Structure of metallic multilayers studied by X-ray absorption spectroscopy

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The use of X-ray absorption spectroscopy (XAS) as a probe of the structure of metallic multilayers is illustrated. The capability of XAS to point out structural anisotropies and strains, essential parameters exhibited by two-dimensional materials, is shown using the examples of Fe/Cu and Co/Cu multilayers.

1. Introduction

Metallic multilayers have recently been the subject of extensive research because of the unusual magnetic properties induced by their two-dimensionality. The discovery of properties such as the giant magnetoresistance of Fe/Cr multilayers, which may radically change the technology of magnetic registration, justifies all the efforts put in the new field of applied physics [1].

In this paper we concentrate on the structural properties of these multilayers and will report some results obtained using X-ray absorption spectroscopy. The potential of this technique applied to the structural characterization of metallic multilayers has been recently demonstrated [2]. It is well known that, by matching the X-ray energy to the energy of a specific absorption edge, XAS allows the local structure around a specific atomic site to be probed selectively. The information obtainable with XAS differs from that obtained with X-ray scattering techniques in that the structural information is site-specific, i.e. it allows the structure around each of the chemical species in a multilayer to be pointed out, and is local, i.e. gives the image of the real rather than the "virtual" crystal [3]. One of the main interests of metallic multilayers is the possibility to stabilize in thin layers crystallographic structures which are unstable in the bulk and exhibit magnetic properties different from those of the bulk material. For example, bcc Cu layers with thicknesses up to $\sim$ 20 Å can be metastable in Fe/Cu multilayers grown on Fe substrates [4]. In the following we give a short review of our latest studies on Fe/Cu and Co/Cu systems [4,5]. For their outstanding magnetic properties, these multilayers have recently been the object of extensive research [6]. The exchange coupling between magnetic layers (Fe) has been shown to exhibit oscillations as a function of the thickness of the non-magnetic spacer (Cu or Co). These oscillations have been observed by various research groups both for MBE grown and for sputtered multilay-
ers. These multilayers also show a large magnetoresistance in the thickness ranges where the exchange is antiferromagnetic [6].

2. Samples

Fe/Cu multilayers with $t_{Fe} = 21$ Å and $t_{Cu} = 6$, 13, 24, 42 and 60 Å were deposited on a 50 Å Fe buffer on Si(100) substrates at $-10{\degree}C$ in a UHV compatible sputtering system. The details of the experimental methods used to characterize these samples and to study their magnetic and transport properties are reported elsewhere [7].

Co/Cu multilayers were prepared by thermal evaporation from tungsten crucibles in an ultra-high vacuum chamber [8]. Co$_x$/Cu$_y$ multilayers (Co$_{10}$Cu$_{10}$, Co$_x$Cu$_5$, Co$_x$Cu$_3$, Co$_x$Cu$_5$, Co$_3$Cu$_3$, where $x$ ($y$) is the number of Co (Cu) monolayers) were evaporated on a 250 Å thick Au layer deposited on a float glass substrate. The results of NMR data presented in a previous publication [9] show that in all the samples Co is present in the fcc crystallographic phase, with a large (38%) concentration of stacking faults having a local hcp environment. The quality of the Co/Cu interfaces was controlled by X-ray reflectivity. The presence of a superstructure peak at around 3° is the fingerprint of rather abrupt Co/Cu interfaces (fig. 1a). Calculations show in fact that if the interfacial roughness is larger than 4 Å, the superstructure peak disappears.

The $\theta$–2θ XRD spectrum recorded for the Co$_{10}$Cu$_{10}$ multilayer (fig. 1b) indicates that the multilayer has a very well defined (111) texture. The observed XRD peaks can be indexed as Au(111) for peak Al, and Cu(111) and Co(111) for peak Cl. The peaks labelled S are due to the superstructure of the multilayer. The good agreement between the experiment and the calculation (obtained by modelling the multilayer as a perfectly regular alternance of layers of the two metals) confirm that a “step-like” model is a good approximation of the multilayer structure and that the Co/Cu interfaces are quite abrupt [5].

3. Experiments and data analysis

X-ray absorption spectroscopy (XAS) measurements were carried out at the 1.85 GeV DCI synchrotron radiation source at the Laboratoire pour l'Utilisation de Rayonnement Electromagnetique (LURE) at Orsay. A Si(311) channel cut monochromator was used. The Co, Cu and Fe K edge absorption spectra of the multilayers were recorded in electron yield mode [3]. The spectra
of the model compounds (Co, Cu and Fe foils) were recorded in transmission geometry. The EXAFS spectra of the multilayers were recorded in two geometries, with the sample surface parallel and nearly perpendicular (80°) to the polarization direction of the X-ray beam, respectively. Since the photoelectron scattering amplitude depends (as \(\cos^2 \theta_i\)) on the angle \(\theta_i\) between the X-ray polarization direction and the position vector of the \(i\)th neighbour of the absorbing atom, differences between the crystal structure in the growth plane and in the growth direction can be pointed out by recording the XAS spectra with the sample surface parallel and perpendicular to the polarization direction respectively.

The data were analyzed using standard methods. Fourier transforms (FT) of the EXAFS spectra were performed in the wavevector region of approximately 3–12 Å\(^{-1}\). The spectra were filtered in real space to isolate the first peak of the FT and back-transformed in \(k\)-space. The Fourier-filtered spectra were fitted using a plane-wave approximation and experimental phase shifts, which include the curved wave corrections [3]. All details on experiments and analysis can be found in refs. [4,5].

4. Results

4.1. Co / Cu multilayers

Fig. 2 shows the Fourier transforms of the CuK edge EXAFS spectra obtained for the Co/Cu multilayers, recorded with in-plane X-ray polarization. For each of the multilayers, the positions and the amplitudes of the FT peaks are very close to those of bulk Cu, up to large distances from the central atoms (~8 Å). This indicates that the fcc structure of Cu layers is highly ordered. This result is confirmed by the least-squares fits of the EXAFS spectra (table 1) which show that the Debye–Waller factors for the Cu neighbour atoms are identical to those of bulk Cu, within the typical ±0.0005 Å\(^2\) error bar. The results of the fits also show that the nearest Co–Co and Cu–Cu distances are independent of the layer thickness, and are different for in-plane or out-of-plane directions, i.e. the layers' structure is anisotropic. For Co layers, the in-plane distance is 2.52 Å (±0.01 Å) and the out-of-plane distance 2.50 Å (±0.01 Å). For Cu layers, the in-plane distance is 2.54 Å (±0.01 Å) and the

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>(R_i) (Å)</th>
<th>(DW_i) (Å(^2))</th>
<th>(R_i) (Å)</th>
<th>(DW_i) (Å(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(In-plane)</td>
<td>(In-plane)</td>
<td>(Out-of-plane)</td>
<td>(Out-of-plane)</td>
</tr>
<tr>
<td>CuK edge</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu (bulk)</td>
<td>2.556</td>
<td>–</td>
<td>2.556</td>
<td>–</td>
</tr>
<tr>
<td>Co(<em>{10})Cu(</em>{10})</td>
<td>2.54</td>
<td>0.0001</td>
<td>2.55</td>
<td>0.0004</td>
</tr>
<tr>
<td>Co(_3)Cu(_5)</td>
<td>2.54</td>
<td>0.0000</td>
<td>2.55</td>
<td>0.0005</td>
</tr>
<tr>
<td>Co(_3)Cu(_3)</td>
<td>2.54</td>
<td>–0.0005</td>
<td>2.55</td>
<td>0.0000</td>
</tr>
<tr>
<td>CoK edge</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co (bulk)</td>
<td>2.51</td>
<td>–</td>
<td>2.50</td>
<td>–</td>
</tr>
<tr>
<td>Co(<em>{10})Cu(</em>{10})</td>
<td>2.52</td>
<td>0.0003</td>
<td>2.50</td>
<td>0.0008</td>
</tr>
<tr>
<td>Co(_3)Cu(_5)</td>
<td>2.52</td>
<td>0.0018</td>
<td>2.51</td>
<td>0.0019</td>
</tr>
<tr>
<td>Co(_3)Cu(_3)</td>
<td>2.52</td>
<td>0.0023</td>
<td>2.51</td>
<td>0.0023</td>
</tr>
</tbody>
</table>

\(R_i\) are the nearest-neighbour distances. \(DW_i\) are the Debye–Waller factors, relative to those of the model compounds used to obtain experimental phaseshifts: bulk Cu for CuK edge spectra and bulk Co for the CoK edge spectra. Typical error bars are ±0.0005 Å\(^2\) for \(DW_i\) and ±0.01 Å for \(R_i\). The coordination number for the nearest neighbour shell has been fixed at 12, as for an fcc or hcp structure.
out-of-plane distance 2.55 Å (± 0.01 Å). In the plane of the layers the Co and Cu lattices are strained with respect to the bulk layers (the first neighbour distance is 2.51 Å in Co and 2.556 Å in Cu). This in-plane strain tends to decrease, but not completely eliminate, the mismatch between the two lattices. The deformation tends to expand (by less than 1%) the Co layers, which have a smaller bulk lattice parameter, and to contract by a similar amount the Cu layers. In the direction perpendicular to the Co/Cu interfaces and in both Cu and Co layers, the nearest-neighbour distances are unchanged with respect to the bulk.

The values of the Debye–Waller factors obtained from the fits of the CoK edge spectra (table 1) indicate that the Co layers are significantly more disordered than the Cu layers. While the copper layers tend to form an almost perfect fcc structure, Co grows in the fcc metastable structure imposed by the Cu substrate. As NMR measurements have shown [9] the stacking of the Co layers is not perfect, and the large Debye–Waller factors are probably due to the presence of defects which tend to locally re-establish the hcp structure typical of the bulk Co phase. The Debye–Waller factors tend to decrease as the layer thickness increases and, for the thickest layer, are larger in the direction perpendicular to the Co/Cu interfaces. This could be due to the formation of large ordered hcp domains in the thicker Co layers.

4.2. Fe / Cu multilayers

In fig. 3 the FeK and CuK near-edge XAS spectra obtained for the Fe/Cu multilayers (tFe = 21 Å and tCu = 6, 13, 24, 42 and 60 Å) are compared with those of Fe and Cu bulk metals. These results show that the structure of the Fe layers is bcc as in the bulk metal and is independent of the thickness of the Cu films in the multilayer. On the other hand, the structure of the Cu layers strongly depends on their thickness. The CuK near-edge XAS spectra evolve with the thickness, from that typical of a bcc structure for tCu = 6 Å to that more typical of a fcc structure for tCu = 60 Å. For tCu = 60, 42 and 24 Å the near-edge spectra show, even if less marked, the features characteristic of the fcc Cu bulk structure. These observations are confirmed by the FT data (fig. 4). The Fourier transforms of the CuK spectra for tCu = 6 Å exhibit the peaks typical of a bcc structure. The large-distance peaks are less marked in the direction perpendicular to the growth plane, probably because of the contribution to the spectra of Fe atoms at the Fe/Cu interface. The Fourier transforms of the CuK spectra for thicker Cu films (tCu = 24, 42 and 60 Å) show the large distance peaks characteristics of a fcc structure. The presence of well-defined FT peaks for larger distances indicates the formation of a fairly ordered Cu fcc phase. On the other hand the small amplitude of the FT peaks with respect to those typical of Cu bulk, points to the presence of a static disorder larger than in the bulk Cu phase. The multilayer with tCu = 13 Å appears to be close to the transition point between the bcc structure for thin Cu films and the bulk-like fcc structure for thicker Cu layers. For this multilayer, while the nearest-neighbour
distance is similar to that found for \( t_{\text{Cu}} = 6 \) Å, no important FT peaks are found for larger distances.

The results of the least-squares fits of the Fourier filtered spectra [4] give more quantitative information about the structural changes within the Cu layers. For \( t_{\text{Cu}} = 6 \) and 13 Å the nearest Cu–Cu distance is 2.50–2.52 Å, 1% larger than the Fe–Fe distance in bulk bcc Fe. For \( t_{\text{Cu}} = 13 \) Å, the bcc structure is very disordered and beyond this thickness the Cu layers relax to the fcc structure typical of bulk Cu. For \( t_{\text{Cu}} = 24, 42 \) and 60 Å the Cu–Cu distance is 2.55 Å, close to the nearest-neighbour distance in fcc Cu (2.556 Å). The process of relaxation is gradual, and a more and more ordered fcc phase is formed as the Cu film thickness increases.

The latter result may explain the “anomalous” behaviour of the Fe/Cu coupling, which has been observed to increase as \( t_{\text{Cu}} \) increases. Since the electron mean free path is expected to be longer in more ordered structures, the progressive ordering probably accounts for the “anomalous” increase of the magnetoresistance as the Cu thickness goes from 24 to 60 Å.

5. Conclusion

Using the examples of Fe/Cu and Co/Cu multilayers, we have shown the potential XAS to characterize the local structure of metallic multilayers. The result of these studies may constitute an important step in the understanding of the exceptional magnetic properties of these multilayers.

References