X-ray-absorption dichroism of Dy at interfaces

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The linearly polarized x-ray-absorption dichroism at the Dy 3d-4f edge is studied for three different kinds of interfaces: Dy on disordered Si(111), Dy on amorphous SiO2, and Dy on polycrystalline Ta. Strong dichroism is observed in all the three interfaces, despite the very different interactions of Dy with the substrates. It is therefore pointed out that the x-ray-absorption dichroism using linearly polarized light is a more widespread, but at the same time complicated, phenomenon than previously suspected.

Since strong magnetic dichroism was predicted in the 3d-4f x-ray-absorption spectra of magnetic rare-earth materials by Thole, van der Laan, and Sawatzky,1 it has quickly become one of the most active research fields in current condensed-matter physics. The experimental proof for this x-ray dichroism was obtained by van der Laan et al. on a single crystal of terbium iron garnet (TbIG), located in a magnetic field of ~2 KG parallel to the [111] surface normal.2 The temperature at the surface of the sample was kept at 55 K. As was expected, the results could be well explained by the magnetic exchange splitting of the Tb4f8 ground state in the presence of a magnetic field. Thus the phenomenon was called magnetic x-ray dichroism (MXD), and it was further pointed out that polarized synchrotron radiation could be used to reveal information about the local rare-earth–metal magnetic moments in solids, thin films, and surfaces. However, a similar strong dichroism was also evident later for both ordered Dy overlayers and epitaxially grown DySi2–x silicide layers on Si(111)(7×7),3 where the substrate was neither magnetically ordered nor located in a magnetic field. It was thus argued, as an alternative to the exchange splitting mechanism, that the crystal-field splitting mechanism could also lead to the dichroism.

In this paper, x-ray-absorption measurements at the 3d-4f edge of Dy are reported for three Dy-deposited interfaces: (1) Dy on an ion-bombed Si(111)-disordered surface; (2) Dy on an in situ grown amorphous SiO2 surface; and (3) Dy on a polycrystalline Ta surface. The basic idea is to check whether x-ray dichroism also exists in systems without well-defined anisotropic single-crystalline structures. In fact, it turns out that strong dichroism does exist in such systems. It is finally concluded that symmetry breaking alone in the Dy ultrathin films can also lead to the dichroism.

The experiment was carried out in a UHV chamber with base pressure lower than 2×10−8 Pa during measurement, and 1×10−7 Pa during Dy evaporation. The coverage of deposited Dy was controlled by a quartz thickness monitor, and the deposition rate used in the experiment was ~2 Å/min. X-ray-absorption measurements (in the total-electron-yield mode) using linear polarized light were performed at the SU22 beam line of SuperACO storage ring at LURE, Orsay. A constant-deviation double-crystal monochromatic of Beryl(1010) was used.

The Si(111) surface was first cleaned in the UHV by ion bombardment followed with post annealing until a clear (7×7) low-energy electron-diffraction (LEED) pattern was observed at room temperature. Then the ordered surface was further sputtered by Ar+ ions so that the surface became disordered. An overlayer of 2 Å Dy was then deposited on top of the disordered Si surface at room temperature. Figure 1 shows the x-ray-absorption spectra taken with the polarization vector of the x ray perpendicular (α=90°) and almost parallel to the surface normal (α=10°), respectively. The three-peak structure, which corresponds to the selection rule for the total angular moment ΔJ = +1, 0, −1, is clearly seen. It is noticed that the intensity of the middle peak (ΔJ =0) increases unambiguously as the polarization vector changes from α = 10° to 90°, relative to the surface normal. It reflects the selection rule for the magnetic quantization number from ΔM = ±1 to mostly ΔM = 0, assuming the quantization axis is along the surface normal.

Being the same as the case of Dy/Si(111) (7×7), the disordered Si(111) substrate here is also nonmagnetic, so

FIG. 1. X-ray-absorption spectra at the Dy 3d-4f edge for 2 Å Dy on a disordered Si(111) substrate, taken with the polarization vector of the x ray oriented perpendicular to the surface normal and almost parallel to the surface normal (an angle of 10°).
the exchange splitting of the ground state of Dy 4f\(^{10}\)(J) caused by an external magnetic field is excluded. On the other hand, it was very unlikely for the Dy overlayer to form well-ordered two-dimensional structures on the disordered Si substrate, so the splitting of the ground state of Dy 4f\(^{10}\)(J) caused by a well-defined axial symmetric local field at the Dy sites—just as the case of Dy/Si(111) (7x7) (Ref. 3)—is also not expected.

Making sure that the dichroism of Dy is not a phenomenon limited to the Si substrate, we prepared in situ a thin film of SiO\(_2\) on top of the Si(111) clean surface, by inletting O\(_2\) gas in the chamber to \(\sim 10^{-1}\) Pa while keeping the substrate at 850°C for two and a half hours. In this case, it was expected that an amorphous SiO\(_2\) overlayer with several hundred Å was formed on top of the Si(111) substrate. On the amorphous SiO\(_2\) surface, a Dy deposition of 2 Å was then performed. Figure 2 shows the x-ray-absorption spectra taken at the two different angles at the Dy 3d-4f edge, from which the dichroism can again be clearly observed. But in this case, not only is the well-defined axial symmetric local field at the Dy sites unexpected, but the coordinated environment around the Dy atoms is also changed. Thus this explanation for the results seems not to be very straightforward from previous points of view.

In addition, the generality of the dichroism of Dy at surfaces and interfaces can further manifest itself in the following experiment. A polycrystalline Ta substrate was cleaned by ion bombardment to remove surface contamination such as carbon and oxygen; then it was exposed to 2 Å of Dy. The x-ray-absorption spectra at the Dy 3d-4f edge are shown in Fig. 3, from which the dichroism can be clearly observed once more. In some sense, this result is more interesting, and perhaps more significant than those just presented above. The reasons are twofold: on the one hand, Ta is of course a non-magnetic substrate, so the exchange splitting mechanism for the dichroism found on TbIG is not expected here; on the other hand, as far as we know, no alloys have yet been found between Ta and Dy, and solid diffusion has never been found between them at room temperature. Therefore, it is evident that even if the crystal-field effect (in the sense that a Dy atom is surrounded by ligands) still plays a role, it should not be the dominant factor. In other words, the mechanism for the dichroism found on the Dy/Si(111)(7x7) would also not be expected here.

Based on all the experimental results presented above, it is clear that the x-ray-absorption dichroism using linear polarized light is a more widespread, but at the same time more complicated, phenomenon than previously suspected. Because all the ultrathin films of Dy in our experiments were prepared on top of disordered substrates, specific adsorption sites on surfaces with well-defined symmetry were avoided. Therefore, it is believed that the dichroism appearing in our experiment manifests itself as a pure surface or interface effect. In other words, the symmetry breaking alone in Dy ultrathin films can also lead to the dichroism. The intuitive picture might be established as follows. For atomic Dy, the lack of the dichroism is expected because of the sphere symmetry. Once a Dy atom is placed on a surface, or located in an interface, the sphere symmetry is immediately broken, leading to the orientation of the Dy magnetic moment fixed in space. In such case, the dichroism should be expected. Of course, the question is whether the electric field is strong enough to lift the degeneration of the ground state of Dy 4f\(^{10}\)(J) to a measurable degree.

It was found that 0.3 Å of Dy deposited on Si(111)(7x7) at 50 K does not show the dichroism, which was explained by the disordering of the Dy adatoms themselves on the surface. However, we have a different explanation for the same experimental result. In our point of view, the lack of the dichroism is not due to the disordering of the Dy adatoms themselves on the surface, but instead is an indication that the temperature is too low to promote chemical bonding between Dy and Si, so that the electric field on the Dy atoms is not strong enough to lift the degeneration of the ground state of Dy 4f\(^{10}\)(J) to a measurable degree.

**FIG. 2.** X-ray-absorption spectra at the Dy 3d-4f edge for 2-Å Dy on an amorphous SiO\(_2\) substrate, taken with the polarization vector of the x ray oriented perpendicular to the surface normal and almost parallel to the surface normal (an angle of 10°).

**FIG. 3.** X-ray-absorption spectra at the Dy 3d-4f edge for 2-Å on a polycrystalline Ta substrate, taken with the polarization vector of the x ray oriented perpendicular to the surface normal and almost parallel to the surface normal (an angle of 10°).
enough to lift the degeneration of the ground state to a measurable degree. As opposed to the low-temperature case, the dichroism is shown here because the temperature we used in our experiment is high enough to promote strong interactions between adatoms and substrates, producing an electric field with reasonable magnitude, despite the fact that the Dy atoms are indeed disordering on the surfaces.

At last, a striking difference is found in the x-ray-absorption spectra at the 3d-4f edges between the TbIG case in Ref. 2 and the Dy/Si(111)(7×7) case in Ref. 3. It is noticed that when the polarization vector of the x ray is perpendicular to the surface normal, the spectrum of TbIG is dominated by the middle peak of the three peak structure, but the spectrum of Dy/Si(111)(7×7) is dominated by the other two peaks. The situations are exactly opposite when the polarization vector of the x ray is almost parallel to the surface normal. Because the 3d-4f x-ray-absorption spectra of rare-earth metals and compounds are due mostly to atomic optical transitions from a 4f"(J) ground state, as determined by Hund's rule for the many possible 3d24fJ+1 final states,1,2 the above streaking difference must indicate that the orientations of the magnetic moments differ by 90° between the two cases. In other words, since the orientation of the magnetic moment of Tb in the former case is unambiguously known along the surface normal, it turns out that the orientation of the magnetic moment of Dy in the latter case is perpendicular to the surface normal, lying in the plane.

Since the basic characters of our spectra are similar to the Dy/Si(111)(7×7) case, it is therefore evident that the orientation of the magnetic moment of Dy also lies in the plane. In fact, the important result can be seen to be quite reasonable by noting that the crystal electric fields, caused by the conduction electrons and ion cores, tend to align the charge clouds and hence the magnetic moments of the Dy 4f electrons lying in the plane.6 Thus it is possible to determine the local magnetic moments by the dichroism, which might be a very useful complementary tool to other techniques such as neutron diffraction and Mossbauer spectroscopy.

In conclusion, the linear polarized x-ray-absorption dichroism at the Dy 3d-4f edge has been studied for three different Dy-deposited interfaces. Strong dichroism is observed at all three interfaces, despite the fact that the interactions of Dy with the substrates are very different. It is pointed out that symmetry breaking alone in Dy ultrathin films can also lead to the dichroism, if the electric field is strong enough.