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Electronic and magnetic coupling between rare-earth adatoms and the Fe(001) surface

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The spin-dependent electronic structure of monolayer coverages of rare-earth metals on Fe(001) has been studied by spin-resolved photoelectron spectroscopy with synchrotron radiation. The highly spin-polarized photoemission from the localized $4f$ levels of Gd, Tb, and Dy on Fe(001) reveals the antiparallel coupling between these heavy rare earths and the Fe spin moment. Exchange-split final-state multiplet terms of the $4f$ spectra of the heavy rare earths are explicitly distinguished by direct observation of opposite polarization. For 1 monolayer of the light rare-earth Nd on Fe(001) the rare-earth magnetic moment couples parallel to the Fe magnetic moment.

The study of the electronic and magnetic properties of low-dimensional systems has recently attracted considerable interest. Several experimental techniques now provide sensitivity to ferromagnetic ordering for a single atomic layer. This progress now allows an investigation of surface, interface, and ultrathin-film magnetic systems. Ferromagnetism has been unambiguously detected in a few cases for $3d$ transition metals in the monolayer thickness range.[1-7] Complex magnetic behavior has been reported as a function of the overlayer thickness and temperature.[7] Critical exponents for the two-dimensional magnetic phase transition at T_c for one Fe monolayer on Au(100) have recently been determined.[8]

Very little information was, on the other hand, available until now on the magnetic and electronic properties of rare-earth ultrathin films and interfaces. A magnetic-resonance study revealed a strong temperature-dependent uniaxial perpendicular magnetic anisotropy in epitaxial ultrathin Gd overlayers on W(110).[9] Remanent in-plane magnetization has been observed for Gd overlayers on Fe.[10,11] This system offers the opportunity of studying the complex interface exchange coupling between the rare-earth overlayers and a magnetic substrate. Spin-resolved Auger-electron spectroscopy measurements[11] and spin-resolved photoemission experiments[10] detected antiparallel coupling between the Gd $4f$ moment and the Fe magnetic moment. Camley[12] discussed the magnetic phase diagram of Gd films on a Fe surface as a function of temperature and external magnetic fields theoretically. Blügel[13] studied the electronic and magnetic structure of Gd on transition-metal (001) surfaces and of Gd impurities in transition-metal hosts within a local-spin-density approximation. For both Gd impurities in Fe and a Gd overlayer on Fe(001), antiferromagnetic coupling between the Gd magnetic moment and the Fe magnetic moment is favored. These calculations also predict a reduction of the Fe surface magnetic moment and $3d$ average exchange splitting due to hybridization of the Fe $3d$ states with the rare-earth $5d$ states.

In this paper we present experimental results on the electronic and magnetic coupling between rare-earth metals and the Fe(001) surface by spin-resolved photoemission with synchrotron radiation. This work extends our previous investigations on Gd overlayers on Fe(001).[10] The spin-polarized emission of the highly localized $4f$ electrons for monolayer coverages of Nd, Gd, Tb, and Dy on Fe(001) has been measured along with the spin-polarized valence-band emission of the Fe substrate, in order to investigate the orientation of the $4f$ spin moments with respect to the Fe magnetic moment.

The rare-earth metals were evaporated *in situ* from W baskets onto the clean Fe(001) surface, in-plane remanently magnetized along the ⟨100⟩ axis. During evaporation the pressure in the experimental chamber rose from 2×10^{-10} to 1×10^{-9} torr. The deposition rate, typically 1 Å/min, was calibrated with a quartz oscillator. Through-

out this paper, one monolayer (1 ML) is defined as the mass equivalent of one monolayer calculated from the bulk densities of the rare earths and an interlayer spacing of 3 Å. As already found for Gd,[10] the sharp low-energy electron diffraction pattern of the pure Fe(001) substrate became less clear with Tb and Dy adsorption and was hardly visible for thicknesses greater than 1 ML. We conclude that these Tb and Dy overlayers do not grow epitaxially. The measurements were performed with monochromatized synchrotron radiation from the storage ring BESSY in West Berlin. Photoemission spectra for normal emission and the component of the spin polarization

$$P(E)=[I^{\uparrow}(E)-I^{\downarrow}(E)]/[I^{\uparrow}(E)+I^{\downarrow}(E)]$$

parallel to the Fe[100] easy axis in the film plane have been measured using a 90° spherical analyzer coupled to a 100-keV Mott detector. $I^{\uparrow,(\downarrow)}(E)$ are the spin-resolved energy distribution curves (SREDC's) for majority (minority)-spin electrons. Measurement of the spin-integrated energy distribution curve $I_0(E)=I^{\uparrow}(E)+I^{\downarrow}(E)$ along with the spin polarization $P(E)$ then allows the calculation of the SREDC's

$$I^{\uparrow,(\downarrow)}=I_0(E)[1\pm P(E)]/2\,.$$

In Ref. 10 we have shown that after deposition of 1-ML Gd onto the Fe, the spectra show a highly polarized feature at about 8.2-eV binding energy corresponding to the photoemission of one Gd $4f$ electron. This emission peak is mainly found in the Fe minority-spin channel, which indicates that the Gd magnetic moment couples preferentially antiparallel to the Fe moment, in analogy with the ferrimagnetic coupling in Gd-Fe compounds and alloys.[14–16] A small peak at the same binding energy in the Fe majority-spin channel indicates that the Gd $4f$ photoelectrons are, however, not fully polarized. Spin-polarized temperature-dependent Auger electron spectroscopy[11] and spin-resolved photoemission spectroscopy[10] experiments show that the Gd $4f$ polarization increases significantly with decreasing temperature. An extrapolation of this trend to lower temperature suggests a polarization of the Gd $4f$ emission near -100% at 0 K,[11] as one would expect for a fully ordered configuration with antiparallel coupling between the adatoms and the substrate magnetic moments. The polarization of the Fe valence states emission also decreases after Gd deposition.[10]

In Fig. 1 we present the SREDC's measured with synchrotron radiation of 70-eV photon energy at a temperature of 170 K of clean Fe(001) and after the deposition of 1 ML of Tb onto the Fe(001) surface. A spin-integrated x-ray photoemission spectroscopy (XPS) spectrum[17] and the calculated final-state multiplet terms for $4f$ photoemission from clean Tb metal are also shown for comparison. The valence-band SREDC's of clean Fe(001) are shown in Fig. 1(a). The minority-spin peak near E_F is due to emission from initial states near $\Gamma_{25}^{\downarrow}$, while the two majority-spin peaks at 1- and 2.6-eV binding energy are due to emission from $\Gamma_{12}^{\uparrow}$ and $\Gamma_{25}^{\uparrow}$, respectively.[10,18] The electronic configuration of Tb in the ground state is $4f^8(5d6s)^3$ with a completely filled majority-spin $4f$ half-shell and a single $4f$ electron of opposite (minority) spin. Emission of this minority-spin electron leads to the high-spin final-state term ^8S at a binding energy of 2.2 eV. The multiplet terms which correspond to the photoemission of one majority-spin electron lie between 7 and 11 eV below E_F. The two multiplet sets, split by the local exchange interaction, which arise from the emission of $4f$ electrons of opposite spin should be found in the two different spin channels, in the presence of long-range ferromagnetic order between the rare-earth adatoms. A broad structure is observed in the Fe minority-spin channel between 7- and 11-eV binding energy which is due to the emission of Tb majority-spin electrons (low-spin final states). These Tb emission peaks are superimposed on a background of inelastically scattered electrons. The posi-

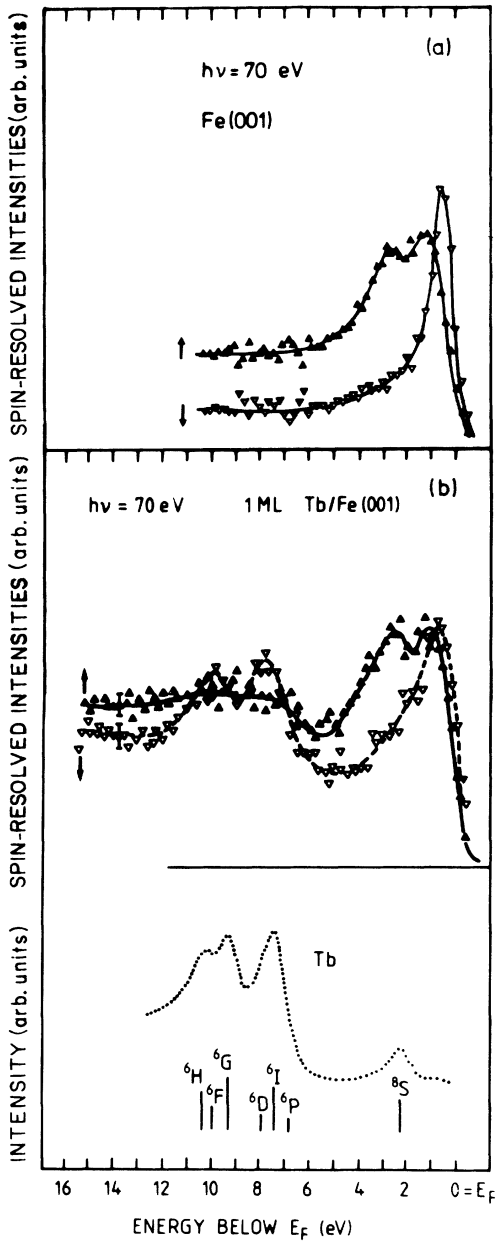

FIG. 1. SREDC's (a) of clean Fe and (b) of 1-ML Tb/Fe(001) for normal emission at 70-eV photon energy, $T=175$ K and spin-integrated XPS spectrum of Tb (Ref. 17).

tions of the two main peaks observed are close to the positions of the ^6G and ^6J multiplet terms as found in XPS experiments.[17,19] As for Gd also the coupling between the Tb $4f$ spin moment and the Fe magnetic moment is mainly antiparallel. The polarization of the Tb $4f$ emission, recalculated from the SREDC's after subtraction of the inelastic background, is not complete, as indicated by the presence of a small feature between 7- and 11-eV binding energy also in the Fe majority-spin channel. The ^8S emission, which should appear in the Fe majority-spin channel in the case of antiparallel coupling is superimposed on the Γ_{25}' emission of the Fe and cannot be observed separately. As for all the other rare-earth overlayer systems we have studied, a reduction of the polarization of the Fe valence emission, within 4 eV from E_F, is observed. The incomplete polarization of the Tb $4f$ emission at 170 K may have different reasons. Spin-resolved photoemission experiments show that at room temperature the polarization of the Tb $4f$ emission is lower than at 170 K, suggesting a decrease of magnetization with temperature in agreement with the strong temperature dependence of the magnetization of Tb-Fe alloys and compounds.[14–16] In amorphous alloys of Fe with rare-earth metals with nonzero orbital component to the magnetic moment (like Tb), locally different magnetic anisotropy and exchange fields lead to locally different easy directions for each rare-earth magnetic moment.[16] In amorphous Tb-Fe alloys the Tb magnetic moments do not order completely antiparallel to the Fe magnetic moment but are spread in a cone of a half-angle θ. Also, crystalline Tb-Fe compounds show high magnetic anisotropies which may lead to easy directions of magnetization different from the [001] directions.[15] Therefore, it is very probable that also for Tb adatoms on Fe(001) anisotropies lead to an incomplete antiparallel alignment of the Tb magnetic moments relative to the Fe magnetic moments and thus to incomplete polarization of the Tb $4f$ emission.

Dy has a $4f^9(5d6s)^3$ ground-state electronic configuration with seven majority-spin and two-minority spin $4f$ electrons. At room temperature Dy is paramagnetic.[20] The SREDC's of 1 ML of Dy on Fe(001), measured with a photon energy of 64 eV at room temperature, are shown in Fig. 2. In Dy the ^7F final-state multiplet term corresponding to the emission of one minority-spin electron at a binding energy of 4 eV is well resolved from the Fe emission in the SREDC's. It appears mostly in the Fe majority-spin channel, while the peaks due to the diverse multiplet terms between 7 and 11 eV below E_F, which describe the emission of one of the Dy majority-spin electrons are found preferentially in the Fe minority-spin channel. Exchange-split final-state multiplet terms are explicitly distinguished by observation of opposite spin po-

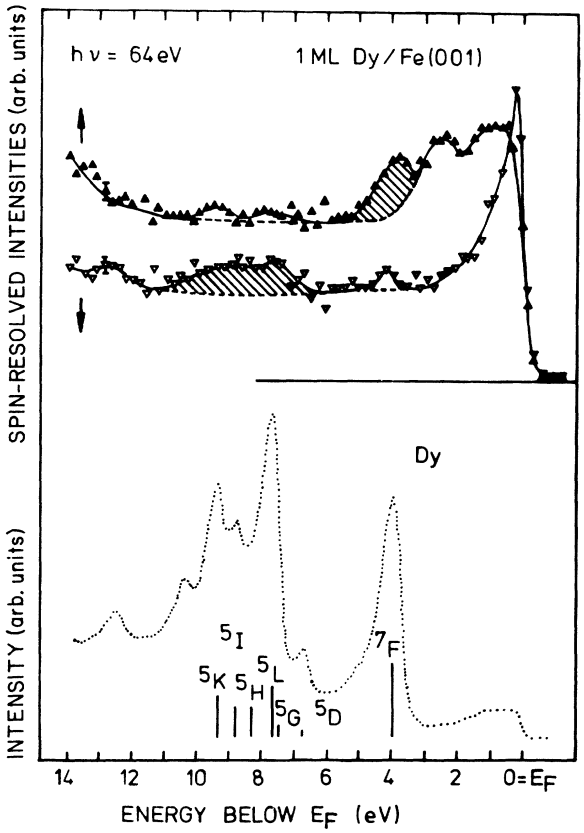

FIG. 2. Spin-resolved energy distribution curves of 1-ML Dy/Fe(001) for normal emission at 64-eV photon energy, $T=295$ K and spin-integrated XPS spectrum of Dy (Ref. 19). In the SREDC's of Dy/Fe(001), the inelastical background is indicated and the Dy $4f$ contribution of the Dy spin moment component antiparallel to the Fe spin moment is shadowed.

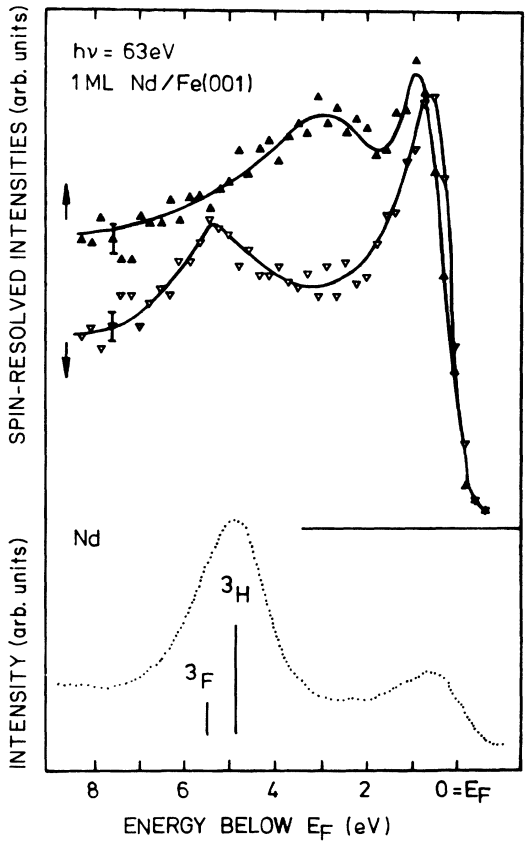

FIG. 3. Spin-resolved energy distribution curves of 1-ML Nd/Fe(001) for normal emission at 63-eV photon energy, $T=295$ K and spin-integrated XPS spectrum of Nd (Ref. 17).

larization. The spectra indicate a mainly antiparallel coupling between the magnetic moments of the Fe and the Dy adatoms. Also, for Dy, the peaks appear on a background of inelastically scattered electrons as indicated in the Fig. 2. Recalculating the polarization from the background-corrected SREDC's shows that the polarization of the Dy $4f$ emission is incomplete. We assume that the incomplete polarization of the Dy $4f$ emission is due to temperature to some extent. The Curie temperatures for Dy-Fe alloys and intermetallics are even lower than those of the corresponding Tb-Fe alloys and compounds.[14–16] Also, for amorphous Dy-Fe alloys, a conical distribution of magnetic moments around an axis antiparallel to the Fe moment has been found.[21] High magnetic anisotropies as in crystalline and amorphous Dy-Fe alloys[15,16,21] might also lead to an incomplete alignment of magnetic moments of Dy adatoms on Fe(001), which would cause a decrease in the polarization of the Dy $4f$ emission.

The SREDC's of 1-ML Nd on Fe(001) measured with a photon energy of 63 eV at room temperature are shown in Fig. 3. Nd has a ground-state electronic configuration $4f^3(5d6s)^3$. At room temperature pure Nd is paramagnetic.[20] The XPS spectrum of pure Nd shows one broad peak at about 4.8-eV binding energy,[17,19] containing the ^3H multiplet term and the weaker ^3F term. For a coverage of 1-ML Nd on Fe(001), this $4f$ emission peak appears in the Fe minority-spin channel on a background of inelastically scattered electrons. As for the heavy rare earths discussed before, the Nd $4f$ spin moments couple antiparallel to the Fe spin moment for this coverage. According to Hund's rule, the Nd magnetic moment is antiparallel to the spin moment due to the high orbital component. Therefore, our results indicate that the magnetic moments of the Nd and the Fe couple parallel. It is remarkable that nearly no $4f$ emission peak is detectable at the same binding energy in the opposite spin channel. This is in contrast to results on amorphous Nd-Fe alloys where a considerable amount of spin canting was found.[16,21] We conclude that spin canting and deviations from parallel alignment due to temperature-induced magnetic disorder are small at room temperature for Nd adatoms on Fe(001). The Nd $4f$ emission peak 5.4 eV below E_F is shifted by about 0.6 eV to higher binding energy as compared to XPS measurements.[17,19]

In conclusion, we have shown that exchange-split final-state multiplet terms of the $4f$ spectra of rare-earth metals appear in spin channels of opposite polarization. The $4f$ spin moments of the heavy rare earths Gd, Tb, and Dy couple antiparallel to the Fe magnetic moment. The polarization of the $4f$ emission is incomplete probably due to both temperature and anisotropy effects. Antiparallel coupling of the Nd spin moment to that of the Fe is also observed for 1-ML Nd on Fe(001). The Nd $4f$ emission is highly polarized.

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