Ferromagnetic coupling in Eu/Gd(0001) observed by spin-resolved photoelectron spectroscopy

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We report on a magnetic analysis by means of spin-resolved photoelectron spectroscopy of an atomically flat heteromagnetic rare-earth interface of 1 ML Eu/Gd(0001). The measurements reveal a high net Eu magnetization at low temperatures reflected by a spin polarization ~15% of the Eu $4f$ state. This magnetic Eu configuration is due to a strong ferromagnetic interlayer exchange coupling across the Eu/Gd interface which overcomes a weak negative intralayer coupling between Eu spins in the hexagonal two-dimensional lattice.

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In metallic rare-earth (RE) systems, due to the localized nature of the $4f$ electrons even in the solid phase, the exchange coupling is well described by the Heisenberg Hamiltonian $H=-JS_iS_j$, where J denotes the effective coupling strength between the localized $4f$ spin moments S_i and S_j. The exchange coupling in RE metals is indirect, mediated by the $6s$ and $5d$ conduction electrons.[1] Gadolinium, due to its localized $4f^7 {}^8S_{7/2}$ ground-state configuration, reveals with 292.7 K the highest Curie temperature among the rare-earth metals. The absence of orbital contributions to the magnetic moment implies that anisotropy interactions are weak and ferromagnetic order is almost exclusively caused by indirect exchange in the framework of the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. Divalent Eu metal, on the other hand, reveals the same ground-state configuration, but crystallizes in a body-centered cubic (bcc) structure with a nearest-neighbor distance of 3.96 Å that is by 10.6% larger than the 3.58 Å interatomic distance of hexagonal close-packed (hcp) Gd. Since additionally the density of states at the Fermi level in Eu is lower than in Gd due to its divalent character, a weaker indirect exchange interaction is manifested leading to antiferromagnetic order below a Néel temperature of T_N=90.5 K. An interesting question concerns the magnetic properties of systems consisting of both Eu and Gd atoms. Unfortunately, divalent and trivalent rare-earth metals do not intermix with each other due to their different ionic radii and bonding properties. For a monolayer Eu on Gd(0001), however, a close-packed (6×6) overstructure has been reported and ferromagnetic coupling of the Eu spins with respect to the Gd substrate has been concluded on the basis of the circular dichroism data.[2] On the other hand, published low-energy electron diffraction (LEED) patterns[3] of the same system reveal a (5×5) overstructure similar to the divalent Sm surface layer of trivalent Sm metal.[4] Yet, since the 1980s, little progress has been made in understanding the coupling in RE superlattices. This is mainly due to the high intermiscibility of all trivalent RE metals, which has prevented preparation of atomically sharp interfaces.[5,6] Thus, a magnetic analysis of atomic layers right at a RE interface has not even been attempted so far. As a consequence, the present-day picture of RE interfaces is still based on the first semiempirical model assuming ideally flat interfaces.[7]

In this contribution, we present spin-resolved photoemission (PE) data from a monolayer of Eu on Gd(0001) surface. In contrast to the earlier study,[2] a (4×4) overstructure was observed that in some cases was rotated by 30° with respect to the Gd(0001) surface. The spin-resolved measurements reveal at 130 K ferromagnetic coupling with respect to underlying Gd substrate with a net spin polarization of the Eu $4f$ emission of about 15%.

Spin-resolved photoelectron spectra (He II, $h\nu$=40.8 eV) were recorded at a temperature of 130 K in angle-integrated mode with a 180° hemispherical energy analyzer (SPECS PHOIBOS 150) combined with a 25 kV Mott detector for spin analysis (from SPECS). The experimental geometry allows us to measure simultaneously two orthogonal components of the spin polarization, P_x and P_y, that give direct information about the respective in-plane surface magnetization. The energy resolution was set to 100 meV. The light incident angle was 30° with respect to the sample surface, and the photoelectrons were collected around surface normal. Spin-resolved measurements were performed in magnetic remanence after having applied a magnetic field pulse of about 500 Oe along the in-plane $\langle 11\bar{2}0\rangle$ easy axis (x axis in experimental geometry) of the thin Gd(0001) film.[8] The experimental setup asymmetry was accounted for in the standard way by measuring spin-resolved spectra for two opposite directions of applied magnetic field.[9,10] The base pressure during the experiment was 8×10^{-11} mbars rising to 5×10^{-10} mbars during sample preparation. Thin Gd(0001) films, with a thickness of 100 Å as measured by a quartz microbalance, were grown epitaxially on W(110) at 200 K by deposition of high-purity Gd metal from an electron-beam heated W crucible. Subsequent annealing at 630 K led to a well-ordered Gd(0001) surface. In the same way, thin Eu films were deposited onto the Gd film at 200 K.

A method to establish a coverage of just one monolayer (1 ML) Eu on Gd is based on the considerably higher cohesive energy between the divalent Eu and the trivalent Gd substrate as compared to the respective quantity between Eu atoms in the second layer. Thus, adsorbing excess amounts of Eu onto well-ordered Gd(0001) and subsequent annealing to 620 K should result in 1 ML Eu/Gd(0001). As stated in a previous study[2] this procedure allows one to prepare the system with high accuracy (1 ± 0.05 ML). Additionally, the annealing process leads to structural ordering of the overlayer,

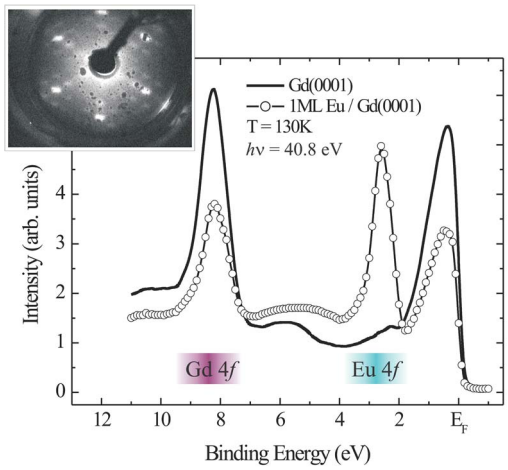

FIG. 1. (Color online) $4f$ photoemission spectrum of 1 ML Eu/Gd(0001). The same $4f^7$ ground states of Eu and Gd give rise to the same ^7F_J PE multiplets, which are well separated by approximately 6 eV. The small O $2p$ signal visible at around 6 eV binding energy corresponds to approximately 0.05 ML of oxygen contaminations. Inset shows the LEED pattern for the 1 ML Eu/Gd(0001) system obtained at the energy of primary electron beam of 50 eV.

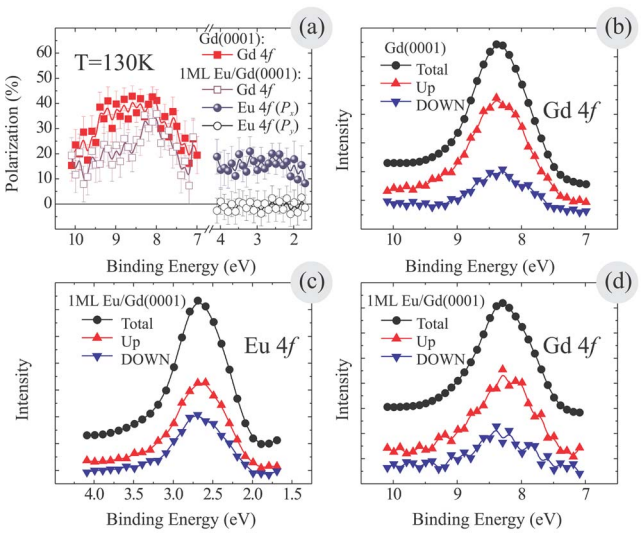

FIG. 2. (Color online) (a) Spin polarization as a function of binding energy of $4f$ photoemission signals of Gd (squares) and Eu (circles) in the Gd(0001) and 1 ML Eu/Gd(0001) systems. (b) Spin-resolved $4f$ photoelectron spectrum of the clean Gd(0001) surface. (c) and (d) Spin-resolved $4f$ photoelectron spectra of Eu and Gd, respectively, in the 1 ML Eu/Gd(0001) system. All spin-polarization plots and spin-resolved spectra are presented for $T = 130$ K.

and formation of a (6×6) overstructure was reported corresponding to an expansion of the Eu-Eu nearest-neighbor distance by 7% as compared to bulk bcc structure Eu metal. On the other hand, published LEED data of the same system reveal a (5×5) overstructure[3] similar to one observed for the (0001) surface of trivalent Sm metal at a temperature of 80 K:[4] There, Sm atoms undergo a surface valence transition to the divalent state and do not fit to the lattice of the trivalent bulk. For Sm, a dissapearence of the superstructure in the LEED pattern was observed at room temperature and attributed to lateral movements of the surface atoms. A similar effect was reported for Eu/Gd(0001). In case of the (5×5) structure the relative increase of the Eu-Eu interatomic distance with respect to Eu bulk amounts to 12.5% instead of 7%.[2] In the present study, a (4×4) superstructure was obtained by the growth procedure described above as demonstrated by the LEED pattern shown in the inset of Fig. 1. In some cases, even a rotation of this superstructure by 30° was observed. Assuming a simple hexagonal arrangement of the Eu atoms at the surface, this structure corresponds to an increase of the Eu-Eu nearest-neighbor distance of 20.5% as compared to bulk Eu metal and, thus, to a considerably lower surface density of Eu atoms as compared to the results of Ref. 2. This would imply that the Eu coverage at the surface depends critically on the temperature and annealing time and the proposed preparation method is not as "safe" as reported. On the other hand, it may also be possible that the assumed two-dimensional hexagonal-packed structure is not valid and the observed superstructures are related to the quality of the Gd substrate. Further structural investigations of this system, e.g., by scanning tunneling microscopy (STM) are, therefore, necessary.

In the elemental bulk lattice (bcc) structure, Eu $4f$ spins reveal a helical antiferromagnetic order below T_N=90.5 K, with interlayer-turn angles near 50° and all spins parallel within (100) planes.[11] At the temperature applied in the present study (130 K) bulk Eu behaves paramagnetically, and possible magnetic ordering at the interface to Gd should be dominated by Eu-Gd interactions, and, thus, only weakly dependent of the actual structure of the Eu film.

PE spectra of the Gd(0001) surface and the 1 ML Eu/Gd(0001) system presented in Fig. 1 show the $4f$ PE signal of both elements reflecting the same (not resolved) ^7F_J final-state multiplet resulting from their common $4f^7$ ground state. The $4f$ PE signals of Eu and Gd are clearly separated from each other by about 6 eV which makes it easy to resolve the signals of the two elements at the interface. At the used photon energy of 40.8 eV the experiment probes mainly the Eu surface and the two adjacent Gd layers, leading to similar $4f$ PE intensities for the Eu adlayer and the Gd substrate.

Spin-resolved photoelectron experiments were carried out both for the pure Gd(0001) surface and the 1 ML Eu/Gd(0001) interface. The results are shown in Fig. 2; 2(a) spin polarization of $4f$ states of Gd and Eu of both systems, 2(b) spin-resolved $4f$ photoelectron spectrum of the Gd(0001) surface, and 2(c) and 2(d) spin-resolved $4f$ photoelectron spectra of Eu and Gd, respectively, of the 1 ML Eu/Gd(0001) system. Experimental data of Eu/Gd interfaces, where the LEED patterns revealed a rotation of the superstructure by 30°, were identical within the error bars to those of systems without rotation. The spin-resolved spectrum of the Gd(0001) surface is well known from the literature[12] and can be deconvoluted into surface and bulk components as a consequence of the surface core-level shifts.[13] The intensity of the individual lines of the ^7F_J multiplet vary as a function of magnetic ordering and experimen-

tal geometry.[14] In order to discriminate bulk and surface contributions, a least-squares fit with two identical Doniach-Sunjic lines was performed describing the underlying multiplet structures by means of the asymmetric parameter.[15] The surface-to-bulk $4f$ core-level shift was found to be 400 meV and consistent with previous measurements of the Gd(0001) surface.[12] The results of this least-squares fit is not shown in order to avoid overloading the figure. The deconvolution of the majority and minority components indicates that the Gd $4f$ spins of surface and bulk are coupled ferromagnetically. The spin polarization of the Gd $4f$ photoemission signal was found to be about 40%, which is in agreement with previous measurements at the same temperature.[12]

Deposition of Eu on top of the Gd(0001) surface and subsequent annealing leads to changes in the spin-resolved spectrum of the Gd $4f$ state. As can be seen in Fig. 2(d) the intensity of the Gd $4f$ surface component is strongly suppressed. This is indicated by the asymmetric shape of Gd $4f$ line as well as by its lower PE intensity as compared to the clean Gd(0001) surface. The spin polarization of the remaining surface component is reduced to about 20% as compared to the clean Gd(0001) surface. At the same time the intensity of the bulk Gd $4f$ component decreases due to the inelastic scattering of electrons in the Eu overlayer, but the spin polarization is only slightly reduced to about 35%. The Gd $4f$ PE signal shows now the typical shape of the ^7F_J multiplet.[16]

The Eu $4f$ PE signal exhibits a clear spin polarization of about 15% [P_x in Fig. 2(a)]. This immediately proves the existence of a net magnetization in the Eu monolayer, i.e., the Eu $4f$ spins are oriented mainly parallel to each other. From the presented data one can also conclude that the Eu $4f$-spins in the 1 ML Eu/Gd(0001) system couple ferromagnetically to the Gd $4f$ spins.

The observed ferromagnetic coupling between Eu overlayer and Gd surface is supported by *ab initio* band structure calculations performed using a full-potential non-orthogonal local-orbital calculation scheme (FPLO)[17] within the local-spin-density approximation (LSDA+U). For the scalar relativistic calculations, the Perdew-Wang functional[18] was used. The same $(6s,6p,5d,4f)$ states were chosen as the basis set for Gd and Eu. For the correlation energy (U) values of 6.7 eV for Gd and 7 eV for Eu were assumed in accordance with Refs. 19 and 20. A $\mathbf{k}$ mesh of $12\times12\times12$ points in the irreducible part of Brillouin zone was used. Pure Gd metal was modeled by a slab of six layers, and one layer of Eu was added on each side of the slab in order to describe the 1 ML Eu/Gd(0001) system. The experimentally observed (4×4) surface reconstruction of the Eu overlayer was not taken into account. The Eu-Gd distance was set to the sum of the respective atomic radii in the pure metals. The slabs were separated by three layers of vacuum. All calculations were carried out for $T=0$ K.

Figure 3(a) shows the $4f$ partial density of states (PDOS) for the surface and bulk Gd atoms in the slab. As a result our calculations confirm the ferromagnetic ground state of the Gd(0001) surface and yield a core-level shift of 0.44 eV which is in good agreement with recent calculations,[21] and

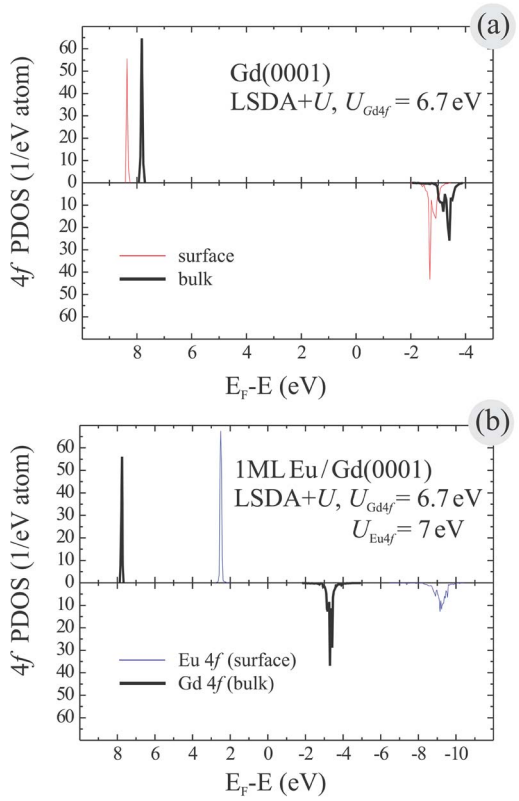

FIG. 3. (Color online) (a) and (b) $4f$ partial density of states (PDOS) of Gd and Eu for the Gd(0001) surface and 1 ML Eu/Gd(0001) system, respectively.

experimental results.[12,22] For the 1 ML Eu/Gd(0001) system [Fig. 3(b)] the surface component of the Gd $4f$ PDOS is absent and one gets only a Gd $4f$ PDOS for the bulk. The calculated position of the Eu $4f$ core level is 2.5 eV, which is in good agreement with the experimental value of (2.6 ± 0.05) eV binding energy. As the most important fact we obtain a clear indication of ferromagnetic coupling of the Eu $4f$ spins with respect to the Gd substrate.

The ferromagnetic coupling in the Eu/Gd heteromagnetic system was firstly observed by Arenholz *et al.*[2] by x-ray magnetic circular dichroism (MCD). In this work the authors performed an analysis of the temperature dependence of the $4f$ MCD signals of Eu and Gd. They show that even at 25 K the Eu $4f$ MCD signal is about 80% of the Gd one and thus the Eu $4f$ spins are not exactly oriented parallel to each other. From the measured temperature dependencies of the $4f$ MCD signals of Eu and Gd,[2] one may conclude that at $T\approx130$ K the $4f$ MCD signal of Eu is about 0.43 of the $4f$ MCD signal of Gd. One may assume that $P_{4f}(T)\sim M_{4f}(T)\sim MCD_{4f}(T)$, where $P_{4f}(T)$, $M_{4f}(T)$, and $MCD_{4f}(T)$ denote the temperature dependencies of polarization, magnetic moment, and MCD signal of the $4f$ state, respectively. In this case we expect for the spin polarization of the Eu $4f$ PE signal a value of $P_{Eu4f}=0.43\times40\%\approx17\%$, which is in good agreement with the experimental value of the spin polarization of the Eu $4f$ state observed in the present study.

For most of the antiferromagnetic phases of RE metals, helical spin arrangements are observed, where all spins

within a plane perpendicular to the helical axis are parallel to each other, while spins of adjacent layers are turned by a certain angle. Thus, one might assume that the reduced spin polarization of the Eu $4f$ signal is due to canting of all $4f$ spins of Eu in the same direction: out of plane or in plane. The absence of first possibility was discussed in work.[2] The later spin arrangement can be discarded on the basis of the present experiment, since the spin-resolved spectra of the Eu $4f$ PE line do not reveal a spin asymmetry in y direction [the corresponding spin polarization P_y is shown in Fig. 2(a) by open circles]. A spin configuration where, due to thermal disorder, individual spins are canted with respect to each other cannot be discriminated from the present experiments. For such a thermal effect, a faster decrease of the magnetization of the Eu layer than of Gd bulk is expected on the basis of the reduced coordination[23] and large interatomic Eu-Eu and Eu-Gd distances, which is in good agreement with the experimental observation.

In conclusion, the magnetic properties of the heteromagnetic 1 ML Eu/Gd(0001) (4×4) interface were studied by means of spin-resolved photoelectron spectroscopy of the $4f$ states. An experimentally observed spin polarization of the Eu $4f$ emission in direction parallel to the one of the Gd substrate is assigned to ferromagnetic coupling between Eu and the subsurface Gd layers in agreement with results of band structure calculations. The obtained spin polarization of the Eu $4f$ state was compared with the previously reported temperature dependencies of dichroism signal which were described by simple layer-resolved mean-field calculations, and good agreement was found between measured and estimated values.

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