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O *K*-edge x-ray magnetic circular dichroism of atomic O adsorbed on an ultrathin Co/Cu(100) film: Comparison with molecular CO on Co/Cu(100)

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We observed O *K*-edge x-ray magnetic circular dichroism (XMCD) of atomic O adsorbed on a fcc Co thin film grown epitaxially on Cu(100). The XMCD of $c(2\times2)$O showed a negative sign at the O1$s\rightarrow2p$ transition. The negative sign indicates parallel alignment of the O orbital moment with the substrate magnetization. This finding is in contrast to the CO/Co/Cu(100) case where a positive XMCD was observed at the O1s $\rightarrow$CO2π^* transition. A possible explanation for this discrepancy is proposed referring to recent theoretical prediction [Pick *et al.*, Phys. Rev. B **59**, 4195 (1999)].

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Magnetic properties of ultrathin metal films have widely been investigated and drastic effects of adsorption of atoms and molecules have been revealed. In the case of oxygen adsorption, enhancement of the Fe magnetization has been reported,[1,2] while significant suppression was found for thin Ni films grown on Cu(100).[3] Moreover, even a reversal of the Mn magnetization has been reported for Mn/Fe(100) ultrathin films.[4] Recently, semiempirical tight-binding calculations have been performed to understand the chemisorption effects of atomic O and molecular CO on the magnetization of Co.[5] It was concluded that atomic oxygen does not essentially affect the Co magnetization while CO is a good magnetization killer. It was also indicated that atomic O couples ferromagnetically with Co while the CO magnetization is antiferromagnetic. A more interesting result is that the magnetic moment of the Co atom just below CO is also antiferromagnetically coupled with the rest Co atoms.

In order to investigate the magnetic effects of molecular and atomic adsorption, information on the local magnetization around the adsorbates is indispensable. Thus the induced magnetic moments of adsorbates have been studied mainly by using spin-polarized techniques. It has been reported that atomic O adsorbed on a Co film is ferromagnetically coupled with Co.[6] In the case of CO adsorption,[7] no splitting of the CO 5σ levels was observed, though no direct information on the surface magnetization seems to have been obtained.

The x-ray magnetic circular dichroism (XMCD) technique is one of the most suitable methods to obtain direct information on the magnetization of adsorbates, since the technique is element specific. For the light elements such as oxygen, the *K*-edge XMCD should be measured instead of $L_{\mathrm{III,II}}$ and $M_{\mathrm{V,IV}}$ edges. Although many interesting features of bulk oxides were clarified from the O *K*-edge XMCD,[8–10] it is much more difficult to accumulate reliable *K*-edge XMCD signals from adsorbates. We have recently investigated O *K*-edge XMCD of submonolayer CO on Ni/Cu(100) (Ref. 11). Moreover, we have reported a preliminary experimental results on CO/Co/Cu(100) (Ref. 12). We believe that these careful works have established reliable measurements of small *K*-edge XMCD signals from submonolayer adsorbates. In the present study, we have measured O *K*-edge surface XMCD spectra of atomic O adsorbed on an ultrathin fcc Co film grown on Cu(100). The magnetic effects of O and CO were discussed by comparing with the theoretical prediction.[5]

A fcc Co film was prepared on a Cu(100) single crystal according to the following procedure. The Cu substrate was cleaned in an ultrahigh vacuum (UHV) chamber by successive cycles of Ar^+ bombardment and annealing at 900 K. The fcc Co film was epitaxially grown at room temperature by evaporation from a resistively heated Co wire. Thickness of the film was monitored by the *in situ* observation of the RHEED (reflection high-energy electron diffraction) oscillations. The $c(2\times2)$O/Co/Cu(100) overlayer was obtained according to the literature.[6] The 2.4 ML [ML (monolayer) is defined as the number of Co atoms with respect to the surface Cu atoms] Co film was dosed with 0.2 L (5×10^{-9} Torr for 40 s) oxygen at room temperature and heated to 410 K. Unfortunately, no LEED optics were installed at the present chamber to detect the $c(2\times2)$ superstructure. Additional dosage with 0.2 L oxygen, however, did not increase the O coverage verified by O *K*-edge jumps. The previous study[6] found a plateau of the O coverage as a function of dosage around the $c(2\times2)$O region, indicating that the present surface prepared by 0.2 L oxygen exposure may correspond to the $c(2\times2)$O/Co overlayer.

The O *K*- and Co $L_{\mathrm{III,II}}$-edge XMCD spectra were taken at room temperature with the bending-magnet station Beamline 11A of the Photon Factory in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-PF).[13–15] We have employed a positive x-ray helicity by using the upper part of the synchrotron radiation orbit plane (+0.4 mrad, ±0.1 mrad width). The circular polarization factor was estimated as $P_c=0.75$ by measuring bulk hcp Co. The energy resolution $E/\Delta E$ was around 500–1000. All the spectra for the thin film were recorded in a partial electron yield mode with a 25-mm diameter microchannel plate, which was placed just below the sample. Retarding voltages of –400 and –500 V were employed for the O *K* and Co *L* edges, respectively. The probing depth for the present setup was ~5 Å. For the NEXAFS measurements, incidence angles θ of x rays were 90° (normal incidence, an electric-field vector parallel to the surface), 55°, and 30°.

The samples were mounted in a Cu coil and were magnetized by a current pulse along the incident x rays. The pulse

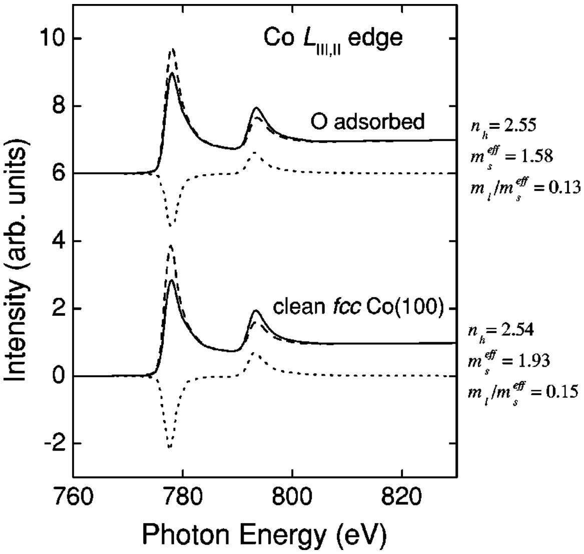

FIG. 1. Co $L_{\mathrm{III,II}}$-edge circular polarized x-ray absorption (solid and long-dashed lines) and XMCD (short-dashed line) spectra for clean (bottom) and O-adsorbed (top) 2.4 ML fcc Co(100) taken at room temperature. The estimated values of n_h, m_s^{eff} (effective spin magnetic moment, m_s+7m_T), and m_l/m_s^{eff} for Co are also given.

currents were large enough (~ 0.05 T) to reach the saturation of magnetization of the Co films, and the remanent magnetization was examined. Since the fcc Co films investigated here are known to be magnetized along the surface plane,[16–18] only the grazing-incidence ($\theta = 30°$) XMCD spectra were recorded. In this configuration, the angle between the magnetization **M** and the x-ray wave vector **k** is 30° or 150°. Typical accumulation time for each data point was 4 s for Co $L_{\mathrm{III,II}}$-edge XMCD and O *K*-edge NEXAFS, and 100 s for O *K*-edge XMCD. The relative photon energy of each spectrum was calibrated with the precision of 0.01–0.02 eV using absorption structures of oxygen contamination on mirrors, appearing in the transmission function measured simultaneously by a Au-coated W mesh placed at the upstream of the sample.[19]

Figure 1 gives Co $L_{\mathrm{III,II}}$-edge circularly polarized and XMCD spectra of clean and O-adsorbed 2.4 ML fcc Co films on Cu(100). The circularly polarized spectra were obtained by division with the I_0 function, linear pre-edge subtraction, and normalization with the edge jumps. The saturation effect of the electron yield measurements[22] was not taken into account for the present ultrathin Co film. On the other hand, for the reference bulk hcp Co (spectrum not shown), the total electron yield spectra were rescaled assuming the electron escape depth of 20 Å (different from that using the partial electron yield). In order to obtain the number of *d* holes, the white-line intensities were estimated by subtracting the step functions for the $L_{\mathrm{III,II}}$ edges from the polarization-averaged spectra.[20] By assuming that the *d*-hole number is proportional to the white-line intensity and that it is 2.50 for bulk hcp Co (Ref. 21), one can obtain n_h as indicated in Fig. 1.

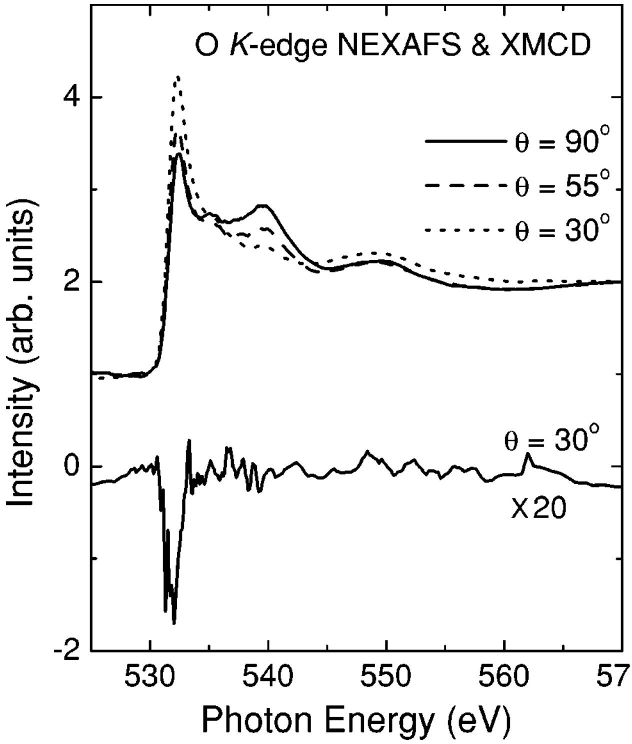

FIG. 2. X-ray incidence angle dependence of O *K*-edge NEXAFS (top) and grazing-incidence O *K*-edge XMCD (bottom) spectra for the $c(2\times2)$O overlayer adsorbed on 2.4 ML fcc Co(100) taken at room temperature.

The XMCD spectra were obtained by the subtraction between the two circularly polarized spectra and the subsequent rescaling with the factor of $P_c\cos\theta$. The value of P_c was determined so that the spin magnetic moment m_s of bulk hcp Co may match the value of $m_s = 1.62$ (μ_B) reported by the transmission XMCD measurements.[23] By employing the well-established sum rules,[24,25] and neglecting the magnetic dipole term m_T, the circular polarization factor was consequently estimated as $P_c = 0.75$. Resultantly obtained m_s^{eff} (effective spin magnetic moment, m_s+7m_T) and m_l/m_s^{eff} (ratio between orbital and effective spin magnetic moments) for clean and O-adsorbed Co films are inserted in Fig. 1. Here, the effective spin moment is given instead of m_s, because m_T is not negligible in the case of ultrathin films. We can apparently find that the effective spin magnetic moment of Co is suppressed with O adsorption (18% reduction relative to that of the clean film). Although some uncertainties remain due to the ambiguities in the evaluation of the *d*-hole number, the observed reduction of m_s^{eff} seems significant.

Figure 2 gives the O *K*-edge NEXAFS and XMCD spectra. The XMCD spectrum was similarly normalized with the factor of $P_c\cos\theta$ as well as the O *K*-edge jumps. In the NEXAFS spectra, distinct angle dependence was observed; the first resonance at ~ 532 eV is enhanced at grazing x-ray incidence, while the second one ~ 540 eV is pronounced at normal x-ray incidence. The first resonance can be ascribed to the transition to the O $2p_z$ level interacting with the Co $3d$ bands.[3] As for the XMCD spectrum, a negative peak is clearly found at ~ 532 eV. The XMCD signal did not change regardless of which direction of the magnetic field was formerly applied (figures not shown), this excluding the possibility of some time-dependent artifacts. Moreover, it has been concluded in the previous report[12] that no artificial XMCD signal is observed with the present setup, which may originate from flipping of the magnetization direction. The reliability of the present XMCD spectra is thus confirmed.

According to the sum rule concerning the *K*-edge XMCD spectrum,[24,26] the orbital magnetic moment m_l is given as

$$m_l = -\frac{2}{3}\frac{n_h}{P_c \cos\theta}\frac{\int_K(\mu^{\uparrow\uparrow}-\mu^{\uparrow\downarrow})dE}{\int_K(\mu^{\uparrow\uparrow}+\mu^{\uparrow\downarrow}-2\mu^{BG})dE}, \qquad (1)$$

where n_h is the number of holes, and $\mu^{\uparrow\uparrow}$ and $\mu^{\uparrow\downarrow}$ are the normalized absorption coefficients in the case where the helicity is parallel and antiparallel to the majority spin of the whole sample. μ^{BG} is the normalized absorption coefficient attributed to the transitions to the continuum. Accordingly, the observed negative XMCD signal implies a positive orbital magnetic moment (parallel to the total magnetization of the Co film) at the $2p_z$ level. The absolute value of the moment cannot be obtained, however, because n_h and μ^{BG} are difficult to estimate.

Before discussing the experimental observations, let us here recall the previous results for CO adsorption on a 4 ML Co film.[12] In the O *K*-edge XMCD spectrum, a positive signal was clearly observed at the $\mathrm{O}1s \rightarrow \mathrm{CO}2\pi^*$ transition. This finding is in clear contrast to the above O/Co/Cu(100) system, which shows a negative XMCD sign. When the sum rule for the orbital moment is similarly applied, we can conclude a negative orbital magnetic moment (antiparallel to the total magnetization of the Co film) at the $\mathrm{CO}2\pi^*$ level.

A similar discrepancy has been found in a theoretical study performed by Pick *et al.*,[5] though they calculated spin magnetic moments whereas we observed orbital ones. In the case of O adsorption on a fcc Co_{13} cluster, they found a ferromagnetic coupling of the O spin magnetic moment $[m_s = 0.06(\mu_B)]$ with the Co cluster. As for the surface Co atom, $m_s = 1.77(\mu_B)$ was reported. On the other hand, the spin magnetic moments of adsorbed CO and one Co atom directly interacting with CO were estimated to be $-0.08\ \mu_B$ and $-0.13\ \mu_B$, respectively. This implies that both the CO molecule and the Co atom just below CO are antiferromagnetically coupled with the total Co magnetization.

Let us try to compare our experimental findings with the theoretical predictions. As described above, the present results imply the positive (parallel to the whole Co film) orbital magnetic moment on the adsorbed O atom, while in the case of CO adsorption the negative one is suggested. The origin of the orbital moments is not clear, but a theoretical study for bulk Ni performed by Igarashi and Hirai[26] is suggestive. They showed that the Ni $4p$ level has little orbital moment if the spin-orbit interaction only in the $4p$ level is taken into account, while a significant $4p$ orbital moment is induced through the hybridization with the $3d$ orbitals of neighboring Ni atoms. In the present study, since the O $2p$ orbital hybridizes significantly with Co $3d$ both in the CO and O adsorption cases, it might be possible to assume that the observed XMCD signals reflect the orbital moments in the Co atoms directly interacting with the adsorbates.

According to this assumption, the present experimental observations seem to coincide with the theoretical predictions.[5] Since the spin magnetic moment of the Co atom should be aligned parallel to the orbital moment due to the Hund rule (more than half filled case), the negative O $2p$ orbital magnetic moment in CO resultantly suggests that the Co atom just below CO has an antiparallel magnetization to the rest of the Co film. On the contrary, in the case of O adsorption all the Co atoms are ferromagnetically aligned. For the verification of the present hypothesis, some sophisticated theoretical studies which directly treats the O *K*-edge XMCD are indispensable.

In conclusion, O *K*-edge XMCD spectra of atomic O adsorbed on an ultrathin fcc Co film grown epitaxially on Cu(100) were successfully recorded to investigate induced orbital magnetic moment on the adsorbate and local magnetization around the adsorbate. The $c(2\times 2)$O overlayer exhibited a negative XMCD sign concerning the O $2p_z$ level. This finding is in clear contrast to the CO adsorption case which gave a positive XMCD for the CO $2\pi^*$ level. According to the sum rule[24,26] for *K*-edge XMCD, these observations suggest, respectively, the parallel and antiparallel alignments of the orbital magnetic moments of atomic O and molecular CO with the total magnetization of the Co films.

These observations were comparatively discussed with the theoretical study,[5] which predicted ferromagnetic and antiferromagnetic interactions for O and CO adsorption on the Co clusters, respectively. We showed a possible interpretation that relates our finings to the previous work, with an assumption that the direction of the orbital moment in the adsorbate is parallel to that of the Co atom directly interacting with the adsorbate. The present work has demonstrated the possibility of the XMCD technique for studying the local magnetization of substrate atoms around adsorbates. Further theoretical works are desired to obtain deeper insight on the magnetic interaction between the adsorbates and substrates.

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