Indication of a non-magnetic surface layer on a magnetic single crystal

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The structural and electronic properties of the surfaces of Sm(0001) and Eu/Gd(0001) were studied by scanning tunneling microscopy and spectroscopy at temperatures between 10 and 110 K. In both systems, an unoccupied surface state is observed that exhibits a temperature-dependent splitting into two states for Eu/Gd(0001), while it is unmixed on Sm(0001). This strongly indicates that the trivalent outermost surface layer of Sm(0001) is non-magnetic despite the antiferromagnetic trivalent Sm substrate. These findings open new opportunities for magnetic studies of ultra-thin Sm films.

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The magnetic properties of trivalent lanthanide (Ln) metal surfaces have been the subject of some controversy in the past. For Gd(0001), e.g., the possibility of an enhanced surface Curie temperature ($T_C$) and an orientation of surface magnetization different from the bulk has been debated. Some of this behavior could be due to the magnetic exchange splitting of surface states that does not follow a simple Stoner-like behavior but is also influenced by spin mixing and short-range magnetic order at higher temperatures $T > 293$ K. The situation is quite different for Sm metal, where a strong deviation of surface from bulk magnetism can be expected due to the well-known surface valence transition. While Sm in the bulk is trivalent and magnetic with an $6H_{5/2}$ ground state $[4f^5(6s5d)^2]$, the reduced coordination at the surface leads to a valence change to divalent Sm with a non-magnetic $7F_0$ ground state $[4f^6(6s5d)^2]$ of 22 %. This valence change is accompanied by a dramatic increase of the ionic radius by 22 % as well as a reconstruction of the Sm(0001) surface. Since Sm metal orders antiferromagnetically (AFM) in the bulk below $T_N = 106$ K, the question arises whether the outermost Sm(0001) surface layer is magnetic or non-magnetic below $T_N$.

The experimental setup consists of a single peak. This strongly indicates that the outermost surface layer of Sm metal is non-magnetic.

The experiments were performed in ultrahigh vacuum (base pressure $< 3 \times 10^{-11}$ mbar) with a home-built low-$T$ STM operated between 10 and 110 K. All Ln-metal films were deposited in situ by electron-beam evaporation of 99.99% pure metals from a Ta crucible onto a clean W(110) single crystal kept at room temperature (RT). The 10-ML-thick Sm films were not annealed upon deposition, since RT deposition readily leads to smooth films. For Eu/Gd(0001), first a 30-ML-thick Gd(0001) film was grown on W(110) and annealed to obtain a smooth, crystalline film, followed by deposition of about 1 ML Eu on the Gd film kept at RT. The samples were then transferred in UHV to the cryogenic STM. STS spectra were recorded with fixed tip position and switched-off feedback loop using standard lock-in techniques (modulation amplitude: 1 mV (rms), modulation frequency: $\sim 360$ Hz). As is well known, the differential conductivity, $dI/dV$, is approximately proportional to the local density of states of the surface ($I = $ tunneling current; $V = $ sample bias voltage).

Fig. 1(a) shows the topography of a 10-ML Sm(0001) film. The surface is atomically flat with ML-high terraces. The close-up view on a terrace shows the hexagonal Moiré pattern of the well-known surface reconstruction caused by the larger radius of divalent Sm surface atoms. The structure was first identified by low-energy electron diffraction as a $(5 \times 5)$ reconstruction (leading to a unit-cell size of 1.81 nm). A recent combined x-ray diffraction, STM, and density-functional-theory study showed that the reconstruction is actually incommensurate with an approximate $(11 \times 11)$ unit cell [red diamond in Fig. 1(a)]. Thus, the Moiré pattern corresponds to an effective $(5.5 \times 5.5)$ unit cell with a size of 2.00 nm; we observe a size of $1.91 \pm 0.09$ nm [blue dashed diamond in Fig. 1(a)], in good agreement with Ref. [8].

In comparison, Fig. 1(b) shows STM images of 1 ML Eu/Gd(0001), with a Moiré pattern very similar to that of Sm(0001). Previously, two different commensurate surface reconstructions have been reported, $(6 \times 6)$ and $(5 \times 5)$ unit cells. It will be interesting to see whether Eu/Gd(0001) exhibits an analogous surface reconstruction but differs in its local $4f$ moments; both Eu and Gd have non-vanishing $4f$ moments ($S = J = 7/2$) and couple ferromagnetically (FM) below $T_C = 293$ K. The outermost divalent Eu layer exhibits also a $d$-like surface state. While we observe a $T$-dependent splitting of the Eu/Gd(0001) surface state, the analogous surface state on Sm(0001) consists of a single peak. This strongly indicates that the outermost surface layer of Sm metal is non-magnetic.
The Tamm-like surface states with $W$ can therefore rule out that this strong spectral feature is caused by a bulk band. Instead, it is reminiscent of the Tamm-like surface states with $d_{x^2}$ symmetry observed for other Ln-metal surfaces [2, 12, 19, 20]. We conclude that the observed peak stems from a surface state of the divalent Sm(0001) surface. Note that a single peak is observed in the present case, quite similar to the surface states on non-magnetic trivalent La(0001) and Lu(0001). Furthermore, STS at various $T$ shows – apart from the expected slight increase of width with increasing $T$ – no significant change of this peak, particularly no indication of magnetic exchange splitting (see below) [20].

In contrast, the STS spectrum of 1 ML Eu/Gd(0001) (Fig. 3) is dominated by two peaks at about 0.1 eV and 0.4 eV above $E_F$, respectively, again showing no dependence on tip position. The two peaks are also within the gap in the center of the projected surface BZ of Gd(0001), reminiscent of the exchange-split surface states of magnetic trivalent Ln metals [20]. In order to check this, we studied the $T$-dependence of the peak positions. With increasing $T$, the peak at 0.1 eV clearly shifts to higher energies, while the peak at 0.4 eV shifts down towards $E_F$, reflecting a decrease of the energy separation of the two peaks with increasing $T$. This strongly supports an interpretation on the basis of magnetic exchange splitting into two (majority- and minority-spin) components separated by $\Delta_{\text{ex}}$. Fig. 4 displays $\Delta_{\text{ex}}$ as a function of $T$. Within the studied temperature range, $\Delta_{\text{ex}}$ decreases approximately linearly with increasing $T$, with a maximum splitting $\Delta_{\text{ex}}(T = 0) = 342 \pm 2$ meV. Extrapolation towards higher $T$ indicates that the splitting would vanish at $273 \pm 20$ K, which is close to the $T_C$ of the FM Gd substrate. We note, however, that the exchange splitting is not expected to decrease linearly with $T$ at higher $T$, and it might not decrease to zero either [3].

To summarize the observations, only one peak can be observed in the STS spectra of Sm(0001), with no significant $T$ dependence, whereas the Eu/Gd(0001) surface exhibits two peaks, with a separation that decreases with increasing $T$. All peaks lie within a local band gap in the center of the projected surface BZs of Sm(0001) and Gd(0001), respectively. We therefore interpret these resonances as signatures of an unoccupied surface state of the divalent Ln-metal surface layers. Similar to the scenario of trivalent Ln metals, the narrow, almost Lorentzian-like peak shapes indicate weak parallel dispersions and hence a relatively high spatial localization of these surface states [13, 18].

The exchange splitting of the Eu/Gd(0001) surface state is caused by FM coupling of the Eu surface layer to the Gd(0001) substrate. The maximum exchange splitting of 0.34 eV is about half as large as that observed for the surface state on pristine Gd(0001), although both surfaces have a spin $S = 7/2$. This can be understood by a reduced spin polarization of the Eu layer relative to the Gd substrate [11, 12]. Additionally, the $\approx 20\%$ larger nearest-neighbor distance of Eu-surface atoms should lead to a smaller interatomic overlap, which should further reduce the exchange splitting.

In previous studies it was shown that the ground-state exchange splitting of electronic bands in the Ln metals

![Image](image-url)
FIG. 2: (Color online) STS spectra of Sm(0001): the large-bias spectrum (top) is dominated by a single peak centered at 0.25 eV above \( E_F \). We interpret this as an unoccupied surface state of the divalent Sm(0001) surface layer.

Although the width of the single STS peak increases slightly to 0.27±0.01 eV at 108 K by thermal effects, while it should decrease towards \( T_N \) if magnetic splitting would play a role. The observed increase in peak width is fully compatible with expectations from both STS data for other Ln-metal surface states and theory \[14, 23\]. Note also that a doubling of the width of the STS peak can be understood if we consider that the spin is not well-defined for the non-magnetic Sm surface state when an excited electron can scatter into both majority- and minority-band states of the bulk electronic structure, whereas in case of Eu/Gd, the (well-defined) spin is conserved. For Sm, this would double the number of available final states and in turn the inverse lifetime (proportional to the peak width). All these considerations support our conclusion that the topmost divalent Sm surface layer on Sm(0001) is non-magnetic despite the magnetically ordered trivalent Sm substrate.

The described observations and conclusions should open new opportunities for atomic-scale local probe stud-
FIG. 4: (Color online) Exchange splitting $\Delta_{\text{ex}}$ of the Eu/Gd(0001) surface state as a function of $T$, decreasing linearly with $T$ in the studied $T$ range.

eties of mixed-valent ultra-thin Sm films (see Ref. [24]). Through the absence or presence of a $T$-dependent exchange splitting, it should be possible to determine the valence state in Sm films. Photoemission experiments on ultra-thin Sm films revealed such valence changes as a function of nominal film thickness that might now be analyzed with high lateral resolution by low-$T$ STM/STS.

It is expected that particularly the combination of high energy resolution with the high lateral resolution of STS will lead to new insight in the topic of mixed valency.

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