Evidence for the Spin Polarization of Copper in Co/Cu and Fe/Cu Multilayers

Stefania Pizzini,* Alain Fontaine, Christine Giorgetti, and Elisabeth Dartyge
LURE, Bâtiment 209D, Université Paris-Sud, 91405 Orsay, France

Jean-François Bobo, Michel Piecuch, and François Baudelet
Laboratoire de Physique des Solides, URA 155 CNRS, Université de Nancy I,
Vandoeuvre les Nancy, France

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Magnetic circular x-ray dichroism on Co/Cu and Fe/Cu multilayers at the K edge of copper shows (i) that the p band of copper is significantly spin polarized by the adjacent Co or Fe atoms, (ii) that the spin polarization of the copper layers strongly depends on the adjacent magnetic layer, and (iii) that the magnetic polarization is not restricted to the interface layer, i.e., it departs from a simple $1/t_{\mathrm{Cu}}$ dependence.

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Fe/Cu and Co/Cu multilayers are intensively studied because of their exceptional magnetic properties, i.e., their giant magnetoresistance and the oscillations of the magnetic coupling between magnetic layers as a function of the copper spacer thickness [1,2]. Models based either on an adaptation of the RKKY theory [3] or on the partial confinement of the d band within the spacer layer [4] are able to predict the periods and the amplitudes of the coupling oscillations.

Spectroscopic techniques aim to identify the electronic states of the spacer metal which mediate the magnetic coupling. The inverse photoemission measurements by Himpsel and co-workers [5,6] on Cu/Co(001), Cu/Fe(001), and Ag/Fe(001) have shown the existence of quantum-well states, created by the quantization of the momentum of the sp band of the overlayer in the direction perpendicular to the film surface. The charge density of the quantum-well states at the Fermi level oscillates as a function of the layer thickness with a periodicity equivalent to that of the magnetic coupling [6]. This strongly suggests that the quantum-well states contribute to the magnetic coupling. Ortega *et al.* [6] and Brookes, Chang, and Johnson [7] showed for the first time that the quantum-well states in Ag/Fe(001) are spin polarized, with a minority character explained in terms of the spin-dependent band structure of the confining Fe layers. The magnetic polarization of quantum-well states in Cu/Co(001) has also been proven by spin-resolved photoemisssion measurements [8–10].

Magnetic circular dichroism in the x-ray domain (MCXD) probes the local magnetic polarization with a very high sensitivity [11]. It has been applied to probe the polarization of spacer layers in sandwiches and multilayers [12,13]. Our first K-edge measurements on Co/Cu and Fe/Cu multilayers showed that a magnetic polarization is induced on the sp band of copper [14]. More recent results on Co/Cu multilayers have shown that a weak magnetic moment is also induced on the $3d$ band of copper [15].

MCXD is sensitive to the orbital momentum of the probed electronic levels and becomes spin sensitive as a result of the spin-orbit interaction [11]. Measurements at the K and $L_{2,3}$ edges of a transition metal allow the magnetic polarization of p-like electrons (sp bands) and d-like electrons to be investigated. The K-edge MCXD signal of transition metals is in general very weak (10^{-3}) since it is induced by the spin-orbit interaction in the $4p$ band. The main advantages of K-edge spectroscopy for the study of magnetic multilayers are its bulk sensitivity and the possibility to probe directly the conduction electrons, which are expected to mediate the magnetic interactions.

In this Letter we show the results of K-edge MCXD measurements on a series of sputtered Co/Cu and Fe/Cu multilayers. The multilayers, deposited on 7 μm thick kapton foil, were prepared by magnetron sputtering in the sequence $\mathrm{Fe}_{50\,\text{Å}}/50(\mathrm{Co}_x\text{-}\mathrm{Cu}_y)/\mathrm{Cr}_{25\,\text{Å}}$ ($x = 8$, 12, 18, and 27 Å, $y = 4$, 8, 12, 16, and 20 Å) and $\mathrm{Cr}_{50\,\text{Å}}/50(\mathrm{Fe}_{12\,\text{Å}}\text{-}\mathrm{Cu}_{8\,\text{Å}})/\mathrm{Cr}_{25\,\text{Å}}$. The samples are polycrystalline and untextured and have good interface quality [16]. The crystallographic structure of the mutilayers is fcc for Co/Cu and bcc for Fe/Cu. The magnetoresistance of the kapton-deposited samples is smaller than that of the same samples deposited on float glass (6% vs 45% for $\mathrm{Co}_{9\,\text{Å}}\mathrm{Cu}_{8\,\text{Å}}$). This is due (i) to the larger roughness of the kapton-deposited substrates which induces a less precise definition of the layer thickness and (ii) to the random grain distribution which has the effect of averaging the magnetoresistance values over all orientations.

K-edge MCXD measurements were carried out in transmission geometry at the energy dispersive x-ray absorption spectrometer of LURE (DCI) [17]. Right circularly polarized ($P_c \approx 70\%$) x-ray photons were selected by positioning a slit at about 3 mrad below the orbit plane of the storage ring. The multilayer samples were positioned in grazing geometry (10°) with respect to the propagation direction of the x rays **k**. X-ray absorption spectra were measured at 300 K in a magnetic field of 0.4 T, whose direction was alternatively switched from parallel to an-

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tiparallel to that of the x-ray beam. The coupling between magnetic layers was always ferromagnetic.

MCXD was measured at the *K* edge of copper and the magnetic atoms (Co and Fe). At the Cu *K* edge good statistics ($S/N \approx 10^5$ for the total absorption spectrum) were obtained with acquisition times of the order of 12 h. The S/N ratio for the MCXD data is of the order of 10 since the difference $(\mu^+ - \mu^-)$ is as small as 10^{-4} (μ^+: $\mathbf{B} \| \mathbf{k}$, μ^-: $\mathbf{B} \| -\mathbf{k}$). The difference spectra $(\mu^+ - \mu^-)$ are normalized to the height of the absorption edge step.

The Cu *K*-edge MCXD spectrum obtained for the $\mathrm{Co}_{12\,\text{Å}}\mathrm{Cu}_{8\,\text{Å}}$ multilayer is presented in Fig. 1 where it is compared with the total absorption spectrum. The signal consists essentially of a negative peak (amplitude 5×10^{-4}) in the vicinity of the inflection point of the absorption edge. The higher energy structures are the magnetic counterpart of the near-edge structure in the total absorption spectrum and will not be discussed here.

The presence of an MCXD signal at the *K* edge of copper in this Co/Cu multilayer shows that the $4p$ band of copper is magnetically polarized.

In Fig. 2(a) we have compared, for the $\mathrm{Co}_{12\,\text{Å}}\mathrm{Cu}_{8\,\text{Å}}$ multilayer, the spectra measured at the *K* edge of copper and cobalt. In the two cases the MCXD signal at the edge position consists essentially of a main peak of the same negative sign. The Cu *K*-edge spectrum is only 3 times smaller than the Co *K*-edge spectrum. The magnetic moment on the $4p$ band of cobalt ($\approx -0.06\mu_B$) is created by the spin-dependent hybridization with the exchange polarized $3d$ band close to the Fermi level. The hybridization tends to align the p moment antiparallel to the $3d$ moment. The same sign found for the MCXD signal at the Cu *K* and Co *K* edges reflects the fact that the $4p$ moments on the two metals have the same orientation. The $4p$ moment on copper is therefore of minority character. This result is in agreement with the spin-resolved photoemission data obtained for Cu/Co(001) [8–10].

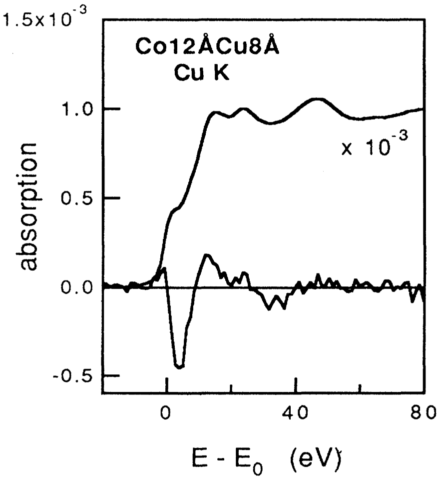

FIG. 1. The Cu *K*-edge MCXD spectrum measured for the $\mathrm{Co}_{12\,\text{Å}}\mathrm{Cu}_{8\,\text{Å}}$ multilayer is shown with the corresponding total absorption spectrum. The latter has been multiplied by 1×10^{-3}.

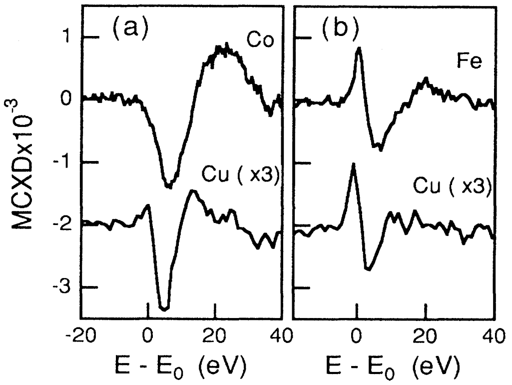

FIG. 2. (a) Cu *K*-edge and Co *K*-edge MCXD spectra of the $\mathrm{Co}_{12\,\text{Å}}\mathrm{Cu}_{8\,\text{Å}}$ multilayer; (b) Cu *K*-edge and Fe *K*-edge MCXD spectra of the $\mathrm{Fe}_{12\,\text{Å}}\mathrm{Cu}_{8\,\text{Å}}$ multilayer. The Cu *K*-edge signals have been multiplied by 3.

The amplitude of the Cu *K*-edge signal measured for the $\mathrm{Co}_{12\,\text{Å}}\mathrm{Cu}_{8\,\text{Å}}$ multilayer is only 3 times weaker than that of the signal measured at the Co *K* edge. Since the amplitude of the MCXD signal is correlated to the $4p$ magnetic moment on the probed atomic species [18], we derive that for this multilayer the $4p$ moment on copper, averaged over the copper thickness (4 monolayers), is of the order of $-0.02\mu_B$, to be compared with the $-0.05\mu_B$ for the cobalt layer.

In order to understand the mechanism responsible for the polarization of the conduction bands of copper, we can discuss the results obtained for the $L_{2,3}$-edge MCXD measurements on a series of similar Co/Cu multilayers [15]. The measurements by Samant *et al.* demonstrate the presence of an induced $3d$ spin moment on copper, aligned parallel to the Co-$3d$ moment. The $3d$ moment is very weak ($0.01\mu_B$ for 13 Å Cu and $0.05\mu_B$ for 4 Å Cu) compared with the $3d$ moment on cobalt ($1.7\mu_B$). In contrast, we have shown that the average spin polarization of the $4p$ band of copper is of the same order of magnitude of that of the $4p$ band of cobalt. It is therefore concluded that this strong $4p$ polarization is induced by the copper $3d$ moment. The polarization of copper is more probably induced by the hybridization of the Cu-$4p$ band with the Co-$3d$ band at the Cu/Co interfaces. The $3d$-$4p$ hybridization is more efficient for the minority $3d$ band since its average energy is closer to the Fermi level and this favors an antiparallel alignment of d and p moments.

The role played by the $3d$-$4p$ hybridization in the polarization of the conduction band of copper becomes clearer when we look at the MCXD results for the $\mathrm{Fe}_{12\,\text{Å}}\mathrm{Cu}_{8\,\text{Å}}$ multilayer [Fig. 2(b)]. When copper is sandwiched between iron layers in the $\mathrm{Fe}_{12\,\text{Å}}\mathrm{Cu}_{8\,\text{Å}}$ multilayer, the Cu *K*-edge MCXD spectrum acquires the double-peaked structure typical of Fe. In the $\mathrm{Fe}_{12\,\text{Å}}\mathrm{Cu}_{8\,\text{Å}}$ multilayer the Cu *K*-edge spectrum is characterized by a strong positive contribution, in contrast to the $Co_{12\,Å}Cu_{8\,Å}$ multilayer where the signal is essentially negative. In both Co/Cu and Fe/Cu multilayers the main features of the Cu *K*-edge MCXD signal are closely related to those of the magnetic atoms adjacent to Cu. The difference between the MCXD spectra of Co and Fe metals can be tentatively explained in terms of the difference of the spin polarization of the $3d$ band of the two metals. Fe is a weak ferromagnetic material with empty states in both the majority and minority $3d$ bands, while Co has empty states only in the minority band. The shape of the *K*-edge MCXD spectra for Fe (double peaked) and Co (single peaked) reflects the $3d$ spin polarization via the hybridization between $3d$ and $4p$ bands [19,20]. The similar shape of the *K*-edge MCXD signal of Co and Cu in Co/Cu multilayers (typical of strong ferromagnetism) and Fe and Cu in Fe/Cu multilayers (typical of weak ferromagnetism) indicates that the $4p$ polarization of copper is induced by the magnetic atom via the $3d$-$4p$ hybridization, which is significant close to the interfaces.

The Co *K*-edge MCXD signal was measured for a series of $Co_x/Cu_{12\,Å}$ multilayers with increasing Co thickness. The shape of the signal does not change with thickness but the amplitude of the signal decreases as the film thickness goes from 100 to 8 Å (Fig. 3). If we correlate the decrease of the MCXD amplitude to a decrease of the $4p$ magnetic moment, this result indicates that in this multilayer the average $4p$ band polarization of cobalt decreases with respect to bulk cobalt. The MCXD amplitude can be fitted with a function decreasing as $1/t_{Co}$, indicating that the Co atoms with decreased $4p$ moment belong to a layer of fixed thickness close to the interface. A vanishing $4p$ moment on Co is obtained for a Co layer 2.6 Å thick, i.e., of 1.3 Å for each interface. It is rather unlikely, however, that the Co atoms at the interface layer have a vanishing $4p$ moment, while the core atoms have unchanged moment. This possibility is also ruled out by the calculations of Samant *et al.* [15]. The decrease of the $4p$ moment is more likely to be gradual and to concern the interfacial layer where Cu and Co are interdiffused. The decrease of the interfacial Co moment with respect to the bulk metal is confirmed by SQUID measurements. The effective magnetization on series of 12 Å thick Co layers measured over a series of samples is 1140 ± 100 to be compared with 1400 emu/cm^3 for bulk Co. These magnetization values indicate that the Co moment reduction is equivalent to the presence of a 2.3 Å dead layer, in very good agreement with the results of magnetic dichroism. The decrease of the Co magnetic moment at the interface is probably due to the hybridization of the $3d$ band of cobalt with the nonmagnetic $3d$ band of copper.

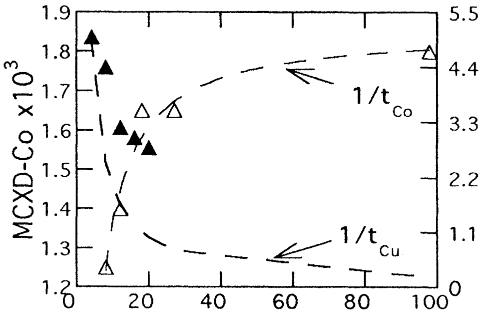

FIG. 3. The thickness dependence of the amplitude of the MCXD signal in Co/Cu multilayers: Co *K* and Cu *K* edges. The amplitude of the Co *K*-edge MCXD signal can be fitted to an $A - B/t$ function; the amplitude of the Cu *K*-edge MCXD signal departs from a $1/t$ dependence.

Some of the details of the Cu *K*-edge MCXD spectra remain to be clarified, in particular, the origin of the small positive peak before the main Cu *K*-edge MCXD signal in Co/Cu multilayers. This peak is probably due to the details of the hybridization between the Cu-$4p$ and Co-$3d$ bands at the interface. The weaker polarization of cobalt at the interface may reduce the occupation of the majority spin band and induce a positive peak in the *K*-edge MCXD spectrum.

One of the questions raised by these results is whether the polarization of the copper $4p$ bands is limited to the interfaces or it is partly extended to the core of the layer. The MCXD results at the $L_{2,3}$ edges of copper in Co/Cu multilayers [15] show that the magnetic polarization of the $3d$ bands of copper decreases rapidly away from the interfaces, so that the magnetic moments are essentially restricted to the interfacial layer. Layer-by-layer calculations confirm that the polarization of the $3d$ band exhibits an RKKY-like oscillatory behavior with a very rapid decay away from the interfaces.

The thickness dependence of the Cu *K*-edge MCXD signal in our $Co_{12\,Å}Cu_x$ multilayers (t_{Cu} ranging from 4 to 20 Å) is shown in Figs. 3 and 4. The signal decreases when the Cu thickness increases, but a very strong polarization is still found for thicknesses up to 20 Å.

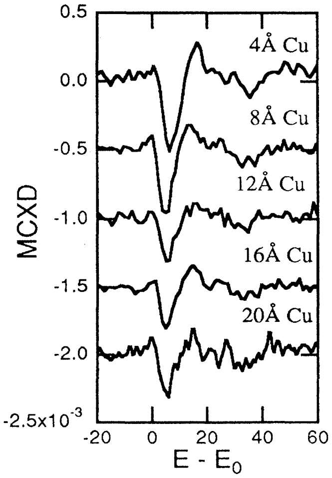

FIG. 4. Cu *K*-edge MCXD signal for a series of $Co_{12\,Å}Cu_x$ (x = 4, 8, 12, 16, and 20 Å) multilayers. The amplitudes of the signals are summarized in Fig. 3.

Even if the extent of our measurements is not sufficient to safely extrapolate the data to very large copper thicknesses, it is clear that the experimental data cannot be fitted with a $1/t_{\mathrm{Cu}}$ function roughly predicted by RKKY theory (see Fig. 3). This large deviation from a $1/t_{\mathrm{Cu}}$ law indicates that the polarization is extended beyond the interfacial region. Our results are consistent with the spin-resolved photoemission measurements on Cu/Co(001) by Carbone *et al.* [8], which show a large spin polarization of copper sp quantum-well states up to at least 10 monolayers of Cu. The measurements in Ref. [8] point out the different character of $3d$ and sp electronic states in copper. Both $3d$ and sp bands are spin polarized by the interaction with the magnetic substrate, but only the widely dispersed sp band exhibits thickness-dependent quantum-well states which allow the polarization to propagate to the interior of the Cu layers. While the polarization of the $3d$ bands appears to decay smoothly with thickness, that of the sp bands is modulated by the quantum-well states [8]. A departure from a $1/t_{\mathrm{Cu}}$ behavior can therefore be expected for the polarization decay.

Finally, our results lead to the following conclusions. In Co/Cu and Fe/Cu multilayers the conduction bands of copper are magnetically polarized via $4p$-$3d$ hybridization at the Cu/M (M = Co, Fe) interface. The $4p$ moments of copper and the magnetic atom (Co and Fe) have the same orientation. The preferential hybridization of the $4p$ band with the $3d$ minority band favors the minority character of the $4p$ spin moments. The magnetic moments of the d band [15] and p band found with $L_{2,3}$ and K-edge magnetic dichroism have opposite sign and similar magnitude ($\approx 0.02\mu_B$). For this reason we cannot exclude that the total magnetic polarization of copper is vanishing. Finally, in Co/Cu multilayers, possibly because of the formation of quantum-well states, the magnetic polarization of copper is not restricted to the interfaces, being relatively strong up to at least 20 Å of copper.

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*Now at Laboratoire de Magnétisme Louis Néel, CNRS, BP 166X, Grenoble, France.

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