

## Strong dichroism in the Dy $3d \rightarrow 4f$ x-ray absorption at Dy/Si(111) interfaces

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We report experimental evidence for strong  $3d \rightarrow 4f$  x-ray-absorption dichroism in rare-earth ions on a nonmagnetic substrate: Dy on Si(111) $7 \times 7$ . The results are discussed by evaluating the role of the crystal-field splitting of the ground state as an alternative to the Zeeman splitting underlying the magnetic x-ray dichroism theory.

Great interest has been raised by the theoretical predictions<sup>1</sup> and experiments<sup>2</sup> of polarization-dependent x-ray-absorption spectroscopy (XAS) with linearly polarized synchrotron radiation in magnetized samples (magnetic x-ray dichroism, or MXD). This was proposed as a tool for investigating magnetism in the bulk and at the surface of solids, complementary to the spectroscopy based on the absorption of circularly polarized light.<sup>3</sup> At this time a large effort, both experimental—based on highly monochromatized x rays of linear and circular polarization—and theoretical, is expended to deepen our understanding of x-ray dichroism.<sup>1,2,4–6</sup>

The atomiclike  $M_{4,5}$  edges ( $d \rightarrow f$  transitions) of rare-earth (RE) garnets<sup>2</sup> and the  $K$  and  $L_{2,3}$  edges of ferromagnetic transition metals<sup>4</sup> have been proven to show dichroism, respectively, in linearly and circularly polarized light. MXD of RE overlayers on ferromagnetic single-crystal surfaces has recently been explored as a probe of surface magnetism.<sup>6</sup>

The origin of the MXD in  $M$ -edge XAS of RE lies in the nonuniform occupation of the ionic ground state—split in Zeeman levels by the external magnetic field—combined with the restrictions induced by the dipole selection rules for the transition.<sup>1</sup> Calculated spectra show large polarization-dependent intensities of the multiplets, suggesting very easy experimental tests of magnetic fields at surfaces and interfaces. Surface MXD studies<sup>6</sup> were carried out on saturated ferromagnetic substrates, and interpreted by extrapolating the theory developed for the case of magnetic Tb-Fe garnets and isolated Dy ions in a magnetic field.

However, the splitting of the atomic levels can have origins other than magnetic. In particular the influence of the crystal field on the splitting of the ground state was previously questioned, but the energy separation of the sublevels was estimated to be small compared with  $kT$  at room temperature, and the detectability of possible crystal-field effects was predicted only at cryogenic temperatures.

We report here experimental evidence for large dichroism, equal or stronger in magnitude than measured in MXD experiments, in the  $3d \rightarrow 4f$  transitions for ordered

submonolayers and monolayers (ML) of Dy on a nonmagnetic substrate: Si(111) $7 \times 7$ , and for epitaxially grown DySi<sub>2-x</sub> silicide layers. In both cases no external magnetic field is present. The modified ground state must therefore be a consequence of strongly anisotropic *local* fields for the Dy ions at the interface such as crystal-field and surface Stark effects.

Si(111) single crystals were mounted on an UHV compatible liquid-He flow cryostat ( $T_{\min} = 50$  K) and could be heated up to 1300 K *in situ* with a base pressure of  $2 \times 10^{-10}$  mbar. Overlayers were evaporated (in a total pressure lower than  $1 \times 10^{-9}$  mbar and at a typical rate of 1 Å/min) from pieces of high-purity Dy onto atomically clean Si(111) surfaces displaying sharp  $7 \times 7$  low-energy electron diffraction (LEED) patterns. XAS measurements (total-electron-yield mode) were performed at SuperACO (Laboratoire pour l'Utilisation du Rayonnement Électromagnétique, Université de Paris-Sud, Orsay, France) using linearly polarized light and a UHV double-crystal monochromator (Ref. 6) equipped with beryl(10 –10) crystals. The angle  $\alpha$  between the surface normal [111] and the direction of polarization of the light was varied between  $10^\circ$  and  $90^\circ$ .

**Submonolayer coverages.** Dy submonolayers (0.3–1 Å; 1 ML =  $7.8 \times 10^{14}$  atoms  $\text{cm}^{-2} \approx 2.6 \text{ Å}$ ) were deposited at both room temperature (RT) and 50 K. In all cases a faint  $7 \times 7$  reconstruction was still observed. Representative XAS Dy  $M_5$  spectra for these samples are reported in Fig. 1. Panel (a) refers to 0.6-Å Dy deposited on Si(111) $7 \times 7$  at RT. The two curves correspond to the two extreme angles  $\alpha = 10^\circ$  and  $90^\circ$  and show strong dichroism. 0.3 Å of Dy condensed on Si(111) $7 \times 7$  kept at  $T = 50$  K [Fig. 1(b)] does not show any polarization dependence in the  $M_5$  spectrum, which is identical to the nondichroic reference spectra obtained for thick Dy metal layers evaporated *in situ* on polycrystalline copper. Dichroism is measured after annealing at  $900^\circ\text{C}$  for 1 sec and subsequent cooling down to 50 K [Fig. 1(c)].

**Higher coverages.** We have extended our study of Dy on Si to higher coverages (up to 10 ML) in order to check whether the dichroic effect originates entirely from the sharp-interface region. The RT evaporation of 2 ML of

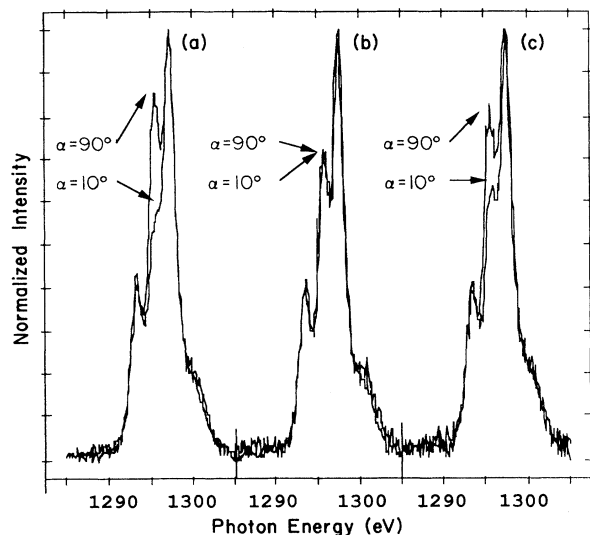


FIG. 1. Dy  $M_5$  absorption edge measured at  $\alpha=10^\circ$  and  $\alpha=90^\circ$  for submonolayer coverages on Si(111)7 $\times$ 7. (a) 0.2 ML deposited at RT. (b) 0.1 ML deposited at 50 K. (c) Same as (b), plus annealing at 900  $^\circ$ C.

Dy on Si(111)7 $\times$ 7 forms an interface layer which displays the same 1 $\times$ 1 LEED pattern of the substrate along with some diffused background. A 2-min annealing at 500  $^\circ$ C leads to a sharp 1 $\times$ 1 pattern. For a 10-ML coverage only a faint 1 $\times$ 1 is observed after RT deposition, which becomes sharp after 2–5-min annealing at 500  $^\circ$ C. The Dy  $M_5$  XAS dichroism is weak in the as-deposited 10 ML, but it becomes very intense after annealing at 500  $^\circ$ C. Similar results are obtained for the 2-ML coverage as shown in Fig. 2. We also explored the temperature dependence of the dichroism by measuring the  $M_5$  spectra while maintaining the sample at constant temperature in the range 300–800 K. The dichroism, evaluated as the

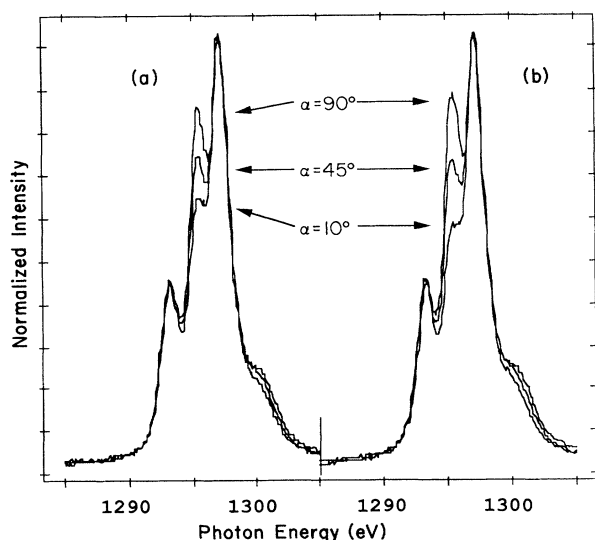


FIG. 2. Dy  $M_5$  edge for 2 ML deposited at RT, before (a) and after (b) annealing at 500  $^\circ$ C for 2 min.

deviation of the measured line shape from the nondichroic reference spectrum, is strongly reduced at 400 K. Measurements taken at 500 K or higher temperatures are indistinguishable from the reference spectrum. This process is found to be reversible: Upon cooling down, the RT dichroism is fully restored. The temperature dependence of the dichroism gives an experimental estimate of the energy separation between the split levels of the ground state.

A first systematic result of our experiment concerns the  $M_5$  line shapes for Dy/Si interfaces: We can obtain directly the polarization selected multiplets by spectra subtraction (see Fig. 3). The line shapes are remarkably identical to the spectra calculated by Thole *et al.*<sup>1</sup> for an isolated Dy ion undergoing the splitting of the  ${}^6H_{15/2}$  ground state in  $2J+1=16$  equally spaced Zeeman levels (ordered for increasing  $M_J$  from  $-\frac{15}{2}$  to  $\frac{15}{2}$ ), due to an external magnetic field.

In the present case there is, of course, no magnetic field from the substrate, and our results call for alternative interpretations with respect to the above theory: The action of a crystal field of axial symmetry splits the ground state into sublevels which are paired with opposite  $M$  values (e.g.,  $\pm \frac{15}{2}, \pm \frac{13}{2}, \dots, \pm \frac{1}{2}$ ) and unevenly spaced in energy. The selection rules for XAS with linearly polarized light cannot distinguish between  $+M$  and  $-M$  ground-state configurations, and so a crystal-field interpretation of the spectra is physically correct and the identity of the excited multiplet spectra shown in Fig. 3 is only apparently surprising.

A large crystal-field effect on XAS implies great sensitivity to the local ligand structure at the interface and in the overlayers. The lattice parameters of AlB<sub>2</sub>-type RE disilicides match ideally to the Si(111) surface, and epitaxial growth has been extensively reported.<sup>7</sup> A recent

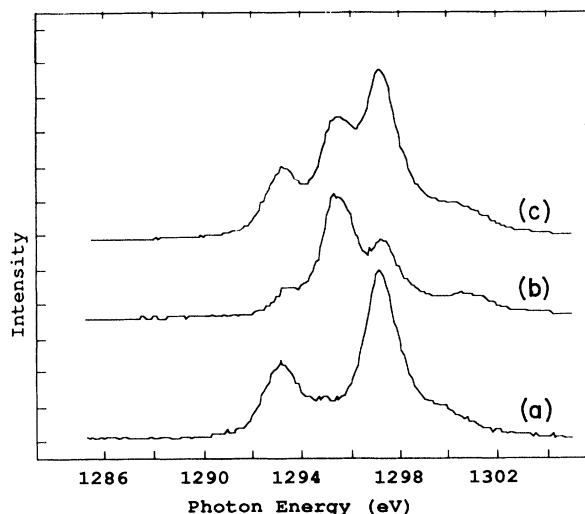


FIG. 3. Deconvolution of the spectra of Fig. 2(b) obtained by subtracting the unpolarized spectrum from the (a)  $\alpha=10^\circ$  and (b)  $\alpha=90^\circ$  spectra. (c) Represents the sum of the two contributions. All the spectra are normalized to the maximum. [These curves compare well with results of the atomic calculations by Thole *et al.* (Ref. 1) for a Dy ion in an external magnetic field (see their Fig. 2 on page 2088).]

photoelectron diffraction study<sup>8</sup> for the isostructural  $\text{YSi}_{2-x}$  shows that even in the sub-ML range the local environment of the metal ion is already the same as in the silicide. The  $\text{DySi}_{2-x}$  structure<sup>9</sup> consists of Dy layers intercalated by defective Si planes. The local environment of Dy ions is given by twelve Si atoms at 3.019 Å located at the vertices of two equivalent copenetrating octahedra, with six atoms each in the Si planes above and below the Dy plane. Second neighbors (3.830 Å) are six Dy atoms at the vertices of a regular hexagon. This structure presents a strong anisotropy for the Dy sites both in the bulk and at the interface. A Dy-rich equivalent structure  $\text{Dy}_5\text{Si}_3$  has been recently detected by x-ray diffraction at glancing incidence for unannealed deposits.<sup>10</sup> In the silicides the 4*f* levels are scarcely involved in the chemical bonding<sup>11</sup> and therefore the 3*d* → 4*f* transitions can rightly be treated as atomiclike, as confirmed by the absence of energy shift in the  $M_5$  spectrum in spite of chemical shifts of the order of 2 eV in the binding energy of the 3*d* electrons.<sup>10-12</sup> This excludes hybridization effects on the observed dichroism. The large splitting of the ionic ground state at the Dy site in the silicide submonolayer and multilayer samples is therefore connected with local fields in the quasi-two-dimensional (2D) graphitic structure of the epitaxial silicides. Clear evidence is given by our results to the importance of the local order at the Dy site. The absence of dichroism for the cold deposits rules out a simple surface electric-field (Stark) effect, which would be at work on every single chemisorbed atom regardless of adatom-adatom ordering or interface compound formation. Accordingly, the intensity of the dichroism is seen to depend on the long-range interfacial ordering (quality of the LEED pattern), which is associated with a larger fraction of Dy atoms sitting in the same local symmetry. The strong dichroism measured on epitaxial multilayers of  $\text{DySi}_{2-x}$  indicates that all Dy planes in the silicide show dichroism and not just the interface or the surface plane. The relevant local field has, therefore, the symmetry of the crystalline site for the rare-earth atom in the silicide and the related dichroism of  $M_5$  XAS transitions possibly represents the most stringent test of the local structural order at epitaxial interfaces from submonolayers to multilayers. Although magnetic fields are not

present at the interface, one should consider other possible contributions to the local field acting on the Dy in the epitaxial layers that might act on the dichroism. An anisotropic structure inducing a large crystal field is likely to imply also a large magnetocrystalline anisotropy. In fact, at cryogenic temperatures the Dy silicide shows antiferromagnetic ordering.<sup>13</sup> Lacking knowledge about the local magnetic properties of  $\text{DySi}_{2-x}$  for  $T \gg T_{\text{Néel}}$ , one cannot exclude the possibility that the anisotropy energy could be so large to determine a 2D local magnetic order of the Dy ions with domains randomly oriented in the planes even at the temperatures of our experiments. Therefore, local magnetic contributions might mix with the crystal field.<sup>14</sup>

The ensemble of our results can be summarized:

(i) Epitaxial  $\text{DySi}_{2-x}$  on Si(111) with highly anisotropic sites for the Dy ions show x-ray-absorption dichroism with variable strength according to the degree of order in the layers. The well-resolved dichroic multiplet structure can be explained by crystal-field splitting of the ground state of Dy in the silicide.

(ii) Disordered submonolayers deposited at cryogenic temperature, i.e., in conditions hindering the structural and chemical ordering of the Dy adatoms, do not show dichroism.

(iii) The measured energy required to reduce (reversibly) the dichroism is of the order of 400–500 K (30–40 meV), which exceeds all the theoretical estimates of the ground-state splitting made thus far.

Our results provide a clear cut evidence for x-ray dichroism in surface and interface systems where no external magnetic field is present, together with well-resolved multiplet spectra and energy limits for the ground-state splitting. This calls for detailed theoretical analysis of the atomic ground state in low-dimensional crystal structures relevant to interfaces. XAS dichroism on atomiclike transitions provides experimental access to surface and epitaxial layer anisotropies and opens up prospects of yielding additional useful information.

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<sup>14</sup>In a nondichroic three-dimensional system, the  $\mathbf{E} \perp \mathbf{H}$  and  $\mathbf{E} \parallel \mathbf{H}$  components of the absorption spectrum for linearly polarized light appear in the ratio 2:1. The existence of magnetically saturated domains with the field direction randomly oriented in a plane would lead to a ratio 1:1 when measuring with  $\mathbf{E}$  in plane and 2:0 when  $\mathbf{E}$  is perpendicular to the plane, giving rise to dichroism of the same sign observed.