Magnetic Splitting of Valence States in Ferromagnetic and Antiferromagnetic Lanthanide Metals

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The magnetic splitting of Δ_2 valence states in the heavy lanthanide metals Gd, Tb, Dy, and Ho was studied in epitaxial films by angle-resolved photoemission, revealing an essentially Stoner-like temperature dependence in all cases. It scales linearly with the $4f$ spin moment, even in the case of the helical antiferromagnet Ho. Such a behavior can be explained by a substantial localization of the corresponding wave function in the c direction. The helical magnetic structure was confirmed for the thin Ho films by *in situ* resonant magnetic x-ray diffraction.

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The magnetic properties of the lanthanide elements are strongly determined by the local $4f$ moments, which persist in the solid state. These metals exhibit a variety of temperature-dependent magnetic structures, including ferromagnetic, conical, and helical antiferromagnetic phases [1–6]. At low temperatures, the heavy lanthanide metals Gd to Tm are characterized by magnetic structures with finite net magnetization. Above their respective Curie temperatures T_C, however, they exhibit antiferromagnetic phases with vanishing net magnetization, except for Gd. Accordingly, Tb to Tm are further characterized by a Néel temperature T_N [1,3]. While it is well established that the magnetic ordering is induced by an indirect exchange between the local $4f$ moments via conduction electrons (RKKY interaction) [3], the influence of magnetic ordering on the valence-electronic structure is largely unexplored and has been discussed essentially only for ferromagnetic Gd [7–15].

The most direct information about well-defined occupied electronic states can be obtained from angle-resolved photoemission (PE), revealing for ferromagnetic Gd a temperature-dependent magnetic splitting of Δ_2 valence states, with a Stoner-like collapse at T_C [8]. Resonances observed in the optical reflectivity of lanthanide metals, on the other hand, have been interpreted in terms of a temperature-independent magnetic splitting [16]. These resonances have been observed in the antiferromagnetic phases as well [16,17], indicating that the magnetic splitting is not related to the net magnetization and that the relevant temperature scale is given by the highest magnetic ordering temperature T_N.

The temperature dependences of magnetic splitting and spin polarization of valence states in ferromagnetic Gd metal were theoretically studied by Nolting *et al.* [11]. Considering two extreme cases, itinerant states were found to be sensitive to the net magnetization, behaving essentially Stoner-like, while the splitting of strongly localized states was shown to be independent of long-range order, persisting even in the paramagnetic phase above T_C [11].

A more complex magnetic structure has been theoretically addressed by Sandratskii and Kübler [10]. They studied an antiferromagnetic structure, consisting of ferromagnetically ordered close-packed planes, with the moments of neighboring planes being rotated by some angle, forming a helix along the c axis. Modeling the temperature-dependent decrease of the $4f$ magnetization of Gd by a decrease of the helix period, the model could reproduce the Stoner-like decrease of the magnetic splitting. Interestingly, this model applies directly to the antiferromagnetic structure of Ho, except for the magnitude of the $4f$ spin moment. The calculations revealed essentially the same splitting for a helix period of $\approx$10 monolayers (ML), as observed in Ho, as for an infinite helix period, i.e., the ferromagnetic case [10]. A substantial splitting may therefore also be expected in the antiferromagnetic phases of the lanthanide metals.

In this Letter, we present a systematic study of the magnetic splitting of valence states in Gd to Ho by means of temperature-dependent PE, with particular emphasis on antiferromagnetic Ho. The metals were studied as epitaxial films on W(110), which, in contrast to bulk single crystals, readily provide the high surface quality required for PE [13]. For such films, the existence of the bulk magnetic structures cannot be anticipated, since they result from a delicate balance between RKKY interaction and magnetostriction, which may be modified due to shape anisotropy [18,19] and strain-induced magnetocrystalline effects [20]. In order to rule out substrate-induced ferromagnetism, the essential question of the magnetic structure of the Ho films was therefore addressed by *in situ* resonant magnetic x-ray diffraction (XRD).

Accordingly, the studies were carried out in two different experimental setups, equipped for PE and XRD, respectively. In both setups, lanthanide-metal films were

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grown in the same way on the same W substrate in ultrahigh vacuum with base pressures of $<10^{-10}$ mbar, as described in Refs. [13,15]. Film thicknesses between 100 and 300 Å were determined with a quartz microbalance and, in case of Ho, also via x-ray reflectivity [21].

XRD experiments were performed at the ID10A beam line (Troïka) of the European Synchrotron Radiation Facility [22]. A photon energy of $h\nu = 8074$ eV was chosen in order to take advantage of the ≈50-fold resonant enhancement of the magnetic scattering intensity upon tuning to the Ho-L_{III} absorption edge [23]. The incident beam was σ polarized, while the scattered intensity was detected in the π-polarization channel [4] using a graphite (006) analyzer crystal, suppressing the signal from charge scattering by a factor of ≈500.

Figure 1 displays the intensity reflected from a 113 ML (≈300 Å) thick Ho film along the specular (00l) direction for various temperatures. The dominant intensity of the (002) Bragg peak, even in the π channel, is due to imperfect polarization analysis. The Laue oscillations around (002) are caused by the finite number of coherently scattering planes [24]. This number agrees well with the film thickness as determined from the reflectivity at small angles, indicating crystalline coherence across the whole film [21]. The increasing background is due to the crystal-truncation-rod scattering from W(110) [25].

As in the case of bulk Ho, magnetic satellites at $(002 - \tau)$ and $(200 + \tau)$ are observed due to the helical magnetic superstructure [4], with a helix period of ≈10 ML at 41 K, characterized by the magnetic modulation vector τ. Within a deviation of ≈3% over the whole temperature range, the helix period is the same as in bulk Ho [5]. A bulklike behavior is also observed for the square root of the integrated satellite intensity, generally used as a measure of the order parameter of the helical phase [5]. As demonstrated in Fig. 4, its temperature dependence can be essentially described by a power law, using the bulk values of the critical exponent $\beta = 0.39$ and of $T_N = 131.4$ K [5]. Another interesting property of the Ho films is inferred from the width (≈$0.018c^*$) of the magnetic satellite that is due to the finite number of magnetic scattering planes. As seen in the inset of Fig. 1, this number agrees with the total number of film layers, revealing magnetic coherence across the whole film for all temperatures studied. From the XRD results, we can conclude that a bulklike helical structure in Ho films on W(110) persists down to thicknesses of ≈300 Å [26].

Angle-resolved PE experiments were performed at the TGM 5 and TGM 1 beam lines of the Berliner Elektronenspeicherring für Synchrotronstrahlung using a VSW-ARIES analyzer, with an angular resolution of 2° and a total-system energy resolution varying between 60 and 150 meV (FWHM).

The most pronounced bulk valence-band features observed in angle-resolved PE from the (0001) surfaces of hexagonal close-packed (hcp) lanthanide metals are due to emission from Δ_2 states [8,11]. Corresponding spectra for Gd, Tb, Dy, and Ho are displayed in the left panel of Fig. 2, revealing a splitting of the Δ_2 states in two components at low temperatures (vertical bars). For ferromagnetic Gd, these components have been shown to be of majority and minority character, respectively [9,12]. The spectra were recorded in normal-emission geometry at $h\nu = 35$ eV, corresponding to an initial electron wave vector close to the center of the Brillouin zone, Γ. In the vicinity of Γ, the splitting turned out to be essentially constant. In the case of Tb, the ^8S component of the $4f^7$ final-state multiplet appears in the region of the Δ_2 emission. Therefore, the Tb spectrum was recorded at an angle of 8° off normal

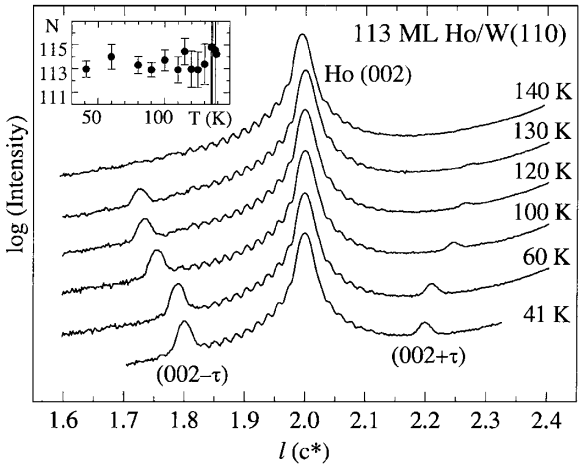

FIG. 1. Resonant x-ray scattering from a 113 ML thick Ho film along the specular (00l) direction, recorded in the π channel. The length l of the scattering vector refers to the reciprocal lattice parameter $c^* = 2\pi/c$ of hcp Ho. The inset displays the number N of coherent magnetic planes.

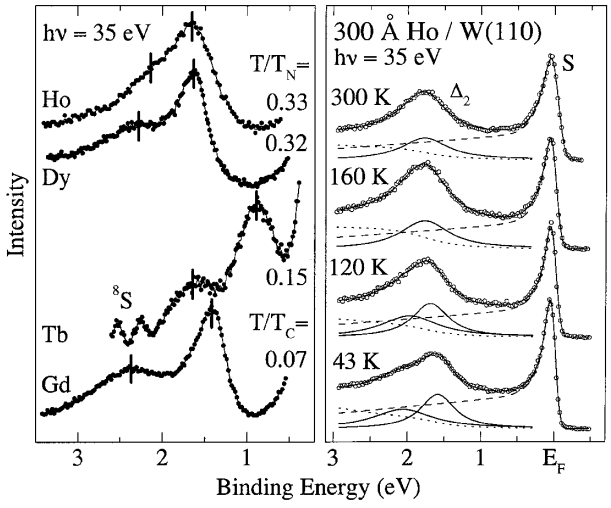

FIG. 2. Angle-resolved PE spectra, recorded from the (0001) surfaces of heavy lanthanide metals in normal-emission geometry (except for Tb; see text). Left panel: systematic behavior of the Δ_2 splitting (vertical bars). Right panel: temperature-dependent spectra for Ho.

along $\overline{\Gamma K}$, where the two contributions are well separated. This is justified, since the other lanthanide metals exhibit no change of the splitting up to this angle. For Ho, the splitting is comparably small; nevertheless, a shoulder can be readily identified.

These spectra demonstrate a magnetic splitting of the Δ_2 states in the heavy lanthanide metals, with a systematic decrease from Gd to Ho. The magnetic origin of the splittings was further confirmed by their temperature dependences, as displayed for the case of Ho in the right panel of Fig. 2 [27]. In addition to the Δ_2 states around 1.8 eV binding energy, these spectra include the surface-state emission (S) at the Fermi energy [12,13]. They show that the splitting decreases with increasing temperature, with no spectral changes observed above T_N (131.4 K).

For a quantitative description, the spectra were fitted by two symmetric Lorentzians for the Δ_2 emission (solid subspectra) and an additional line for S. The finite experimental resolution was taken into account by a Gaussian broadening. Identical fit procedures could be applied in a consistent way to the spectra of all lanthanide metals studied, resulting in the temperature dependences of the magnetic splittings displayed in the left panel of Fig. 3. In agreement with the results obtained previously for Gd [8,12], all systems reveal a Stoner-like behavior with a splitting that essentially vanishes at the highest magnetic ordering temperature, denoted here by T^* [28]. These data show that T^* defines the relevant temperature scale for magnetic splitting, independent of the net magnetization.

The zero-temperature splittings, $\Delta E(0)$, readily obtained by extrapolation, are displayed in the right panel of Fig. 3. From Gd to Ho, $\Delta E(0)$ scales linearly with the $4f$ spin moment, in accordance with the picture of local exchange interaction between valence electrons and $4f$ moments [2,3]. While such a scaling has been anticipated for the lanthanide metals [29,30], the present data represent the first direct experimental observation.

Unlike the other metals studied here, Ho remains antiferromagnetic down to the lowest temperatures of the present study. Nevertheless, the extrapolated $\Delta E(0)$ scales systematically with the full $4f$ spin moment and the temperature dependence of the magnetic splitting is the same as for the other lanthanides. Obviously, the vanishing net magnetization has no noticeable influence on the magnetic splitting of the Δ_2 states. The substantial $\Delta E(0)$ of Ho is in agreement with the helical model of Sandratskii and Kübler [10]. The temperature dependence of the splitting, however, cannot be understood in terms of a decreasing helix period only. Without taking the increasing disorder of the $4f$ moments within the close-packed planes into account, a Stoner-like collapse would require a decrease of the period to <5 ML [10], while the XRD data establish the persistence of the helix across the whole film with a period of ≥ 7 ML up to T_N.

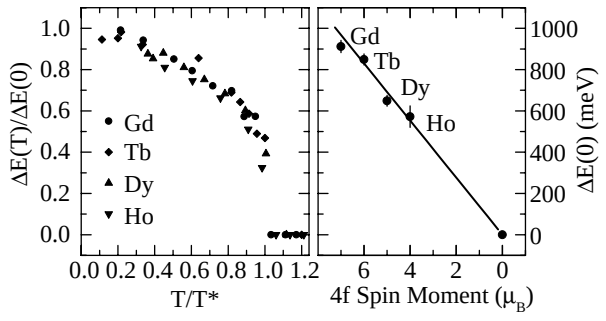

FIG. 3. Left panel: temperature dependence of the magnetic splitting $\Delta E(T)$ of the Δ_2 states of various lanthanide metals, normalized to the zero-temperature splitting, $\Delta E(0)$. T^* denotes the highest magnetic ordering temperature in each case. Right panel: zero-temperature splittings versus $4f$ spin moment; the solid line represents a linear relationship.

The influence of the decaying ferromagnetic order on the valence-electronic structure in Gd was studied by Nolting *et al.* [11], revealing that a Stoner-like decrease of the magnetic splitting corresponds to a delocalized wave function, which is sensitive to long-range ferromagnetic order. Hence, $\Delta E(0)$ in Ho might be expected to vanish or at least to be reduced by averaging the magnetization across several planes along the helix. Within this model, a consistent picture of Stoner-like temperature dependence of the Δ_2 splitting *and* its scaling with the full $4f$ spin moment in the helical phase can be obtained by assuming a wave function with considerable itineracy in the basal plane and a high degree of localization with respect to the c axis. Such a wave function would not sense the antiferromagnetic alignment of the close-packed planes along the c axis, but only the ferromagnetic order within the planes, which persists in the antiferromagnetic phase.

Considerable localization of the Δ_2 states with respect to the c axis is indeed indicated by the experimentally observed dispersion, with a substantially smaller bandwidth along ΓA than along ΓK [8]. Anisotropic behavior of the corresponding wave function with 73% $d_{3z^2-r^2}$ character at Γ is also revealed by band structure calculations [31], which were performed for paramagnetic Ho within the local density approximation. Fitting a tight-binding model to the calculated band structure results in hopping parameters of $\approx$0.40 eV within the close-packed planes, and $\approx$0.28 eV in the perpendicular direction. While these considerations support our interpretation to some extent, they cannot account quantitatively for the observed behavior. A detailed theoretical study of the temperature-dependent magnetic splitting, e.g., by combining the approaches of Refs. [10] and [11], however, is beyond the scope of the present paper.

Another interesting result is given by the similarities of the temperature dependences of the $(002 - \tau)$ intensity and of the Δ_2 splitting in Ho (Fig. 4). Since the latter is presumably determined by the decay of the ferromagnetic order in the close-packed planes, one might speculate on a similar mechanism for the decrease of the magnetic-satellite intensity, resulting from the decrease of the

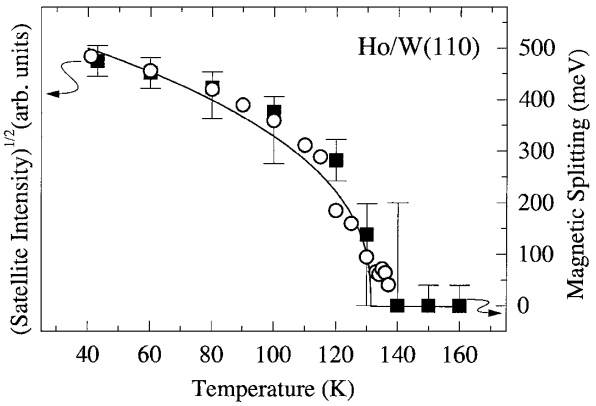

FIG. 4. Temperature dependences of the Ho Δ_2 splitting (solid squares) and of the square root of the integrated $(002 - \tau)$ intensity (open circles). The solid line represents a power law with $T_N = 131.4$ K and $\beta = 0.39$ (from [5]).

magnetic moment of the planes rather than the decay of the helical order. On the other hand, no indication for such a mechanism is evidenced from the XRD studies of the magnetic coherence lengths in bulk Ho at T_N, neither within the close-packed planes nor along the c axis [5]. There might, however, remain room for such a speculation, since the temperature dependence of the magnetic-satellite intensity in Ho is still not fully understood, as the corresponding critical exponent β does not exhibit a mean-field scaling and the universality class of the helical antiferromagnets is still unclear [6].

In summary, a systematic angle-resolved photoemission study of Δ_2 states at Γ has been presented for Gd to Ho. It establishes a linear scaling of the magnetic splitting of these states with the $4f$ spin moment, in agreement with the concept of exchange between valence and localized $4f$ states. No anomaly is observed in the helical antiferromagnetic structures, revealing that T_N defines the relevant temperature scale for the splitting. This behavior can be interpreted in terms of a wave function with substantial confinement to the close-packed planes, being sensitive only to the ferromagnetic order of the planes.

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