

Magnetism and electron redistribution effects at Ni/Co interfaces

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The electronic structure at the Ni/Co interface has been characterized using differences in $L_{2,3}$ x-ray-absorption spectra (XAS) recorded before and after deposition of Ni overlayers on Co films. Strong changes in the Co and Ni absorption spectra suggest a high degree of d -charge redistribution between the Co and Ni d states for submonolayer coverages of Ni. X-ray magnetic circular dichroism shows that the change in the d -state occupancies results in an increased Co spin moment and a reduced Ni spin moment. The effects are interpreted in terms of a modified exchange splitting of the Ni and Co d bands determined using line-shape analysis of Co XAS. The results are compared with the predictions of first-principles band-structure calculations invoking the local spin-density approximation.

I. INTRODUCTION

Data storage technology has benefited widely from the discovery of artificial materials not found in nature such as magnetic multilayers and amorphous alloys.¹ These materials often exhibit important phenomena such as perpendicular magnetic anisotropy (PMA) and giant magnetoresistance. At the same time they provide a challenge for theorists to explain the microscopic origin of low-dimensional magnetism. For instance, the prediction and confirmation of PMA in Ni/Co multilayers is a prime example of how theoretical calculations can be used to tailor novel materials exhibiting technologically important properties.² Using first-principles local-spin-density calculations Daalderop *et al.*² showed that the Ni/Co interface anisotropy is controlled by d -state occupancy near the Fermi level. However, other studies have shown that predicting the effects of electron mixing and hybridization at ferromagnetic interfaces remains a challenge even for state-of-the-art calculations.^{3,4} Experimental determination of such effects, and their influence on interface magnetism, is therefore essential from both a theoretical and technological point of view.

In a recent study, Dhesi *et al.*⁵ reported on the electronic and magnetic structure of ultrathin Ni films grown on 4 ML films of Co. A marked reduction in the Ni spin moment, as the film thickness was decreased from 2 ML to 0.2 ML, was attributed to an increased electron localization. In the present study we show that, in addition to changes in the Ni hybridization, electron redistribution plays an important role in determining the magnetic properties at the interface of Co and Ni. We use high-resolution x-ray absorption spectroscopy (XAS) with circularly polarized radiation to monitor electronic structure and interface magnetism in an element-specific manner for Ni films grown on Co. Deposition of Ni on Co, results in a redistribution of charge, which increases the Ni d -state occupation and reduces the d occupancy of Co. X-ray magnetic circular dichroism (XMCD) shows that this redistribution increases the Co spin moment and reduces the Ni spin moment. Features in the Co $L_{2,3}$ spectra, which are resolved for the first time, are used to interpret the interface magnetism in terms of a modified density-of-states (DOS).

The results are compared with first-principles band-structure calculations, which predict negligible hybridization and charge rearrangement at the Ni/Co interface.

II. EXPERIMENT

The Cu(001) substrate was prepared by repeated cycles of Ar⁺ ion bombardment and annealing to 700 K in UHV. Co was deposited onto the Cu(001) surface at temperatures between 270 and 300 K followed by deposition of Ni at similar temperatures. The films were not annealed to avoid interdiffusion and the pressure rise during deposition of either Co or Ni was $< 1 \times 10^{-10}$ mbar. The thickness of the Ni and Co films was calibrated by a quartz crystal monitor and by edge jumps in the XAS spectra. All coverages reported in this study are accurate to within 10%. The morphology and growth mode of the films was determined using high-resolution low-energy electron diffraction and is described in more detail elsewhere.⁵ The electronic and magnetic properties of the thin films were investigated using 85% circularly polarized light at beamline ID12B of the European Synchrotron Radiation Facility, Grenoble. The $L_{2,3}$ absorption spectra were recorded in total electron yield mode with the light incident at 45° after remanent magnetization of the films parallel to the sample surface. The energy resolution of the incident x-rays was better than 0.45 eV. XMCD spectra were recorded by reversing the remanent magnetization of the thin films and by reversing the helicity of the incident radiation. The angle-dependence of the XMCD indicated that all films reported here exhibited an in-plane easy direction of magnetization. All XAS spectra presented were normalized to a constant edge jump in order to obtain ground-state moments per atom. Saturation effects are negligible for the given geometry and thin Ni films used in this study.⁶

III. RESULTS AND DISCUSSION

Figure 1 shows the isotropic Co $L_{2,3}$ edges for a 4 ML Co film grown on Cu(001) before (dashed line) and after (drawn line) deposition of a Ni ML. The spectra, split by the $2p$ spin-orbit interaction into an L_3 and L_2 structure, show fea-

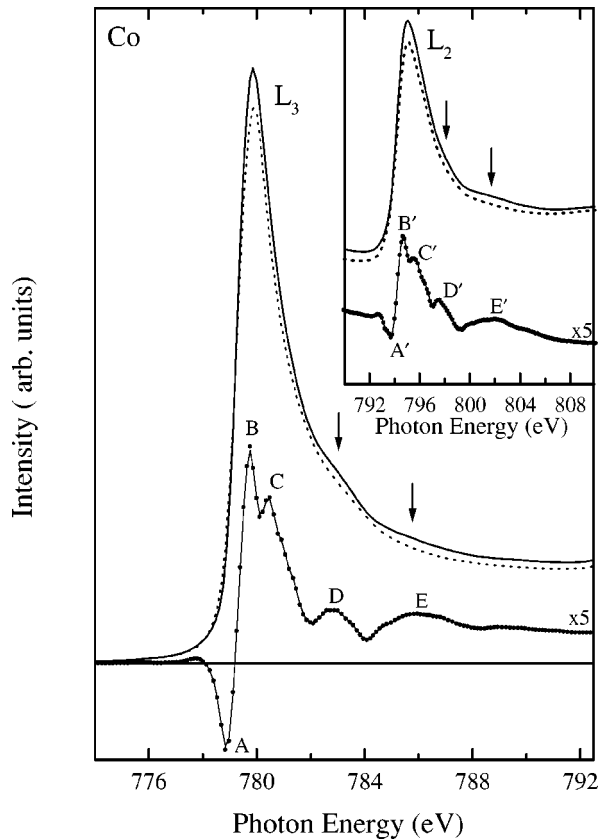


FIG. 1. Co L_3 XAS for 4 ML Co grown on Cu(001) before (dashed line) and after (drawn line) deposition of 1 ML Ni. The difference spectrum (dots) is shown with a Fourier smoothing (drawn line). The energy positions of the resolved features with respect to the L_3 maximum are $A = -1$, $B = -0.1$, $C = 0.6$, $D = 3$, and $E = 6.1$ eV. The inset shows the Co L_2 edge with the energy positions with respect to the L_2 maximum as $A' = -1.4$, $B' = -0.3$, $C' = 0.5$, $D' = 2.6$ and $E' = 6.4$ eV.

tures due to transitions from the core level to the unoccupied s and d states. The d states largely dominate because of the much larger radial matrix element. After addition of the Ni overlayer the intensity at the $L_{2,3}$ edges increases and additional satellite structures are resolved, as indicated by the downward pointing arrows. Furthermore, the line shape of the difference spectrum shows that the increase in intensity is not uniformly distributed across the edges. At least five features, labeled $A-E$, can be resolved in the L_3 difference spectrum of Fig. 1. The line shape of the difference spectrum (circles) was confirmed by repeated measurements for varying Ni overlayer thicknesses. The L_2 difference spectrum shows almost the same features (inset Fig. 1). Features $A-E$, which are directly related to the structure in the XAS spectra, have not been reported previously. For Ni, the origins of satellite features in the $L_{2,3}$ edge XAS spectra remain controversial. In a one-electron model the XAS satellites are explained in terms of critical points in the DOS.^{7,8} In a configuration interaction (CI) approach, the satellites are due to d -weight fluctuations in the initial state.^{9,10} However, the application of the CI model to metallic Co is complicated by the large number of configurations in the final state.

The removal of the transitions into the continuum and s states is accomplished, in the standard manner, by subtracting

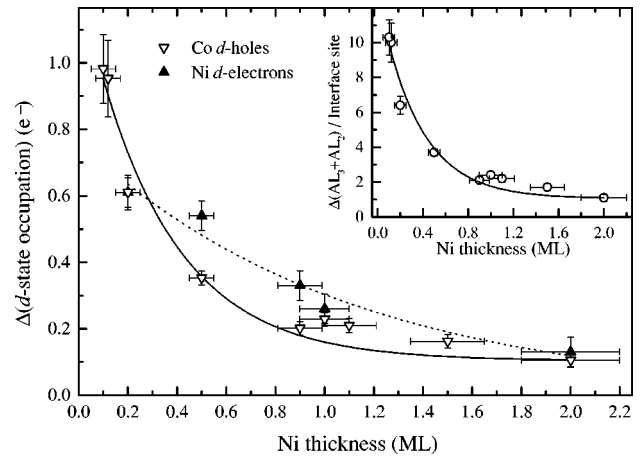


FIG. 2. The increase in the number of Co d holes (open triangles) and corresponding increase in Ni d -state occupancy (solid triangles). The lines are a guide to the eye. The inset shows the increase in the integrated area over the Co $L_{2,3}$ edge as a function of Ni overlayer thickness.

tion of a steplike background aligned at the maxima of the L_3 and L_2 edges with relative heights of 2:1. The integrated intensity over the $L_{2,3}$ edges is then proportional to the number of unoccupied d states. The thickness dependent trend in the Ni d -state occupation, extracted from the Ni $L_{2,3}$ edge, is shown in Fig. 2 (solid triangles). The procedure used to determine this has already been described in a previous report.⁵ The rise in the occupation of the d states for decreasing Ni film thickness is similar to the case for Ni thin films grown on Cu(001).¹¹

The increase in the integrated intensity over the Co $L_{2,3}$ edge in Fig. 1 shows that the occupation of the Co d states decreases after the addition of a Ni film. The inset of Fig. 2 shows the background subtracted change in the integrated Co $L_{2,3}$ intensity for varying Ni coverages. The data have been normalized to the Ni overlayer thickness in order to reflect the intensity rise due solely to the Co-Ni interface sites. In order to transform the intensity changes in the inset of Fig. 2 into d -state occupation changes we adopt the following procedure. Figure 2 shows that the Ni d -state occupancy increases by ~ 0.61 electrons going from a 2 ML to a 0.2 ML Ni film. In the case of the Ni/Cu interface the electron mixing has been shown to be dominated by the d states.¹² If, in the same manner, the Ni- d -Co- d hybridization dominates then the increase in the Ni d -state occupancy can be equated with the decrease in the Co d -state occupancy. By taking the total change in the number of Ni d electrons (0.61) equal to the corresponding change in the Co integrated intensity for the 0.2 ML Ni overlayer, the trend in the Co d -state occupancy can be established (Fig. 2, open triangles). The decrease in the Co d -state occupancy at the interface sites follows the increase in Ni d -state occupancy over a wide range of Ni thicknesses. The deviation between the two curves might be ascribed to factors such as small amounts of s - d hybridization. Also, for the lower Ni coverages, cluster formation at step edges may result in electron confinement, which would also increase the Ni d -state occupancy.¹³ Nevertheless, the trends in d occupancy exhibited in Fig. 2 are strong evidence for a charge redistribution from the Co towards the more localized Ni d states. In a one-electron

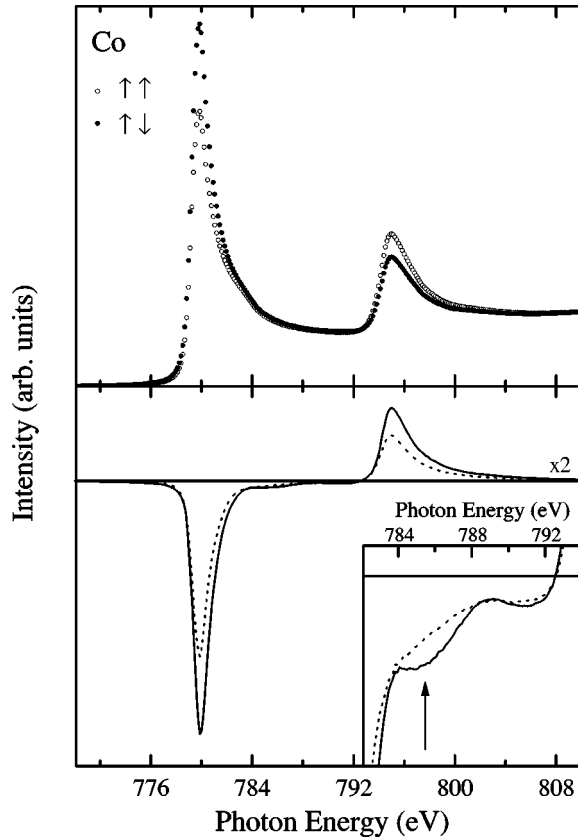


FIG. 3. Co $L_{2,3}$ XAS for a 4 ML Co film with remanent magnetization parallel (open dots) and antiparallel (closed dots) to the light helicity. The resulting XMCD for the 4 ML Co film (dashed line) together with the XMCD for a 4 ML Co film covered with 1 ML Ni (drawn line). The inset shows the dichroism line shape in between the L_3 and L_2 edges before (dashed line) and after (drawn line) deposition of the Ni overlayer.

scheme, a change in the d -state occupation shifts the relative positions of the minority and majority DOS for both Ni and Co and would result in modified magnetic moments. Such energy shifts have been predicted for the Ni/Cu interface and ascribed to hybridization between Cu and Ni d states.¹²

In order to determine the interface magnetic properties we used XMCD. Figure 3 shows the XAS spectra for a 4 ML Co film with the magnetization direction parallel (open dots) and antiparallel (closed dots) to the light helicity. The resulting dichroism (drawn line) is compared with that after deposition of 1 ML Ni (dashed line). The nonuniform distribution of signal increase is again emphasized by the change in the line shape of the dichroism in between the two edges (inset Fig. 3). The additional feature (indicated by the arrow in the inset of Fig. 3) has been observed for bulk Co.¹⁴ In the CI approach, the decrease in the Co d -state occupation would increase the electron correlation resulting in the appearance of extra features in the XAS (marked by the arrows in Fig. 1) and XMCD spectra. In the one-electron model, the addition of Ni alters the Co DOS, which would also result in shifted spectral weights. The increase in the dichroism might be related to an increase in the Co Curie temperature (T_c) as the film thickness is increased.¹⁵ However, for a 4 ML Co film grown on Cu(001), T_c is ~ 1000 K (Ref. 16) so that no significant increase in the saturation magnetization should

TABLE I. Ni and Co orbital and spin moments for the structures in this study together with the experimental values for bulk fcc Co (Ref. 19) and Ni (Ref. 4). The corresponding theoretical values for each structure are also given in Ref. 20 and Ref. 21.

	Co $\langle L_z \rangle$	Co $\langle S_z \rangle$	Ni $\langle L_z \rangle$	Ni $\langle S_z \rangle$
4 ML Co/Cu(001)	0.23(1)	0.70(5)		
1 ML Ni/4 ML Co/Cu(001)	0.26(1)	0.95(5)	0.06(2)	0.18(3)
fcc bulk metal (exp.)	0.153 ^a	0.775 ^a	0.06(2) ^b	0.27(3) ^b
fcc bulk metal (th.) ^c	0.08	0.76	0.05	0.31
NiCo/Cu(001)	0.28(2)	0.93(3)	0.07(2)	0.33(3)
Ni ₅₀ Co ₅₀ (th.) ^d	0.07	0.81	0.05	0.33

^aReference 19.

^bReference 4.

^cReference 20.

^dReference 21.

arise from an increase in film thickness at room temperature. The orbital moment, $\langle L_z \rangle$, and spin moment, $\langle S_z \rangle$, obtained by applying the sum rules to the XMCD spectra^{17–19} are given in Table I. It is expected that the magnetic dipole term can be neglected because the measurements were performed near the magic angle.²² Table I shows a dramatic increase in the Co spin moment after the deposition of the Ni and a Ni spin moment considerably smaller than the bulk value. In addition, the Co $\langle L_z \rangle / \langle S_z \rangle$ ratio decreases from 0.33(1) to 0.27(1) after the addition of the Ni overlayer. The determination of this quantity does not involve an estimation of the number of unoccupied Co d states and further shows that the addition of the Ni alters the Co magnetic structure. Figure 4 shows XAS spectra for a 2 ML Ni film, grown on a 4 ML Co film, recorded using the same experimental geometry as for the spectra of Fig. 3. The resulting dichroism (drawn line) is also shown together with the dichroism recorded for a 0.2 ML Ni film grown on 4 ML of Co (dashed line). The decrease in the dichroism, as the Ni film thickness is reduced, shows that the Ni magnetic moment is dependent on the degree of charge redistribution at the interface. The inset of Fig. 4 shows the change in the XMCD line shape as the Ni film thickness increases and also reflects modifications in the Ni electronic structure at the interface. A detailed analysis of the changing Ni XMCD line shape is presented elsewhere.⁵ The Ni $\langle L_z \rangle / \langle S_z \rangle$ ratio decreases from 0.52(10) to 0.33(7) for the two Ni film thicknesses. From Table I it can be seen that the increase in this ratio is due to a reduction in the Ni spin moment compared to the bulk value. Similar results have been reported by Srivastava *et al.*²³ for the Ni/Cu(001) interface. The Co and Ni XMCD spectra therefore show that the magnetic structure on both sides of the interface is substantially altered by the charge redistribution. In the present case, the complications of using the CI model to interpret the Co spectra means that another approach may be more appropriate.

In a one-electron model, a redistribution of d electrons from Co to Ni results in a larger exchange splitting for Co and a smaller splitting for Ni; hence, an increased Co spin moment and decreased Ni spin moment. The XAS final state contains an extra $3d$ electron compared to the ground state, which effectively screens the $2p$ core hole. XAS is then a

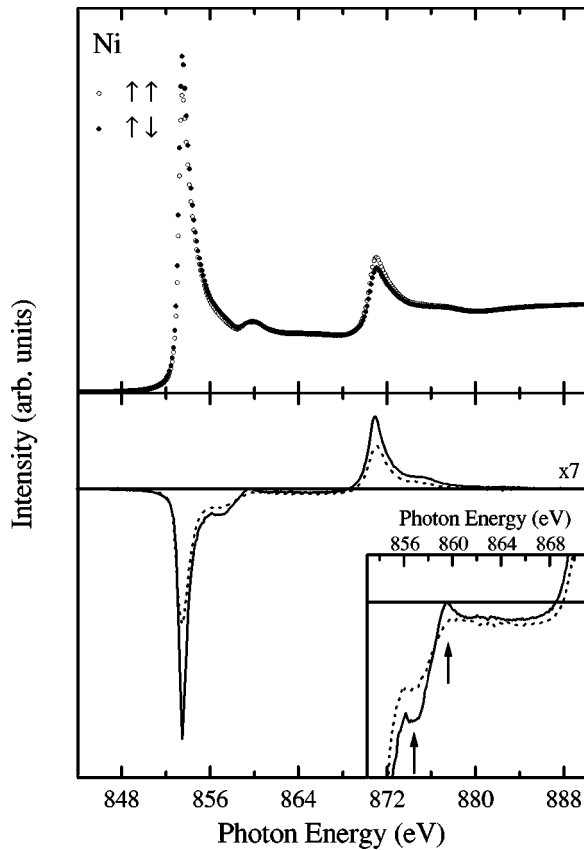


FIG. 4. Ni $L_{2,3}$ XAS for a 2 ML Ni film with remanent magnetization parallel (open dots) and antiparallel (closed dots) to the light helicity. The resulting XMCD for the 0.2 ML Ni film (drawn line) together with the XMCD for the 0.2 ML Ni film (dashed line). The inset shows the dichroism line shape in between the L_3 and L_2 edges for the 0.2 ML (dashed line) and 2 ML (drawn line) Ni film.

sensitive probe of the ground state DOS and the line shapes of the XAS spectra may be used to determine changes in the ground-state electronic structure. Features B , C , D and E could then be related to a decreased occupation of Co d states with minority character. The onset of the spectra are more sensitive to changes in the DOS near the Fermi level. The negative peak A of Fig. 1 then reflects an increased occupation of a small quantity of Co majority d states. However, it should be emphasized that the removal of energy shifted states related purely to the Co surface could also result in the appearance of feature A in the difference spectrum.²⁴

To confirm that features A – E in the difference spectrum of Fig. 1 represent modifications to the DOS, the measurements were repeated for a NiCo alloy formed by codeposition of 4 ML of Co and 0.7 ML of Ni. Figure 5 shows the L_3 XAS spectra for the alloy (dashed line) and the Ni overlayer structure (from Fig. 1, drawn line). The difference between the two spectra is also shown with features A – E marked. The difference spectrum implies that the redistribution of charge is not the same for the alloy and overlayer structures. Further, the XMCD for the alloy shows that the Co and Ni spin moments are both larger than the bulk values in direct contrast to the case for the Ni overlayer (c.f. Table I). It should be noted here that this is not a T_c effect since T_c for such an alloy will be almost the same as for 4 ML of Ni.¹⁶

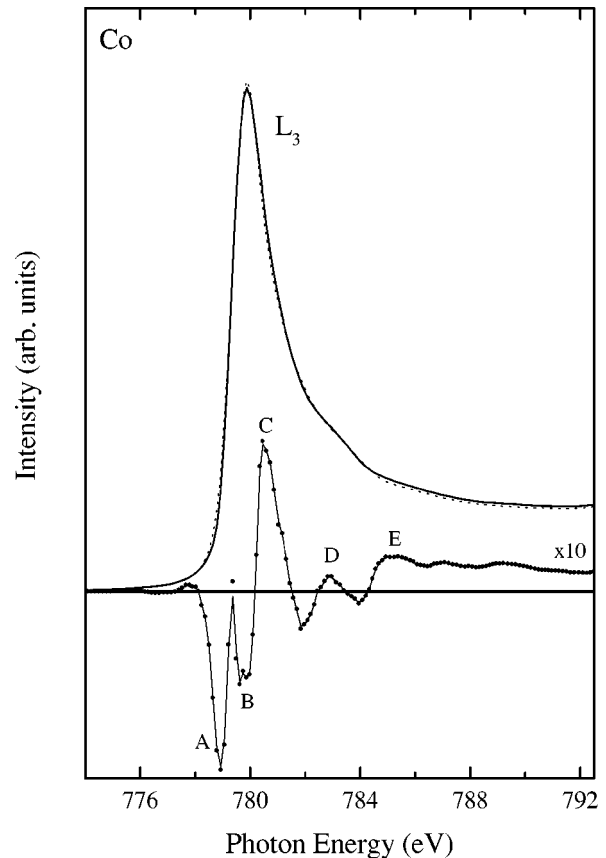


FIG. 5. Co L_3 XAS for 4 ML Co grown on Cu(001) after deposition of 1 ML Ni film (drawn line) and for a NiCo alloy formed by codeposition of 4 ML Co and 0.7 ML Ni onto the Cu(001) surface (dashed line). The difference spectrum (dots) is shown with a Fourier smoothing (drawn line).

The difference in the d -charge redistribution between the alloy and overlayer structures is therefore reflected in the relative intensities of features A – E in the difference spectra (cf. Fig. 1 and Fig. 5). Even though the origins of features A – E are difficult to determine, the combined use of high-resolution XAS and XMCD shows that XAS spectra can yield information regarding the spin-polarized DOS.

The spin moments in Table I contradict the results of recent band-structure calculations for the Ni/Co interface.^{25,26} Using the Korringa-Kohn-Rostoker approach, Ernst *et al.*²⁶ have calculated the magnetic and electronic properties at the Ni/Co interface, and found no change in the d occupancy of the Ni or Co. They also found that the interface Ni and Co spin moments are close to their bulk values. Since these calculations can only be applied to systems with translation symmetry, they are less appropriate for determining interface properties at submonolayer coverages. However, even for the 1 ML Ni on Co structure Fig. 3 shows a d -state occupation change of ~ 0.2 electrons (Fig. 2) as well as modified interface magnetic moments (cf. Table I). The discrepancy between our experimental results and the theoretical predictions may be due to the difficulty in calculating a spin-dependent exchange correlation energy at the interface of two ferromagnetic materials since calculations for the Ni/Cu interface have proved to be highly accurate.¹²

Table I also shows an increase in $\langle L_z \rangle$ after the addition of the Ni to the Co. The increase in $\langle L_z \rangle$ will affect the

magnetocrystalline anisotropy (MCA) through a modified orbital anisotropy.²⁷ This is because the charge redistribution directly influences the population of the *d* bands whose symmetry favors either out-of-plane or in-plane magnetization. Transverse XMCD measurements, for 3 ML Co films grown on 33 ML of Ni show that it is the Co orbital anisotropy, which aligns the Ni moments in-plane.²⁸ In the absence of the Co film the Ni film exhibits PMA due to the bulk magnetoelastic anisotropy.²⁹ The microscopic origin of the spin reorientation, after the addition of the Co, could then be assigned to an increased in-plane orbital anisotropy due to charge redistribution at the interface.

IV. CONCLUSIONS

In summary, we have shown that high-resolution XAS and XMCD using circularly polarized synchrotron radiation provides a valuable tool with which to study interface electronic and magnetic structure. It is found that the element-specific magnetic structure at the Ni/Co interface is highly sensitive to changes in the interface electronic structure. Dur-

ing the initial stages of interface formation the Ni spin moment decreases and the Co spin moment increases. This effect is explained in terms of a modified exchange splitting arising from the charge redistribution between the *d* states. The details of the electronic structure changes are observed in the Co isotropic $L_{2,3}$ edge line shapes, which reflect the unoccupied spin-polarized DOS. The method of subtracting high-resolution XAS spectra has enabled the observation of at least five features in the Co $L_{2,3}$ edges previously not reported. This technique could be used to monitor subtle changes in hybridization, electron transfer, and exchange-splitting in magnetic ultrathin films using the improved intensity of linear polarization. Monitoring charge redistribution at the interface and controlling the MCA therefore becomes a possibility for future studies.

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