X-ray Reflectivity at the L Edges of Gd

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Preparations are underway for the experimental investigation of the roughness of magnetic interfaces in rare-earth multilayers by combining the grazing-angle X-ray scattering technique with the resonant magnetic scattering of hard X-rays. Theoretical considerations show that for small scattering angles, 2θ, the asymmetry ratio, A = [I(+)-I(-)]/[I(+)+I(-)], depends on 2θ and varies as 1/cos θ. The first step towards the goal of determining the magnetic roughness has been taken by measuring the chemical roughness (via specular reflectivity) of a Gd thin-film sample at five photon energies close to the L3 absorption edge, which yielded the dispersion corrections, f' and f'', to the Gd atomic form factor in good agreement with the calculation of Cromer & Liberman [J. Chem. Phys. (1970), 53, 1891-1898].

Keywords: resonant X-ray magnetic scattering; magnetic multilayers; specular reflectivity; interface roughness; Gd atomic form factor; anomalous-dispersion correction; L absorption edge.

1. Introduction

X-ray scattering is a powerful technique for probing the structure of buried interfaces. One can evaluate the r.m.s. roughness, σ, from measured specular reflectivity profiles and fit a model height-height correlation function, C(h(R)), to diffuse scattering data to determine the in-plane and vertical correlations as well as the Hurst parameter, h, in a fractal model of interface roughness (Sinha, Sirotta, Garoff & Stanley, 1988; Holy & Baumbach, 1994). Compositional or chemical interfaces in multilayers have for several years been probed through grazing-angle reflectivities and diffuse scattering as determined by the Thomson cross section. A natural extension to the conventional X-ray study of the roughness involves the characterization of magnetic interfaces. This magnetic roughness is seen through the spin-dependent scattering of X-rays. Magnetic scattering is, in general, much weaker than charge scattering, but the magnetic signal can be significantly enhanced at the absorption edges of the sample material through the resonant exchange scattering process (Namikawa, Ando, Nakajima & Kawata, 1985; Gibbs et al., 1988; Hannon, Trammell, Blume & Gibbs, 1988). At synchrotron sources the incident photon energy can be tuned to these absorption edges. Magnetic roughness scatters conduction electrons in magnetic multilayers in a distinct way from chemical roughness and is thus important with regard to the properties of giant magnetic resistance structures which find applications in magnetic recording devices.

Previous studies of the magnetic interface roughness were conducted at the L edges of a 3d transition metal, Co (Kao et al., 1994; Mackay, Teichert, Savage & Lagally, 1996). In these cases, soft X-rays of 0.8 keV were used, which is restrictive in two ways: the accessible area in momentum-transfer space is limited, and instrumental precisions are sacrificed as vacuum conditions are required to minimize absorption. These difficulties are removed at the L edges of rare-earth atoms located in the hard X-ray region. Hard X-rays allow us to explore larger areas in reciprocal space, enabling a more thorough characterization of magnetic interfaces. Goniometry under ambient conditions is easier to perform and hence can be made more accurate.

In this paper, preliminary non-magnetic measurements of specular reflectivities at the L edges of Gd are presented. While the technique by itself is a new method of experimentally determining the anomalous-dispersion terms f' and f'', we are here more concerned with its application to the measurement of magnetic roughness. Precise knowledge of f' and f'' is important to determine the chemical roughness, and hence, in comparison, the magnetic roughness. Information about the magnetic roughness is obtained from the difference reflectivity signal measured under directionally opposite magnetic fields. It can then be compared with the summed average reflectivity signal dominated by the electronic contribution. We first present...
preliminary theoretical considerations involved in such an experiment using hard circularly polarized X-rays, and then present the resonant non-magnetic scattering data used to obtain on-edge optical constants.

2. Theoretical considerations

X-ray magnetic scattering is largely enhanced when 2p or 3p electrons of the L or M shell undergo low-order electric multipole transitions to outer shells or bands. Because of the Pauli exclusion principle, the transition can only occur to unfilled states. This results in an exchange interaction sensitive to the spin states of the d and f orbitals. The L and M levels are split into well resolved multiplets due to the strong spin-orbit coupling, which leads to enhanced resonant exchange scattering. This is the reason we are interested in rare-earth elements with L absorption edges in the hard X-ray region. The K edges of transition metals, which are more important in applications, are also located in the hard X-ray region, but only weak magnetic effects are expected at these edges because there is no spin-orbit energy splitting of the s electrons. In the rare-earth elements a dipole transition occurs by 2p → 5d excitation and a quadrupole transition occurs by 2p → 4f excitation. The 5d orbital here is spin-polarized through interaction with the 4f moments. The amplitude scattering factor of a magnetic atom is given by (Hannon, Trammell, Blume & Gibbs, 1988)

\[ f = -f^{(mag)} = -(\hat{e}_x \cdot \hat{e}_\gamma)(f_0 + f' + if'') \]

where \( f^{(mag)} \) represents the non-resonant magnetic scattering, which is very small. Under the resonance condition, \( f' + if'' \) is rewritten within the dipole approximation as

\[ f_{res} = C[(\hat{e}_x \cdot \hat{e}_\gamma)(F_{11} + F_{1-1}) - i(\hat{e}_x \times \hat{e}_\gamma) \cdot z(F_{11} - F_{1-1}) + (\hat{e}_x \cdot z)(\hat{e}_\gamma \cdot z)(2F_{10} - F_{11} - F_{1-1})]. \]  

where \( \hat{e}_x \) and \( \hat{e}_\gamma \) is the polarization of the incident (scattered) beam, \( z \) is the direction of the magnetization, and \( F_{1m} \) is the dipole transition strength. The first term in \( f_{res} \) is independent of the magnetization, which represents the anomalous charge scattering. The scattered intensities to be observed are dominated by the electronic scattering, of which \( f_0 \) is the origin of the largest contribution. To extract the magnetic signal we apply directionally opposite magnetic fields on the sample and collect two sets of intensity data, \( I(+) \) and \( I(-) \). The sign of \( z \) is reversed by the reversal of the magnetic field. When \( I(+) - I(-) \) is calculated at each scattering vector Q, only the term linear in \( z \) survives and all other terms cancel out. Dividing the difference by the sum defines the asymmetry ratio, \( A \):

\[ A = [I(+) - I(-)]/[I(+) + I(-)]. \]  

The largest contribution to \( A \) comes from the cross term of \( f_0 \) and the second term in (2) which is linear in \( z \). There are two important points to be noted here.

(a) In grazing-angle scattering of hard X-rays, the scattering angle \( 2\theta \) is as small as a few degrees. In this case the asymmetry ratio \( A \) depends on \( 2\theta \) and varies as \( \tan(2\theta) \) for linearly polarized incident X-rays (de Bergevin, Brunnel, Calera & Vettier, 1992), but as \( 1/\cos\theta \) for circularly polarized X-rays. This requires circularly polarized incident X-rays for a good signal-to-noise ratio.

(b) When the incident X-rays are circularly polarized, the external magnetic field must be applied parallel to the plane of scattering. Otherwise, the magnetic effects may not be detected.

Theoretical estimates of the strength of the dichroic effect for Gd show a magnetic circular dichroic signal as large as 6% at the L2 edge and 3% at the L3 edge (Carra, Harmon, Thole, Altarelli & Sawatzky, 1991). Effects of this magnitude have been observed with a bulk Gd sample at 200 K (Namikawa, 1992). The quadrupole component was claimed to be less than 10% of the total signal (Lang et al., 1994). The magnitude of the \( 2p \rightarrow 5d \) dipole excitation is dependent on the spin of the 4f states, and is therefore largest for Gd and its compounds.

3. Non-magnetic near-edge X-ray reflectivity from a Gd film

A Gd film of 70 Å in nominal thickness was prepared by electron-beam evaporation on an Si(100) substrate at room temperature in an \( 8.5 \times 10^{-9} \) Torr base-pressure chamber. The deposition rate was 0.1–0.3 Å s\(^{-1}\). The top surface was capped with a 50 Å-thick protective Al layer. Gd has absorption edges at 7.243 (L3) and 7.930 keV (L2), which lie comfortably within the hard X-ray range obtained from synchrotron sources. At these energies the 1/e X-ray penetration depth in crystalline Gd is \( \sim 50 \) Å for incidence angles smaller than the critical angle for total external reflection (0.32° at the L1 edge). Crystallinity of the sample is unimportant in the present experiment. The prepared sample is chemically stable and can be studied in ambient conditions. It did not show a ferromagnetic hysteresis curve at room temperature, but did show one at 5 K. The Curie temperature for thin-film Gd may be lower than the bulk value of 293 K.
Table 1
Structure parameters determined from X-ray reflectivity.

Figures in parentheses are estimated standard deviations in the units of the least-significant digit. $d_{AI}$ and $\rho_{AI}$ are the thickness and mass density of the top Al layer; $d_{Gd}$ and $\rho_{Gd}$ are the thickness and mass density of the second Gd layer; $\sigma_1$, $\sigma_2$, $\sigma_3$ are the r.m.s. roughness at the air/Al, Al/Gd and Gd/substrate (Si) interfaces, respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>$d_{AI}$</td>
<td>52.3 (15) Å</td>
</tr>
<tr>
<td>$d_{Gd}$</td>
<td>65.4 (14) Å</td>
</tr>
<tr>
<td>$\rho_{AI}$</td>
<td>0.98 (2) $^*$</td>
</tr>
<tr>
<td>$\rho_{Gd}$</td>
<td>1.01 (1) $^*$</td>
</tr>
<tr>
<td>$\sigma_1$</td>
<td>5.3 (8) Å</td>
</tr>
<tr>
<td>$\sigma_2$</td>
<td>7.9 (10) Å</td>
</tr>
<tr>
<td>$\sigma_3$</td>
<td>1.5 (8) Å</td>
</tr>
</tbody>
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$^*$ Normalized to the bulk crystal densities.

X-ray reflectivity measurements were performed without applying a magnetic field on the sample, using linearly polarized synchrotron X-rays, on bending-magnet beamline 20B of the Photon Factory, KEK, Tsukuba, Japan (Fig. 1). The double-crystal Si(111) monochromator on this beamline was tuned to five different photon energies between 7.0 and 7.4 keV, spanning the $L_3$ edge of Gd. A slit, 0.1 mm in vertical aperture, placed in front of an NaI detector, defined the out-of-plane momentum resolution of the set-up at $2.2 \times 10^{-3}$ Å$^{-1}$. For each energy, rocking (sample) scans were made for fixed detector positions to keep track of the specular rod. We estimated the specular intensity in each scan by integrating the photon counts under the sharp peak after stripping off the broad diffuse scatter, which was plotted against the scattering angle $2\theta$ to give a reflectivity profile.

To obtain initial estimates of the structure parameter values for the sample, we fitted the data collected with 7.0 keV photons using Parratt's formulae (Parratt, 1954), with the $f'$ and $f''$ parameters for Gd fixed at the values from Cromer & Liberman (1970). Subsequently, the five data sets for the different photon energies were simultaneously fitted with common structure parameters and energy-dependent $f'$ and $f''$ parameters for Gd. The structure parameters were the Al and Gd layer thicknesses ($d_j; j = $ Al, Gd), the mass densities

Table 2
$f'$ and $f''$ values for Gd determined from X-ray reflectivity measurements at five photon energies $E$.

Figures in parentheses are estimated standard deviations in the units of the least-significant digit.

<table>
<thead>
<tr>
<th>$E$ (keV)</th>
<th>$f'$</th>
<th>$f''$</th>
</tr>
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<tbody>
<tr>
<td>7.000</td>
<td>-9.5 (13)</td>
<td>3.5 (15)</td>
</tr>
<tr>
<td>7.100</td>
<td>-11.2 (21)</td>
<td>3.9 (14)</td>
</tr>
<tr>
<td>7.243</td>
<td>-21.2 (13)</td>
<td>2.9 (17)</td>
</tr>
<tr>
<td>7.263</td>
<td>-17.3 (24)</td>
<td>10.3 (20)</td>
</tr>
<tr>
<td>7.400</td>
<td>-17.1 (15)</td>
<td>10.3 (12)</td>
</tr>
</tbody>
</table>

Figure 2
Specular reflectivities measured (data points) at photon energies of 7.0, 7.1, 7.263 and 7.4 keV. Lines show least-squares fits.
of the layers \((\rho; j = \text{Al, Gd})\), and the r.m.s. roughnesses for the air/Al, Al/Gd and Gd/Si interfaces \((\sigma_j; j = 1-3)\). There were a total of 22 variable parameters including the scale factors. Some of the fits are shown in Fig. 2. Data in the low scattering-angle regions (not shown) were excluded from the fits because of possible harmonic contamination.

Table 1 lists the refined structure parameters and Table 2 shows the \(f'\) and \(f''\) values for Gd determined for the five photon energies used. The \(\sigma\) values shown represent the chemical roughness at the layer interfaces. The Gd layer is found to have a thickness smaller than the design value by 10%. Both Al and Gd layers have high mass densities close to the crystal values.

4. Discussion

The experimental \(f'\) and \(f''\) values for Gd near the \(L_3\) edge are in good agreement with the calculations by Cromer & Liberman (1970) for isolated atoms (Fig. 3). They also agree well with more recent calculations by Creagh (1996). The rather large standard deviations associated with the experimental values prohibit discussion on the deviations and an attempt to see EXAFS effects (Stanglmeier, Lengeler, Weber, Goebel & Schuster, 1992). The good agreement may be surprising in view of the quality of the fits in Fig. 2. Reasonable fits are achieved with respect to the positions of the peaks and the valleys in the oscillatory specular profiles. The systematic deviations in the peak--valley modulation amplitude suggest the presence of a thin oxide layer on top of the Al layer. Our fits used
Cromer–Liberman calculations (Cromer & Liberman, 1970) for the Al and Si form factors. This may account for the good agreement of the absolute $f'$ and $f''$ values for Gd with the Cromer–Liberman calculation.

Specular reflectivities for our Gd sample only show dips at the L edges when plotted in $2\theta - E$ space (Fig. 4). This is different from the case of the Co sample from which Kao et al. (1994) observed dips and peaks near the L edges in E-scan traces for small and large scattering angles, respectively. The peaks in the Co case arise from the enhanced tails of Fresnel reflectivity profiles at slightly higher photon energies than the absorption edge. This enhancement is caused by the predominant contribution of $\beta^2$ to $2\kappa^2 + \beta^2$ which determines the specular reflectivities at large 2$\theta$ angles, where $1 - \delta$ and $\beta$ are the real and imaginary parts of the refractive index $n$ of Co ($n = 1 - \delta - i\beta$).

5. Conclusions

We have determined the non-magnetic anomalous-dispersion terms $f'$ and $f''$ of the Gd atomic form factor near the L$_3$ absorption edge from specular reflectivity data, which are in good agreement with the Cromer–Liberman calculation. It is to be noted that $f'$ and $f''$ are independent free parameters in our data fit. The values of these quantities at the absorption edge are important for evaluating the roughness of the chemical interface in Gd films, which is to be compared with the magnetic roughness. Information about the roughness of magnetic interfaces will be obtained from similar reflectivity measurements taken with incident circularly polarized X-rays at the Gd L edges, under a flipping magnetic field applied parallel to the sample surface and to the plane of scattering. It may be appropriate to point out here that, to our knowledge, no theory is yet available which incorporates the quantum excitations and the scattering of circularly polarized X-rays by magnetic interfaces.

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References