Effects of impurities on Tamm-like lanthanide-metal surface states

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The effects of isolated residual-gas adsorbates on the local electronic structure of the Dy(0001) surface were spatially mapped by scanning tunneling microscopy and spectroscopy at 12 K. Less than 15 Å away from an adsorbate, a strong reduction of the intensity and a significant increase of the width of the majority component of the surface state due to impurity scattering were observed, with essentially no change of the minority component; this reflects a high lateral localization of the Tamm-like surface state. Furthermore, an adsorbate-induced state was found that behaves metastable.

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One challenge in surface science has always been the study of pristine surfaces, and improvements in ultrahigh vacuum technology and surface preparation techniques have led to continuous progress towards this goal. The absence of surface impurities is particularly important when linewidths of surface states, which are determined by hot-electron and hole dynamics, i.e. by the lifetimes of excited electronic states, are spectroscopically monitored by hot-electron and hole dynamics, i.e. by the lifetime when linewidths of surface states, which are determined by hot-electron and hole dynamics, i.e. by the lifetime.

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The role of clean surfaces is best reflected in the development of spectroscopic results on noble-metal surfaces over the recent decades. Problems due to surface impurities are particularly severe for surface-integrating methods, like angle-resolved photoelectron spectroscopy (ARPES), where it is almost impossible to monitor the properties of pristine surfaces since even a single adsorbate influences the electronic lifetime of the surface state over distances of a few hundred Å.

It has been shown that laterally localized probes, such as scanning tunneling microscopy (STM) and spectroscopy (STS), can reliably measure linewidths on pristine parts of a surface. Even though a careful ARPES study has been able to reproduce the STS results on noble-metal surfaces, we consider this an exception due to these rather inert metals. In case of more reactive surfaces, such as those of the transition metals, a comparable surface cleanliness has not been reached so far.

Recently, we demonstrated that STS is well suited for studying the dynamics of excited surface states on lanthanide metals. The ability to identify and select locally clean surface areas for spectroscopic studies is of utmost importance for these highly reactive metals. However, a comparison of linewidths on Gd(0001) determined by ARPES and STS and time-resolved photoemission calls for further studies regarding the role of defect-scattering contributions on the widths of surface states. Therefore, we have studied the local influence of residual-gas adsorbates on the electronic structure of the (0001) surface of dysprosium metal (Dy) by STM and STS. We discuss the induced changes in the majority and the minority components of the surface state, and we report on the appearance of a novel adsorbate-induced state. The lateral extensions of the adsorbate-induced features provide quantitative information on the localization of the Tamm-like Dy(0001) surface state with $d_{2z}$-symmetry. The results are compared with the properties of the laterally more extended $sp$-like Shockley-surface states on noble metals.

The experiments were performed in ultrahigh vacuum (UHV, base pressure $< 3 \times 10^{-11}$ mbar) with a home-built low-temperature STM operated at 12 K. A 30-monolayer (ML) thick Dy film was deposited in situ by electron-beam evaporation of 99.99% pure Dy metal from a Ta crucible onto a clean W(110) single crystal kept at room temperature. With thoroughly degassed evaporators, the vacuum stayed below $5 \times 10^{-10}$ mbar during deposition. Subsequent annealing of the film to $\approx 800$ K led to a smooth hcp(0001) surface. STS spectra were measured with fixed tip position and switched-off feedback control using standard lock-in techniques (modulation amplitude 1 mV (rms), modulation frequency $\approx 360$ Hz).

As is well known, the differential conductivity, $dI/dU$, is approximately proportional to the local density of states (LDOS) of the surface. Here, $I$ is the tunneling current and $U$ the sample bias voltage. Typical acquisition times for a single spectrum ranged from 10 seconds to 2 minutes. All spectra are raw data, i.e., the mutual normalization depends only on the feedback parameters prior to opening the feedback loop (here $\approx 300$ mV, 1 nA). The sample bias was chosen such that tunneling into bulk states dominates. The systematic error of this normalization can be estimated to $\approx 10\%$ by comparing the background intensities (e.g. at $U < -200$ mV).

Fig. displays STM images of a terrace on the Dy(0001) surface with residual-gas adsorbates of $\approx 0.01$ ML nominal coverage. The apparent height of the adsorbates in the STM images is bias dependent: Below $-100$ mV, they appear as depressions in the Dy film, while above $-100$ mV, they show up as protrusions. Even though we cannot identify with certainty the nature of these adsorbates, there is strong evidence that they are either atomic or molecular hydrogen, which is by far the dominant impurity in well-degassed lanthanide-metal evaporators. Furthermore, quadrupole mass spectroscopy during Dy deposition revealed that the increase in pressure is almost completely caused by a rising partial pressure of hydrogen. In addition, hydrogen is known to
cause a contrast reversal in STM images of Gd(0001).

The observed bias dependence of the apparent height of the adsorbates can be understood by comparing STS spectra on a clean part of the Dy surface with those on adsorbates. Fig. 2 displays representative STS spectra on a clean part of the Dy surface with those on adsorbates. Fig. 3 summarizes the lateral dependence of the fit parameters, with the top panel displaying a linescan of the topography through an adsorbate. A fit with a Gaussian results in a width of $9 \pm 1$ Å (FWHM). In the following, the minimum of this topographical cross section is defined as the center of the adsorbate. The intensity of the adsorbate-induced state as a function of lateral displacement (green triangles in the bottom panel) is also well described by a Gaussian, with its maximum at the center of the adsorbate; its width is $8.3 \pm 0.5$ Å (FWHM), identical to that of the topography.

The presence of the adsorbate significantly alters the spectrum: The LDOS of the MAC is halved, while its width is doubled. In addition, a new peak appears that is only present close to an adsorbate. This adsorbate-induced state can be described by a Lorentzian function. The resulting fit curves are shown as solid lines in Fig. 2. It turns out that the only spectral features that are systematically altered by the adsorbate are intensity and width of the MAC as well as the intensity of the adsorbate-induced state, while both position and width of the latter remain unchanged. As discussed above, the MIC remains essentially unchanged.

On the other hand, the lateral change of the linewidth of the MAC (red squares) is again comparable to the behavior of the other parameters, with a width of $12 \pm 2$ Å (FWHM). At the adsorbate, the linewidth is $\Gamma = 39 \pm 2$ meV, i.e., twice as large as the intrinsic linewidth on the pristine surface ($\Gamma = 19 \pm 5$ meV). Since $\Gamma$ corresponds to the sum of the intrinsic and the defect-scattering linewidth, the latter can be calculated as $\Gamma_{\text{def}} = \Gamma - \Gamma_0 = 20 \pm 6$ meV; it shows that defect scattering doubles the inverse lifetime of the MAC. We note that already at rather small distances from the adsorbate ($> 15$ Å), the measured linewidth equals the intrinsic linewidth of the defect-free surface.

In summary, the spectroscopic features close to an ad-
FIG. 2: (Color online) Local tunneling spectra of a Dy(0001) surface ≥ 15 Å away from any adsorbate (top) and at various distances relative to an adsorbate (marked by arrows in the STM image). The intensity of the MAC (at ≃ −100 mV) is halved on an adsorbate, while the width is approximately doubled. In addition, an adsorbate-induced state appears at U ≃ 100 meV. The solid lines are results of the fit analysis.

sorbate are found to be influenced over lateral dimensions that correspond to the extension of the adsorbate as reflected in the topographical cross section (see Fig. 3, top panel), i.e. ≃ 10 Å. These dimensions reflect the localization of the surface state and are in conformity with the very flat dispersions of the surface states on these closed-packed lanthanide-metal surfaces corresponding to large effective masses |m*/m| > 5.6,7 If we neglect the contribution of the adsorbate and ascribe the observed lateral changes to the surface state alone, we arrive at the conclusion that the overlap of d2z-like orbitals of two surface atoms at a distance larger than three lattice constants (with a = 3.59 Å) must be negligibly small. This supports a recent finding that the exchange splittings of lanthanide-metal surface states deviate from the overall bulk magnetizations.14,15 Due to high spatial localization, these Tamm-like surface states are more sensitive to short-range than to long-range magnetic order.

Most of the described observations can be generalized to the series of lanthanide metals as a whole. While the adsorbate-induced state was observed solely on Dy(0001), all the other lanthanide metals that have been studied so far (cf. Ref. 17) exhibit analogous surface defects with comparable effects on the MAC. On the (0001) surfaces of Gd, Tb, and Er, e.g., adsorbates were found that exhibit contrast reversals in the apparent heights

FIG. 3: (Color online) Top: Topographical cross section through a single adsorbate at U = −300 mV. Bottom: Lateral dependences of the width (Dy↑, red squares) and the dI/dU intensity of the MAC (blue circles) and comparison with the dI/dU intensity of the adsorbate-induced state (green triangles).

of STM images at bias voltages of −200 mV, −100 mV, and −50 mV, respectively. In all three cases, these voltages correspond to the positions of the respective MACs, and the contrast change can again be explained by a reduction of the surface-state intensity and a simultaneous broadening of the peak. On Lu(0001), adsorbates were identified that also reduce and broaden the surface state. However, a contrast reversal could not be observed in this case, presumably due to the fact that the surface state in this case is directly at EF.13 In all cases, the lateral extensions of the adsorbates were found to be between 9 and 12 Å.

A comparison with Shockley-type surface states on noble-metal surfaces reveals that the lateral extensions of these states are an order of magnitude larger than those of Tamm-like surface states on lanthanide-metal surfaces. The explanation of this significant difference is simple: The lifetimes, τ, of surface states on lanthanide metals are much shorter than those on noble metals. Furthermore, the group velocities, vg, of electrons or holes in surface bands are smaller for lanthanide-metal surfaces than for noble-metal surfaces due to larger effective masses. Since the mean-free path is the product of these two quantities, i.e., λ = vgτ, it is dramatically reduced in case of the lanthanide metals. Whereas electrons and holes in noble-metal surface states are considered to be good approximations for a quasi-free electron gas, the present results make it clear that this picture breaks down for the surface states on lanthanide metals. Their small λ also explains why STM images of lanthanide-metal surfaces do not exhibit standing-wave patterns typical for the (111) surfaces of noble metals.

The strong effects of an adsorbate on the linewidth of the MAC explain why in case of Gd(0001) even high-resolution ARPES measurements led to much larger
Even though the origin for these jumps is unknown, it is obvious to assume that they are caused by the influence of the tunneling current on the adsorbate state itself, e.g. by electronically or vibronically exciting the adsorbate or by charging it. Then, no further electrons can tunnel into this state, and the LDOS feature of the adsorbate-induced state disappears in STS. As the jumps occur preferentially around 100 mV and no dependence on the tip-sample distance was observed, we infer that a tunneling electron must have sufficient energy to switch the adsorbate to an excited state. Usually, each jump-down of the adsorbate state (i.e., when it disappears in the spectrum) is followed by an upward jump (i.e., when the state reappears); this indicates that the excited state is metastable: within the timescale of a few seconds, the adsorbate relaxes to its ground state. Consistently, STM images at a bias of 100 mV have a three times larger noise along the slow scanning direction with respect to images taken below 10 mV or above 1 V.

Further studies are necessary to clarify the exact nature of the adsorbates (atomic or molecular hydrogen), e.g. by experiments with controlled deposition of various gases on clean Dy(0001) surfaces as well as by experiments aiming to clarify the nature of the switching process. It will be interesting to check whether this switching behavior can be influenced or controlled in a reliable way.

Note that the lifetimes of these excitations seem to be of the order of 1 to 10 seconds, which is unusually long.

In summary, we have shown that single residual-gas impurities (most probably hydrogen) on Dy(0001) exert strong influences on the LDOS as well as on the linewidths of the occupied MAC. In addition, a metastable adsorbate-induced state appears in the STS spectra. All of these features are confined within 10 Å (Gaussian FWHM) around the adsorbate, which is a direct measure of the spatial extension of the surface state itself. This confirms recent studies of lanthanide-metal surfaces, which could only be understood by assuming that the surface states are fairly localized.

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