

X-ray dichroism as a probe of the electronic ground state in ultrathin rare-earth overlayers

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We present polarization- and temperature-dependent Tb M_5 x-ray-absorption total-yield spectra of Tb submonolayer overlayers on a Ni(110) surface. Strong polarization dependencies are observed. This dichroism is found to decrease with layer thickness, increase upon annealing, and, for annealed layers, increase upon cooling. Although the observed spectral shapes can be reproduced with an atomic calculation including a magnetic field only, we suspect (surface) crystal fields may play an essential role.

The purpose of this paper is to present the first results of strong polarization effects, or dichroism, in the $M_{4,5}$ absorption spectra of submonolayer films of a rare-earth metal on a magnetic substrate. We show that these effects are singularly sensitive to the interface morphology and argue that x-ray dichroism provides us with a powerful new tool for the study of magnetic and crystal-field interactions at surfaces and interfaces. The method is illustrated for the example of Tb or Ni(110) with as little as 0.25 monolayer.

The background for these measurements can best be described in an atomic-like model for the rare-earth (RE) $M_{4,5}$ absorption¹⁻⁵. In these spectra a RE $3d$ electron is excited to the empty $4f$ states and a complicated multiplet structure is observed corresponding to the final-state $3d^9 4f^{n+1}$ multiplet, which can be simulated to a very high degree of accuracy with atomic multiplet calculations.¹

Of course the transition is subject to dipole selection rules ($\Delta J = 0, \pm 1$, $\Delta M = 0, \pm 1$, no $J = J' = 0$), so that the actual spectral shape reflects only a subset of the total final-state multiplet. It has been shown previously that the subset depends critically on the nature of the initial state $|JM\rangle$. Strong linear dichroism can be, and has been observed, in these $M_{4,5}$ lines with linearly polarized light.²⁻⁵ In this earlier work the deformation from spherical symmetry of the $4f$ shell, from which the dichroism has to originate, was assumed to originate from the influence of magnetic interactions (Zeeman splitting) on the initial state $|JM\rangle$ and has been described as magnetic x-ray dichroism.²⁻⁴ We will use this picture as a starting point for the description of the effects observed here because it allows us to characterize our spectra by a single parameter, the linear dichroism coefficient C . The disadvantage of this approach is that one neglects the role of crystal electric fields, which also can break the spherical symmetry, but are much less important in the rare-earth series than in, e.g., the $3d$ transition metals where they dominate the multiplet structure.^{6,7}

In this work we will present x-ray-absorption (XAS) spectra obtained at various angles of photon incidence for thin layers of Tb on Ni(110) single crystals. The linear dichroism coefficient will then be determined by comparing experimental data with simulations and this information will be used to discuss the extent to which the measured C values deviate from a free-ion behavior.

The Ni(110) crystal ($10 \times 5 \times 1.5$ mm³) was cut from the

boule by spark erosion with an easy direction of magnetization [111] along the longest dimension. After polishing, the sample was annealed for 12 h at 650 °C under a hydrogen flow at a pressure of 10^{-4} Torr to remove sulphur impurities from the sample.

The sample was mounted by spotwelding it on two W/Rh wires (diameter 0.45 mm) which were connected to a helium cold finger. The lowest temperature achieved on the sample was 70 K. Temperatures were measured with a K -type thermocouple which was also spotwelded on the back of the sample. Also, the sample could be heated to 1300 K by electron bombardment on the back surface while the cryostat was kept cold. The cryostat could be rotated around its vertical axis without breaking vacuum by means of a differentially pumped rotary feedthrough. Further details of the experimental setup are described elsewhere.⁵ After insertion in the vacuum the sample was further cleaned in vacuum by the usual cycles of sputtering and annealing. 1×1 low-energy electron diffraction (LEED) surfaces were obtained with C contamination as judged from Auger spectra less than 10% of a monolayer (the limit of detection). No sulfur contamination was found.

The sample could be magnetized along the [111] direction by a small c-shaped electromagnet with a gap of 11 mm that embraced the sample, leaving a vacuum gap of 0.5 mm between both sides of the sample and the magnet's poles. The magnet could be pulsed to a maximum field strength of 5 kG. *Ex situ* magneto-optical Kerr effect (MOKE) measurements performed after completion of the absorption experiments showed the sample could be saturated easily. However, the remanent magnetization was found to be only $\sim 70\%$ of the saturation value. The apparent failure to arrive at a single domain state in remanence is ascribed to the size of the vacuum gap between the poles and the sample and to crystal defects induced by the spotwelding method of mounting the crystal.

Tb overlayers were deposited on the Ni sample from a Knudsen cell furnace with a rate of ~ 1 Å/min. During deposition the sample temperature stayed at 300 K. Layer thicknesses were determined with an oscillating quartz crystal monitor with an estimated systematical error of 40%; relative errors are estimated to be less than 5%. During annealing and evaporation the base pressure of 2×10^{-10} Torr rose to 1×10^{-9} Torr. When speaking of a Tb monolayer in the following we mean a single layer of

of the hcp lattice of Tb metal, which has a thickness of 2.85 Å.

The x-ray absorption spectra were accumulated using the total electron yield method. Linear polarized synchrotron radiation was obtained from a newly constructed windowless UHV double-crystal monochromator at Super-ACO, Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (LURE), Orsay⁵ equipped with Beryl crystals. In describing the dichroism spectra below we will use the polarization angle α , defined as the angle between the electric polarization vector of the light and the [111] direction, which both lie in the plane of the synchrotron ring. At normal incidence $\alpha=0^\circ$; spectra were accumulated at angles between -45° and $+80^\circ$ off-normal incidence.

The $3d^9 4f^{n+1}$ final-state multiples are divided in $3d_{5/2}$ (M_5) and $3d_{3/2}$ (M_4) parts by the $3d$ core-hole spin-orbit interaction. We will consider here only the Tb $3d_{5/2}$ spectrum; the $3d_{3/2}$ was found to display only very small dichroism effects, conforming to our predictions.^{2,4} In Fig. 1 we reproduce room-temperature normal-incidence Tb $3d_{5/2}$ spectra of as-deposited overlayers with increasing thicknesses, obtained by successive additions of new material to previously deposited layers. As for all spectra discussed here, the spectra were normalized to constant peak height after subtraction of a linear background extrapolated from the pre-edge region.⁸

The bottom curve is typical for polycrystalline (unoriented) material, consisting of two peaks flanked by shoulders of around one third of the main peak height. The spectra of the thinner layers are seen to display dichroism: The right-hand side peak is seen to decrease in intensity, in accordance with our earlier results.^{3,4} This dichroism is strongly dependent on the thickness of the overlayer; the effect is clearly largest for the $\frac{1}{4}$ monolayer (ML) film, and decreases already before completion of the first monolayer. From the dependence of the signal strengths of the Tb M_5 and Ni L_3 edge intensities as a function of thickness we found the sampling depth of Tb M_5 XAS in total electron yield mode to be ~ 60 Å.⁵ The spectra of Fig. 1 thus represent the layer-integrated signal. Therefore the dichroism asymmetry is a weighted average of the signal from the interface Tb layer and that of the following layers, and apparently already the second layer is very much less ordered. As will be discussed below, cooling these as-deposited overlayers to 70 K led to a very slight increase of the effect.

By contrast, annealing of the interface caused an increase of the measured asymmetry. Figure 2 shows the strong increase in the peak asymmetry of the room-temperature normal-incidence spectrum of a 2-ML film upon annealing for 5 min at 920 K. We found that for initial coverages ≥ 2 monolayers the intensity of both the Auger and the XAS Tb:Ni signal ratios decreased upon annealing to a nearly constant value that was independent of the deposited layer thickness for initial thicknesses of above two ML's. Also a range of clear LEED patterns were observed. This behavior is compatible with the formation of a surface compound similar to what has been found in a number of detailed studies of the kinetics of rare-earth overlayers on different Ni and

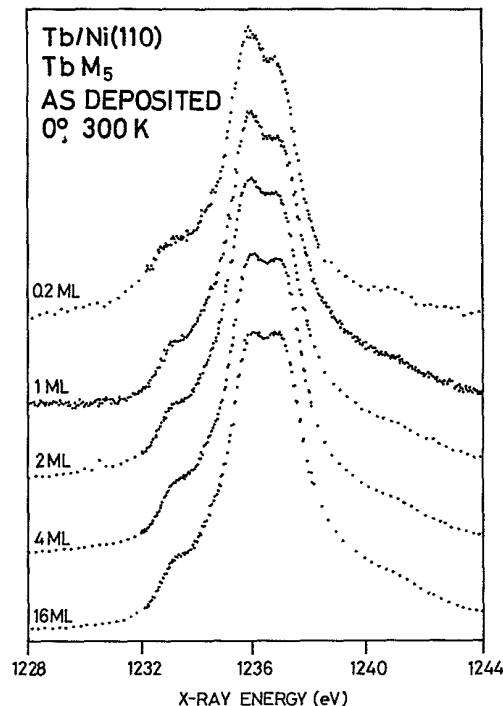


FIG. 1. Tb M_5 XAS spectra of Tb overlayers of increasing thickness. The total thickness was obtained by evaporating new material on top of the previous layer. The spectra were taken at room temperature and at normal incidence.

Cu crystal faces.⁹⁻¹⁵

The general behavior of these systems has been found to be quite complex, but some traits common to all systems can be discerned. At room temperature the rare-earth overlayer has been found to grow in a disordered layer-by-layer mode,¹⁰⁻¹² although some intermixing of the interface layers may occur.¹⁰ At higher deposition temperatures or after annealing, thin layers are found to form structures, with a wide variety of complex LEED

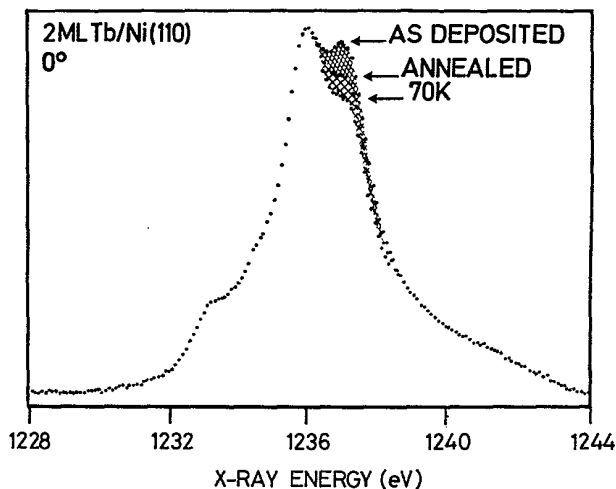


FIG. 2. Evolution of the normal incidence Tb M_5 spectrum of a 2-ML film on Ni(110). Arrows indicate the height of the right shoulder after deposition ($C=0.04$), after ($C=0.08$), and after cooling to 70 K ($C=0.16$). The first two spectra were acquired at room temperature.

patterns occurring for different choices of thickness, deposition temperatures, and crystal faces.^{10,13} Also, by annealing at higher temperatures the amount of overlayer material decreases,¹⁴ although it is unclear at present whether the material diffuses into the bulk or evaporates from the surface. The results for annealed surfaces have been interpreted as indicating the formation of a surface compound with a thickness in the range of one monolayer.^{10,14} The same marked tendency to passivate the substrate with the formation of sharp reacted interfaces is generally observed in RE/semiconductor systems.¹⁵ The structure of this surface compound appears in most cases^{10,12,14} to be unlike that of any of the known bulk RE TM intermetallic compounds.^{15,16}

The spectra of the annealed layers were found to depend more strongly on temperature, as exemplified by the lowest curve in Fig. 2. As in the as-deposited layers, the dichroism in the annealed case was strongest for the thinnest films. That the observed effect is indeed a manifestation of dichroism is proven by Fig. 3, which gives a representative pair of measurements at room temperature of an annealed film of 2-ML thickness taken at $\alpha=0^\circ$ and $\alpha=70^\circ$: at $\alpha=0^\circ$ the high-energy peak is highest, while at 70° the situation is reversed.

We start the discussion by noting that the observation of dichroism at room temperature indicates a total splitting of the atomic ground state of the order of some hundreds of Kelvin. All Tb-Ni intermetallic compounds have ordering temperatures below 180 K. Also the effect decreases with increasing thickness. This means the observed overlayer dichroism has to originate from ordering induced by the interface, i.e., the Ni magnetization or the interface symmetry, and is not a property of a hypothetical surface compound.

In order to describe the dichroism effects we use the

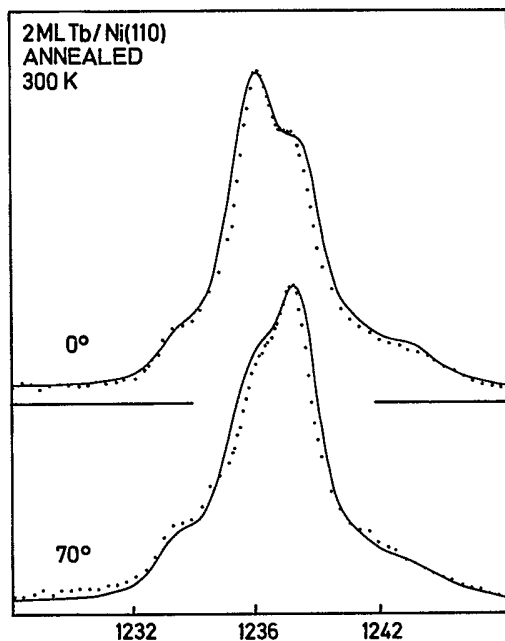


FIG. 3. Dotted line: room-temperature Tb M_5 spectra of a 2-ML Tb film after annealing. Solid line: theoretical fits with dichroism parameters $C=0.18$ (0°) and $C=0.25$ (70°).

linear dichroism parameter C which represents the ratio of the $\Delta M=0$ ($E\parallel H$) to the $\Delta M=\pm$ ($E\perp H$) contributions to the spectrum. Within the free-ion model and with linearly polarized light, for any combination of temperature, magnetic field, or polarization angle α the shape of the spectrum is determined by the value of C . As described in Refs. 3–5 it can be shown that C is the product of an angular-dependent term C_α and a magnetization, i.e., temperature- and field-dependent term C_M^3 . The angular term C_α has the form

$$C_\alpha = \frac{3}{2} \cos^2 \alpha - \frac{1}{2}, \quad (1)$$

and can take values between $-\frac{1}{2}$ and 1. Of course, C_α may take on other forms in real materials where the spin structure may be more complicated, e.g., in the case of helical or umbrella structures.³

C_M is a term defining the occupation of the Zeeman-split $|M\rangle$ levels and thus is temperature dependent. From Eq. (5) of Ref. 3 we find for Tb^{3+} ($J=6$)

$$C_M = (\langle M^2 \rangle - 14)/22, \quad (2)$$

where $\langle M^2 \rangle$ is the average value of the square of the magnetic quantum number M in the initial state $|JM\rangle$. In the free-ion model $\langle M^2 \rangle$ is a function of the reduced temperature $\Theta = kT/g\mu H$ only given by the expression

$$\langle M^2 \rangle = J(J+1) + \langle M \rangle \coth(\frac{1}{2}\Theta), \quad (3)$$

with $\langle M \rangle$ having the normal Brillouin behavior $-JB_J(J/\Theta)$. The C_M term completely describes the temperature and field dependence of the linear magnetic dichroism. C_M ranges between 0 and 1, so that $C = C_M C_\alpha$ also has values between $-\frac{1}{2}$ and 1.

By fitting the measured spectra with the atomic predictions it is possible to obtain experimental values for C as is demonstrated in Fig. 3, which contains our best simulations of experimental spectra at two angles. The calculated spectra are a little broader than in the experiment, which indicates a limitation in the accuracy of the F and G Slater integrals used to calculate the spectra.^{1–5} The important point, however, is that the calculations simulate the overall structure well and this procedure can be used to determine C within 0.05. The values obtained from the spectra in Fig. 3 are 0.18 (0°) and -0.25 (70°), respectively, which corresponds to $C_M = 0.18$ and 0.77.

The apparent variation with α of C_M from 0.18 to 0.77 indicates that the model used is in some way at variance with the simple model of ordering of the Tb atomic moments along the Ni[111] easy axis. The major problem lies in our failure to magnetize the Ni in a single domain as was indicated by the MOKE measurements. Since domains pointing out of the surface are energetically unfavorable, we try here the assumption that the surface magnetization consists of domains ordered along the two in-plane easy directions ($[111]$ and $[1\bar{1}\bar{1}]$). If we assume a two-domain model with equal population of the two domains the expected angular dependence becomes $C_\alpha = \frac{5}{6} \cos^2 \alpha - \frac{1}{2}$. This greatly reduces the discrepancy in C_M (from 0.6 to ~ 0), and the experimental value for which $C_\alpha = 0$ is correct to within experimental error. The uncertainty with respect to the actual domain occu-

pancy means that for the present results we cannot use the angular dependence of the C parameter, which is a powerful tool. However, we can make use of this domain structure, because at grazing incidence the electric field vector of the incoming light is perpendicular to both domains. Even at 70° the C_α values are very similar for the two domains. This makes the values for $C_M=0.77$ at 70° reasonably reliable. From Eq. (2) we find $\sqrt{\langle M^2 \rangle}$ is 5.6, while the saturation value is 6. This shows the overlayer is very highly ordered, and to our knowledge this is the first experiment that supplies this information for an overlayer system.

However, we should not rule out that the deformation of the $4f$ -electron cloud giving rise to dichroism also can be due to crystal-electric-field (CEF) interactions. For the RE $4f$ shell the CEF splitting can be of magnitude comparable to the exchange splitting,¹⁷ and thus likewise is too small to be directly visible as broadening in the final-state multiplet with the present experimental resolution (~ 20 meV and ~ 30 meV, respectively). However, the splitting of the 13-fold degenerate atomic ground state of Tb^{3+} ($J=6$) by the CEF may be completely different from the simple Zeeman splitting, leading to a completely different temperature dependence of the dichroism, or C_M .

In the present experiment the RE ions have the reduced symmetry of the surface. The highly anisotropic surroundings of surface ions are known to lead to dichroic effects in XAS and SEX-AFS spectra of adsorbates.^{18,19} For rare-earth materials surface CEF effects have been the subject of theoretical studies which show that the surface CEF is likely to have a strong axial component normal to the surface, so that to a first approximation, one would expect the $4f$ shell of a surface rare-earth ion to be distorted along the surface normal. In our experiment this distortion is superimposed on the distortion produced by the exchange interaction along the [111]. We cannot rule out that CEF effects contribute significantly to the effects observed here. In principle it is possible to distinguish between CEF and exchange effects with circularly polarized x-rays, but presently it is impossible to use the circularly polarized radiation emitted by the synchrotron out of the plane of orbit of the electrons, because with Beryl crystals the energy of the $Tb M_{4,5}$

lines correspond to a Bragg angle of 45° , where the transmission of the perpendicular polarized component of the radiation is effectively zero.

In this study of the $Tb/Ni(110)$ system we have shown that x-ray dichroism measurements on submonolayer coverages of rare-earth metals on ferromagnetic substances are not only feasible, but give quantitative information derivable from dichroism studies, especially the temperature dependence (not discussed here), gives insight into the size of the splitting of the ground state by magnetic or crystal electric fields. When circularly polarized x-rays will become available, that will allow one to separate magnetic and crystal-field effects.⁵

Only a few years ago x-ray dichroism effects were almost unknown and magnetic effects of the order of 10^{-3} would have been considered large. Effects of the order of 30% have been observed in several systems^{3,20} and in principle 100% effects are possible.^{2,4} These first data on overlayers show the potential of the x-ray dichroism method as a probe for interactions that break the spherical symmetry of the $4f$ shell of rare-earth elements, and thus is a valuable new tool for the study of rare-earth overlayers. A detailed study relating the dichroism with changes in the LEED signal has not yet been performed, but is certainly very interesting. Also, the kind of information derivable from dichroism studies, especially the temperature dependence (not discussed here), gives insight into the size of the splitting of the ground state by magnetic or crystal electric fields. When circularly polarized x-rays will become available, that will allow one to separate magnetic and crystal-field effects.⁵

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