temperature after the described cleaning cycles are presented as open dots in Fig. 1 for a photon energy of 40.8 eV (He II). The dominating spectral feature is a peak at about −6 eV, which is associated with oxygen contamination. At first sight, this is very surprising because no oxygen was

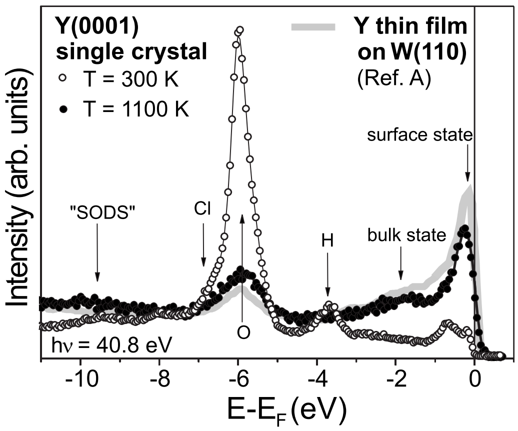

FIG. 1. Photoemission spectra of a yttrium single crystal with (0001) surface at 300 K (open dots) and at 1100 K (filled dots). The gray line represents photoemission data obtained from a thin yttrium film grown on W(110) (taken from Ref. 5).

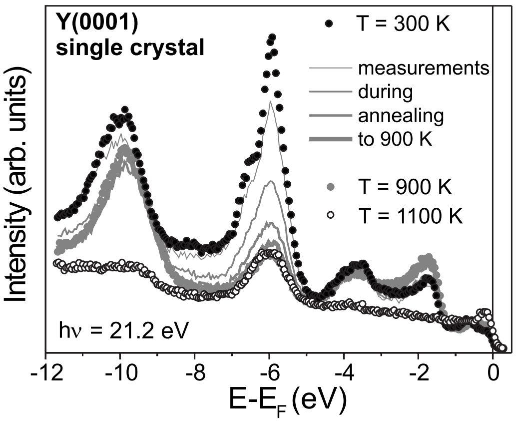

FIG. 2. Photoemission spectra of a Y(0001) single-crystal surface taken at room temperature (black dots) during the annealing process from 300 to 900 K (gray lines), at 900 K (gray dots), and at 1100 K (open dots).

detected with AES on the warm surface after annealing. Beside the dominating oxygen peak, a hydrogen-induced peak can be seen at about −4 eV. The surface state at the Fermi energy appears only with small intensity. Additionally, there is a feature at −0.75 eV which we associate with the surface state being shifted in binding energy due to the presence of oxygen. A similar behavior was observed on Gd(0001) and Lu(0001).[6] The fact that the Y surface state and the oxygen-induced surface state are simultaneously observed on the same surface reflects the localized character of the *d*-like surface state.

The SODS is expected at −9.6 eV but hardly visible in the spectrum, as shown in Fig. 1. It should be mentioned that the SODS intensity strongly depends on the history of cleaning cycles performed before a UPS measurement. Therefore, in the following, we will discuss only relative changes in the SODS feature rather than its absolute intensity. As an additional observation, we found that the SODS increased with time, especially when the gas discharge lamp used as the photon source was operated at high discharge currents necessary for operation in the He II regime. This led us quite early to the assumption that the SODS might be related to surface contamination.

The black dots in Fig. 1 represent photoemission data from the same Y(0001) surface but at a temperature of 1100 K. The oxygen peak at −6 eV is strongly reduced and the SODS as well as the H-induced feature at −4 eV are completely gone. The same is true for the oxygen-induced surface state at −0.75 eV that is no longer visible in the data obtained from the hot surface. However, the "true" yttrium surface state shows up with high intensity at about −0.2 eV. The data are in perfect agreement with data obtained from a thin Y(0001) film grown on W(110) (gray line) taken from Blyth *et al.*[5]

To get a better view of what happens when the Y(0001) single crystal is heated, we took a series of photoemission spectra during the annealing process from room temperature to 900 K. The results are presented in Fig. 2. For intensity reasons, the experiment was performed at a photon energy of 21.2 eV (He I). The open dots show UPS data obtained at room temperature. Note that the peak intensities relative to each other are different from those in Fig. 1 due to the different excitation energies. As already mentioned, the intensity of the SODS strongly depends on the history of cleaning cycles. In the measurements shown in Fig. 2, it shows up with rather high intensity. We found a correlation between an increased carbon signal in AES and UPS measurements with an intense SODS feature.

The gray lines in Fig. 2 represent UPS data taken during the annealing process from 300 to 900 K. Clearly, the oxygen peak is gradually reduced with rising sample temperature. Additionally, the SODS shifts by about 200 meV to lower binding energy. Further, a peak at −2 eV, which was previously associated to a bulk transition, slightly gains intensity upon heating. The gray dots show data with the sample at a constant temperature of 900 K.

In the case of further heating up to 1100 K, all spectral features almost completely vanish (open dots), except the oxygen peak at −6 eV. Simultaneously, the surface state at −0.2 eV strongly gains intensity. The result is a spectrum similar to the one shown in Fig. 1, except for a lower intensity of the surface state as a consequence of the different photon energy.

So far, we assumed that the SODS is correlated to contamination and we learned how to remove it at high temperatures. To further explore the origin of the so-called SODS, we performed an adsorption experiment with CO_2. The results are shown in Fig. 3. For a sample temperature of 300 K [Fig. 3(a)], the oxygen peak at −6 eV is rapidly gaining intensity and width with increasing CO_2 exposure. Additionally, the peak at −2 eV increases and a new feature at −3 eV appears. This behavior is similar to Gd(0001), where a two-peak structure shows up around −2 to −3 eV upon CO exposure, indicative of the formation of stable carbonates at the surface.[7,12] Due to the dominant, broad oxygen peak and the changing background intensity, the behavior of the SODS at −10 eV cannot be conclusively evaluated from a CO_2-adsorption experiment at 300 K.

When the same experiment is performed at a sample temperature of 900 K [Fig. 3(b)], the situation is very different.

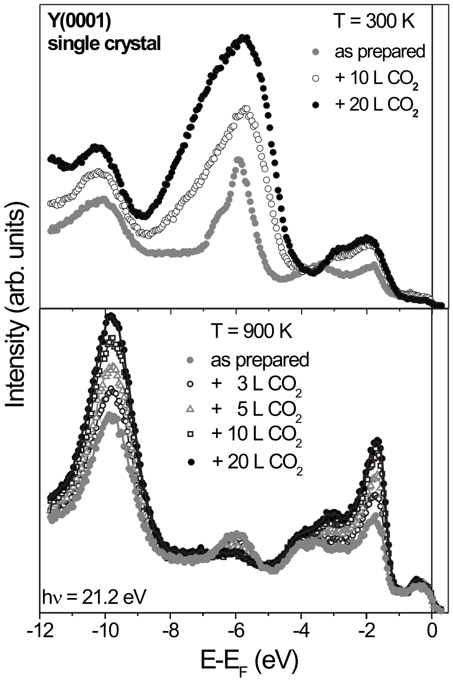

FIG. 3. Photoemission spectra of adsorption experiments with CO_2 performed on the Y(0001) single crystal at two sample temperatures, 300 and 900 K. The filled gray dots indicate the spectra as obtained from the nominally clean sample. The open dots, triangles, and squares show spectra for increasing CO_2 exposure. The filled black dots represent an exposure of 20 L CO_2 ($1\ \mathrm{L} = 1.33 \times 10^{-4}$ Pa s).

At this temperature, the oxygen peak at −6 eV does not gain intensity upon adsorption of CO_2. In contrast, both the peak at −2 eV and the SODS gain intensity. This finally proves that the SODS is related to the formation of carbon compounds on the surface and is not, as suspected for more than 20 years, an intrinsic property of the Y surface. When the sample is cooled down to room temperature, the spectrum [black dots in Fig. 3(b)] remains unchanged for days under UHV conditions, except for a slow rise of the oxygen peak. This proves that a stable, inert surface is obtained.

Figure 4 compares the Y(0001) single-crystal data from the literature (gray line)[10] with our results for 20 L CO_2 on Y(0001) (open and black dots). Except for small quantitative differences in the oxygen-induced intensity at −6 eV and the H-induced intensity at −4 eV, the spectra are qualitatively identical. As mentioned above, the presence of the oxygen peak at −6 eV is accompanied by a small peak shift of the SODS to higher binding energies. This can again be seen by comparing the data obtained at sample temperatures of 900 K (black dots) and 300 K (open dots).

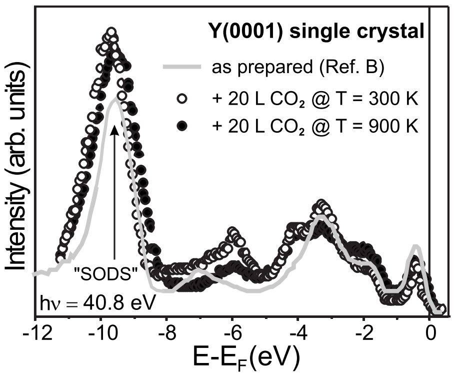

FIG. 4. Photoemission spectra of a Y(0001) single-crystal surface taken from Ref. 10 in comparison with our results from 20 L CO_2 on Y(0001) at a temperature of 900 K (black dots) and after cooling down to 300 K (open dots).

In this Rapid Communication, our experiments on Y(0001) provide evidence that the "surface-order-dependent state" at about −10 eV, observed in photoemission spectra from many rare-earth single crystals, is in fact due to stable carbon compounds. This terminates a longstanding conflict between experiments performed on single crystals and on thin films. We proved that heating the Y single crystal leads to desorption of contaminants from the (0001) surface and to identical UPS spectra as obtained from thin films. In summary, the surface-state emission just below the Fermi level and a bulk-derived feature at −2 eV are the only spectral features in photoemission of Y(0001) that originate from a clean surface.

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