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Indication of a nonmagnetic 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 unsplit on Sm(0001). This strongly indicates that the divalent outermost surface layer of Sm(0001) is nonmagnetic despite the antiferromagnetic trivalent Sm substrate. These findings open opportunities for magnetic studies of ultrathin 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.[1] Some of these behaviors could be due to the magnetic exchange splitting of surface states that does not follow a simple Stoner-type behavior but is also influenced by spin mixing and short-range magnetic order at higher temperatures T.[2,3] More recent experiments have convincingly shown that the magnetic properties of most Ln-metal surfaces are essentially the same as in the bulk.[4,5]

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.[6] While Sm in the bulk is trivalent and magnetic with an $^6H_{5/2}$ ground state $[4f^5(6s5d)^3]$, the reduced coordination at the surface leads to a valence change to divalent Sm with a nonmagnetic $^7F_0$ ground state $[4f^6(6s5d)^2]$.[6,7] This valence change is accompanied by a dramatic increase in the ionic radius by 22% as well as a reconstruction of the Sm(0001) surface.[8,9] Since Sm metal orders antiferromagnetically in the bulk below $T_N=106$ K,[10] the question arises whether the outermost Sm(0001) surface layer is magnetic or nonmagnetic below T_N.

The present study shows that Sm(0001) exhibits a previously unnoticed d-like surface state that allows to address this question by studying its magnetic exchange splitting via scanning tunneling spectroscopy (STS) as a function of T ($10 \leq T \leq 110$ K). For comparison, a monolayer (ML) of Eu on Gd(0001) was studied that exhibits an analogous surface reconstruction but differs in its local $4f$ moments: both Eu and Gd have nonvanishing $4f$ moments ($S=J=7/2$) and couple ferromagnetically below $T_C=293$ K.[11,12] 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 nonmagnetic.

The experiments were performed in ultrahigh vacuum (base pressure $<3\times10^{-11}$ mbar) with a homebuilt low-T scanning tunneling microscope (STM) operated between 10 and 110 K.[13] 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.[9] 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,[14] 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: ≃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).

Figure 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

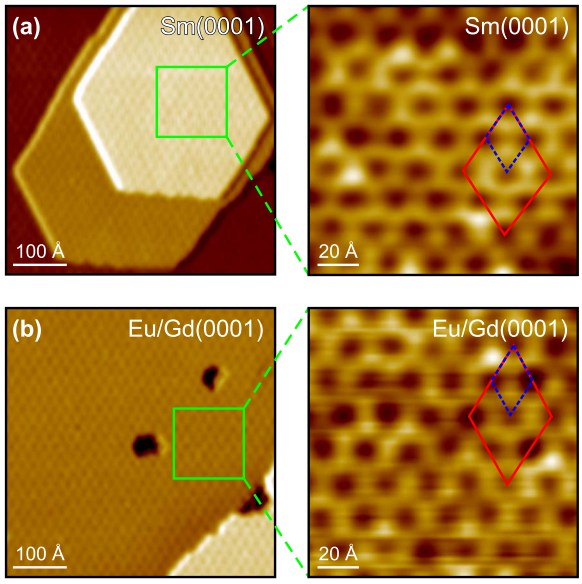

FIG. 1. (Color online) (a) STM images of 10 ML Sm(0001)/W(110). The close-up image reveals the hexagonal Moiré pattern of the (11×11) surface reconstruction (large red diamond), with an effective (5.5×5.5) unit cell in STM topography (dashed blue diamond). (b) STM images of 1 ML Eu/Gd(0001) reveal striking structural similarities. Small holes in the surface layer indicate that the amount of deposited Eu is slightly less than 1 ML.

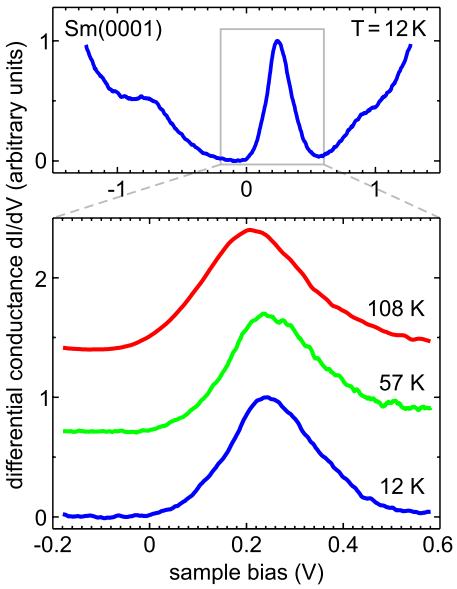

FIG. 2. (Color online) STS spectra of Sm(0001): the large-bias spectrum (top) is dominated by a single peak centered at 0.25 eV above E_F. We interpret this as an unoccupied surface state of the divalent Sm(0001) surface layer.

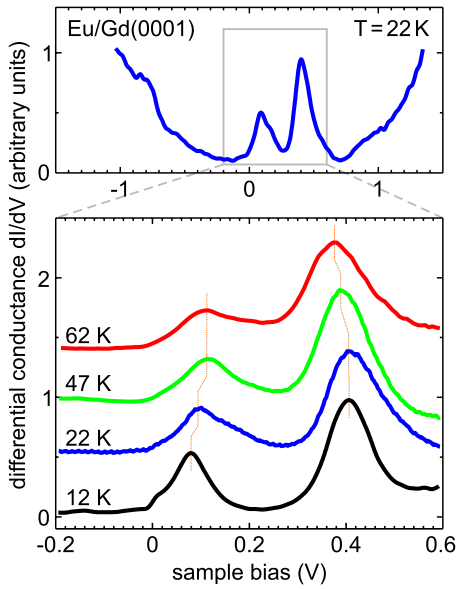

FIG. 3. (Color online) STS spectra of 1 ML Eu/Gd(0001): the large-bias spectrum (top) is dominated by two peaks at 0.1 and 0.4 eV above E_F, respectively. STS spectra at various T (bottom) show that the peak at 0.1 eV shifts to higher energies with increasing T, while the one at 0.4 eV shifts to lower energies, indicative of an exchange-split surface state.

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 (5×5) reconstruction (leading to a unit-cell size of 1.81 nm).[8] A recent combined x-ray diffraction, STM, and density-functional-theory study showed that the reconstruction is actually incommensurate with an approximate (11×11) unit cell [red diamond in Fig. 1(a)].[9] Thus, the Moiré pattern corresponds to an effective (5.5×5.5) unit cell with a size of 2.00 nm; we observe a size of 1.91 ± 0.09 nm [blue dashed diamond in Fig. 1(a)], in good agreement with Ref. 9.

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, (6×6) and (5×5),[11,15] which would lead to apparent Moiré-pattern sizes of 2.18 and 1.82 nm, respectively.[16] We find a size of 2.03 ± 0.06 nm (blue diamond), very similar to the Sm(0001) reconstruction. This Moiré pattern is not compatible within the limits of error with either one of the reported reconstructions. We suggest that the Eu monolayer is also best described by an (11×11) reconstruction (red diamond), with an effective (5.5×5.5) Moiré pattern (blue dashed diamond). This underlines that Sm(0001) and Eu/Gd(0001) are well suited for a direct comparison because both their surface reconstructions are identical and the lattice constants of the hexagonal bulk basal planes are the same for Sm(0001) and Gd(0001) (a=3.63 Å).[17]

The STS spectrum of Sm(0001) (Fig. 2) is dominated by a narrow resonance at 0.25 meV above E_F=0, independent of the tip position on the reconstruction pattern. At this energy, all trivalent Ln metals exhibit a gap in the center of the projected surface band structure, i.e., around the $\bar{\Gamma}$ point of the Brillouin zone (BZ).[18,19] We can therefore rule out that this strong spectral feature is caused by a bulk band. Instead, it is reminiscent of the Tamm-type surface states with d_{z^2} symmetry observed for other Ln-metal surfaces.[2,13,20,21] 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 nonmagnetic trivalent La(0001) and Lu(0001). Furthermore, STS at various T shows—apart from the expected slight increase in width with increasing T—no significant change of this peak, particularly no indication of magnetic exchange splitting (see below).[22]

In contrast, the STS spectrum of 1 ML Eu/Gd(0001) (Fig. 3) is dominated by *two* peaks at about 0.1 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.[21] 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 toward E_F, reflecting a decrease in 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 Δ_{ex}. Figure 4 displays Δ_{ex} as a function of T. Within the studied temperature range, Δ_{ex} decreases approximately linearly with increasing T, with a maximum splitting $\Delta_{ex}(T=0)=342\pm2$ meV. Extrapolation toward higher T indicates that the splitting would vanish at 273 ± 20 K, which is close to the T_C of the ferromagnetic (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]

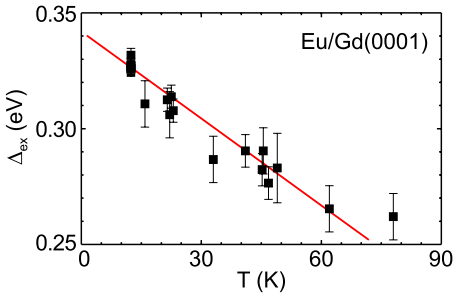

FIG. 4. (Color online) Exchange splitting Δ_{ex} of the Eu/Gd(0001) surface state as a function of T, decreasing linearly with T in the studied T range.

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-type peak shapes indicate weak parallel dispersions and hence a relatively high spatial localization of these surface states.[13,19]

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 $\simeq 20\%$ 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 does not depend on the total magnetic moment. Instead, it scales almost linearly with the $4f$ spin.[21,23,24] From the measured exchange splitting of Eu/Gd(0001), we can estimate the expected splitting for $S=3$ (the spin of divalent Sm) to about 0.29 eV. The Sm spectra in Fig. 2 do not allow for such a large splitting. One may argue that the exchange splitting of Sm might be much smaller, because bulk Sm is antiferromagnetic (AFM). However, within each of the closed-packed basal planes of the Sm(0001) crystal, the atomic moments are FM coupled, leading to a local spin polarization of the subsurface layer.[10] Note that a significant exchange splitting has also been observed for the surface state on the complex AFM Nd(0001).[3]

We also studied the possibility of describing the STS spectrum of Sm(0001) by two unresolved components since the single peak in the Sm spectrum has a width of 0.22 ± 0.01 eV [full width at half maximum (FWHM)] at 12 K; i.e., it is about twice as broad as the peaks in the Eu/Gd(0001) case. Satisfactory fits could only be obtained for a peak separation of less than 0.10 eV, i.e., less than half the exchange splitting expected for a magnetic divalent Sm surface. An argument against magnetic splitting is given by the fact that 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 toward 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.[3,14,25] 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 nonmagnetic Sm surface state when an excited electron can scatter into both majority- and minority-band states of the bulk electronic structure, whereas in the 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 nonmagnetic despite the magnetically ordered trivalent Sm substrate.

The described observations and conclusions should open opportunities for atomic-scale local probe studies of mixed-valent ultrathin Sm films (see Ref. 26). 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 ultrathin 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 insight in the topic of mixed valency.

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