

## X-ray-absorption study of the magnetic moments in thin Ni layers on Fe(100)

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We performed magnetic circular x-ray dichroism (MCXD) measurements on thin epitaxially grown layers of Ni on bcc Fe(100). These measurements show that at room temperature the layers are magnetically ordered. Values for the orbital, spin, and total magnetic moments are estimated and compared to calculations.

In the last ten years the search for materials with novel magnetic properties has partly been directed to thin surface layers of 3d transition metals (TM). They can serve to study magnetism of quasi-two-dimensional structures or of interfaces, which are of major importance for the magnetic properties of multilayers. Some of these thin layers show magnetic anisotropy perpendicular to the film plane, which makes them interesting candidates for high-density magnetic storage media. Another important aspect is that with the modern molecular-beam epitaxy techniques it is sometimes possible, by choosing the right substrate, to stabilize thin layers in crystallographic phases which at room temperature do not exist in the bulk materials. Examples are bcc Co on Fe(100) thin films,<sup>1</sup> fcc Fe on Cu(100),<sup>2</sup> and bcc Ni on Fe(100) (Refs. 3 and 4) and Fe(110).<sup>5</sup> Parallel to these experimental achievements considerable theoretical effort has been put into calculating magnetic moments in surfaces and overlayers.<sup>6,7</sup> For many systems an increased magnetic moment with respect to the bulk is expected, though until now little experimental evidence has been given.<sup>8</sup>

Several experiments using low-energy electron diffraction<sup>3</sup> (LEED) and reflection high-energy electron diffraction<sup>4,5</sup> have established that Ni grows epitaxially on Fe(100) and Fe(110) up to 6–8 monolayers (ML). The magnetic properties of these Ni layers however are less clear. Calculations done by Moruzzi *et al.*<sup>9</sup> show that bulk bcc Ni is nonmagnetic, but gets ferromagnetic when the lattice is expanded, which is the case if Ni is grown epitaxially on an Fe substrate.<sup>3,10</sup> The calculations of Lee *et al.*<sup>11</sup> give strongly enhanced magnetic moments for 1 and 2 monolayers of Ni on Fe(100), with respectively 40 and 15% enhancement over the bulk fcc values. The experiments do not solve this point: the results of Wang *et al.*<sup>3</sup> and Heinrich *et al.*<sup>4</sup> suggest that the Ni layers might be nonmagnetic, while the results of Wiczorek *et al.*<sup>5</sup> indicate that they are ferromagnetic.

We tried to clarify this discrepancy measuring the  $L_{2,3}$  absorption edges ( $2p \rightarrow 3d$  transitions) of thin layers of Ni on an Fe(100) single crystal. It is possible to extract information about ground-state magnetic properties of the

measured element from x-ray-absorption spectra,<sup>12,13</sup> using circularly polarized light. For this one needs absorption spectra with the helicity of the light parallel and antiparallel to the magnetization direction in the sample. This technique, magnetic circular x-ray dichroism (MCXD), which in the soft x-ray range was first applied to the  $L_{2,3}$  edges of a Ni single crystal,<sup>14</sup> has already been used to determine magnetic moments in multilayers and alloys,<sup>15,16</sup> though one has to be careful with its quantitative interpretation.<sup>15,17</sup>

The substrate we used was an Fe(100) single crystal of  $9 \times 5 \times 1 \text{ mm}^3$  with the [010] axis in the length direction of the sample. It contained a low percentage of Si (< 3%) for stabilization. The crystal was mounted on a horseshoe magnet and introduced into an ultrahigh-vacuum chamber (base pressure  $1 \times 10^{-10}$  mbar). There it was cleaned by many cycles of ion bombardment and subsequent annealing at 700 °C, until contaminants (mainly C and S) were no longer detectable with Auger electron spectroscopy (AES).

The magnetic quality of the crystal was checked using the magneto-optical Kerr effect. It appeared that the crystal showed 100% remnance at zero field and a coercive field of 40 G. This value was increased to 80 G after evaporating ( $\sim 10 \text{ \AA}$ ) Fe on top. Before each evaporation of Ni the substrate was thus cleaned and annealed until the correct square LEED pattern was observed. After that about 10 Å of Fe was evaporated followed by a slight heating of the substrate to 200 °C to restore the LEED. The cleanliness of the surface was checked again with AES.

Both the Ni and the Fe layers were evaporated from high purity (> 99.99%) rods using electron bombardment. The evaporation rate was measured with a quartz crystal balance and the thickness of the deposited Ni layer was also checked by comparing the intensities of the LVV and MVV Auger lines with those of the Fe substrate. We estimate the accuracy of this procedure to be about 20%. During the evaporation the pressure was kept below  $1 \times 10^{-9}$  mbar. We carefully examined the LEED for all the layers and noticed that for Ni

thicknesses up to 4–5 ML there is no change with respect to the clean Fe(100) pattern while for  $\sim 10$  ML no clear pattern is visible anymore. This is in agreement with earlier observations.<sup>3–5</sup>

During Ni evaporation the Fe substrate was kept at room temperature (RT) or at least not intentionally heated. The maximum reading on the thermocouple during Ni deposition corresponded to about 50°C. Comparing the Auger spectra for the as deposited layers with those taken after a thermal cycle evidenced the occurrence of interdiffusion already below 300°C and extremely short annealing times (10 sec at peak temperature).

The Ni  $L_{2,3}$  absorption edges were measured on beamline SA22 of the storage ring Super-ACO in the laboratory LURE, Orsay, France. This line is equipped with a double-crystal monochromator with natural Be(10 $\bar{1}$ 0) crystals which give a resolution of about 0.3 eV at the Ni  $L_3$  edge. We used high precision vertical slits to select the portion of the light coming from the bending magnet 1 mrad below the plane of the ring. The light is elliptically polarized with negative helicity and the degree of circular polarization  $\xi_2$  is about 0.9. Monochromatizing at  $\sim 850$  eV with Beryl crystals implies two Bragg reflections close to 67° reducing  $\xi_2$  to about 0.55 at the sample position.<sup>18</sup>

The spectra were collected with the light in grazing incidence (15°) using total electron yield. In this configuration one has to be aware of saturation effects, but these are not expected for the thin Ni layers used in our experiment ( $\leq 4$ ML, with 1ML  $\approx 1.43 \text{ \AA} \approx 1.2 \times 10^{15}$  at. cm $^{-2}$ ). The data were all collected at room temperature, with the Fe crystal remnantly magnetized after a current pulse of about 5 A through the wires around the horseshoe magnet. From *ex situ* measurements the intensity of the field was estimated to be about 100 G per ampere. The relative orientation between the helicity of the light and the magnetization in the Fe(100) was changed simply by reversing the direction of the current through the magnet wires.

Let us briefly recall the sum rules for x-ray absorption as deduced by Thole and co-workers<sup>12,13</sup> applied on the  $L_{2,3}$  edges of the 3d TM. We define the total integrated 3d intensity of the unpolarized spectrum as  $\mu_{\text{tot}}$  and the integrated  $L_3$  and  $L_2$  intensities of the difference curve of the two spectra, taken with opposite helicities of the light, as  $A_3$  and  $A_2$ , respectively. For the expectation value of the orbital moment of the  $d$  shell,  $\langle L_z \rangle$ , in the direction of the propagation vector of the light we then get  $\langle L_z \rangle = 2(A_3 + A_2)n/\mu_{\text{tot}}$  and for the spin moment  $\langle S_z \rangle = \frac{3}{2}(A_3 - 2A_2)n/\mu_{\text{tot}} - \frac{7}{2}\langle T_z \rangle$ , where  $n$  is the number of holes in the 3d band and  $\langle T_z \rangle$  is the expectation value of the magnetic dipole operator. In the following analysis, the  $\langle T_z \rangle$  term will be neglected, which requires some comment. In the 3d transition metals,  $\langle T_z \rangle$  essentially measures the anisotropy in the spin field which is caused by crystal-field effects on the spatial distribution of the electrons.<sup>19</sup> This term is zero for a bulk cubic system, but can be important in reduced symmetry, as is the case for a surface layer.<sup>20</sup> A nonvanishing  $\langle T_z \rangle$  should also imply the presence of linear dichroism,<sup>21</sup> i.e.,

different absorption spectra when the electric vector of the linearly polarized photons is oriented parallel and perpendicular to the surface. This was also calculated for the surface layer of bcc Fe.<sup>22</sup> We have carefully looked for linear dichroism in the thin Ni/Fe(100) layers, without finding any evidence for it. In absence of reliable calculations that state at least the sign of the  $\langle T_z \rangle$  term for an in-plane quantization axis in the 1-ML bcc Ni/Fe case, we have decided to proceed with the above-mentioned approximation. To calculate  $\langle L_z \rangle$  and  $\langle S_z \rangle$  we adopted two different procedures:

(a) The total absorption spectra (the sum of the spectra for both directions of magnetization) were normalized to a baseline measured in the same conditions on the clean Fe crystal (Fig. 1). A double-step function was subtracted to account for the background of  $2p \rightarrow 4(sp)$  transitions. The first step coincided with the spectra before the  $L_3$  and just before the  $L_2$  edge, while the second was shifted to the  $2p$  hole spin-orbit energy and coincided with the spectra after the  $L_2$  edge. This step function is shown in the inset of Fig. 1. The integrated area of the resulting curve gave  $\mu_{\text{tot}}$ , while  $A_2$  and  $A_3$  were calculated directly on the difference between normalized spectra

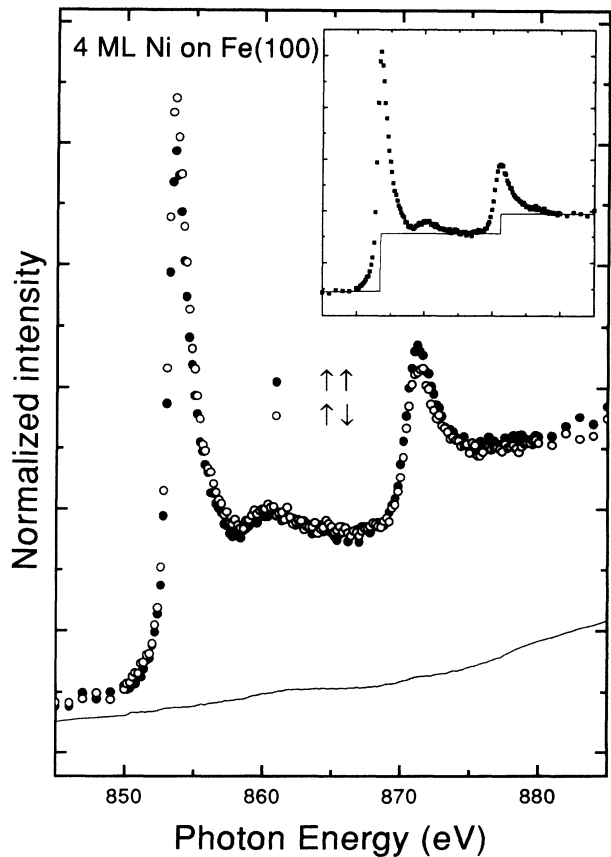


FIG. 1.  $L_{2,3}$  absorption edges for 4 ML of Ni on Fe(100) with helicity of the light and Ni majority spin direction parallel (filled circles) and antiparallel (open circles), together with the background taken on clean Fe. The inset shows the total absorption spectrum after normalizing to the Fe background, and the step function used to get  $\mu_{\text{tot}}$ .

for opposite magnetizations.  $n$  was taken equal to 1.

(b) The second procedure is similar to the one adopted by Wu *et al.*:<sup>15</sup> we used the MCXD curve of a Ni single crystal, measured in the same conditions, and the commonly accepted values of  $\langle L_z \rangle$  and  $\langle S_z \rangle$  for Ni ( $0.06\mu_B$  and  $0.27\mu_B$ ) to deduce  $n/\mu_{\text{tot}}$ . The theoretical error in the orbital sum rule is small<sup>22</sup> ( $< 10\%$ ), but can be considerable in the sum rule for the spin, especially for the earlier TM. For Ni, however, it seems to be quite accurate:<sup>17</sup> the deduced values for  $n/\mu_{\text{tot}}$  using  $\langle L_z \rangle$  or  $\langle S_z \rangle$  show a difference of only 3%. With the obtained value of  $n/\mu_{\text{tot}}$  the magnetic moments for Ni atoms in other configurations can now be determined by normalizing the spectra to those of pure Ni, supposing that the intensity per hole is independent of the number of holes.<sup>15,23</sup> The obtained value of  $n/\mu_{\text{tot}}$  was corrected for saturation effects in the bulk Ni reference<sup>17</sup> and the calculated values of  $\langle L_z \rangle$  and  $\langle S_z \rangle$  for the incomplete alignment of magnetization direction and light propagation vector.

The values we report in this paper are obtained using method (b) and deriving  $n/\mu_{\text{tot}}$  from the sum rule for the orbital moment. The values derived otherwise fall well within the given error bars.

In Fig. 1 we show the raw spectra for a 4-ML-thick Ni layer. To be able to compare them with the Ni metal spectrum, we subtracted a properly normalized and smoothed background measured in the same conditions on the clean Fe. After that the spectra were normalized before the  $L_3$  and after the  $L_2$  edge. The experimental error on the derived values for  $\langle L_z \rangle$  and  $\langle S_z \rangle$  introduced in the whole procedure is estimated to be about 20%.

In Fig. 2 we compare the MCXD curves of 1, 2, and 4 ML of Ni with the curve for the single crystal. Even without drawing quantitative conclusions, it can be seen directly that the thin Ni layers are magnetic (since dichroic) and that the difference curves are smaller than for fcc Ni. The curves for the different thicknesses are remarkably similar. These observations are at variance with the calculations of Lee *et al.*<sup>11</sup> for 1 and 2 ML of Ni on Fe(100): they find values for the total moment of  $0.87\mu_B$  and  $0.69\mu_B$  (for the  $d$  electrons), respectively, compared to  $\sim 0.60\mu_B$  for bulk fcc Ni. In Table I we compare the experimentally deduced magnetic moments for the different layers with the calculated values for the total moments. Also the values obtained for a Ni(110) single crystal are given. The noise on the curves, in addition to the uncertainty caused by the above-mentioned

TABLE I. Measured orbital and spin moments for different layer thicknesses. Theoretical values are for 1 and 2 ML Ni/Fe(100) (Ref. 11) and for bulk bcc Ni expanded at the lattice parameter of bcc Fe (Ref. 9).

Layer thickness	$\langle L_z \rangle$ ( $\mu_B$ )	$\langle S_z \rangle$ ( $\mu_B$ )	Total moment ( $\mu_B$ )	Theoretical value
1 ML	$0.05 \pm 0.03$	$0.14 \pm 0.06$	$0.33 \pm 0.12$	0.87 (Ref. 11)
2 ML	$0.03 \pm 0.03$	$0.13 \pm 0.04$	$0.29 \pm 0.09$	0.69 (Ref. 11)
4 ML	$0.07 \pm 0.03$	$0.18 \pm 0.04$	$0.43 \pm 0.09$	0.44 (Ref. 9)
fcc Ni	$0.06 \pm 0.02$	$0.27 \pm 0.03$	$0.60 \pm 0.06$	

normalization procedure, introduces a large error in the derived values. In the calculations of Lee the spin-orbit splitting in the  $3d$  band was not included and therefore we cannot compare separately the orbital and spin moments.

There are some experimental conditions which might influence the measured magnetic moments. With the technique we used, MCXD, only the component of the magnetic moments along the propagation direction of the incoming light is measured. We put this direction  $15^\circ$  off the magnetization direction of the Fe crystal, and are essentially not sensitive to the components of the moments normal to the [010] direction. The strong exchange interaction expected between the Fe and Ni moments makes it unlikely however that the Ni moments do not align with the Fe magnetization. A second point is that the measurements were done at room temperature: for some thin layers of TM it is known that the Curie temperature can be quite different from the one for the bulk material.<sup>24</sup> This means that the moments at room temperature might not be completely saturated. To test this point we performed additional measurements on thin (2 and 3 ML) Ni layers at RT and  $100 \pm 10$  K. The values we found were coherent with those in Table I and not depending on the temperature within the given error bars. Hence, thermal disorder cannot explain the large difference (a factor 2) between the calculated and measured magnetic moments. A similar discrepancy between experiment and theory was also found for Cr overlayers

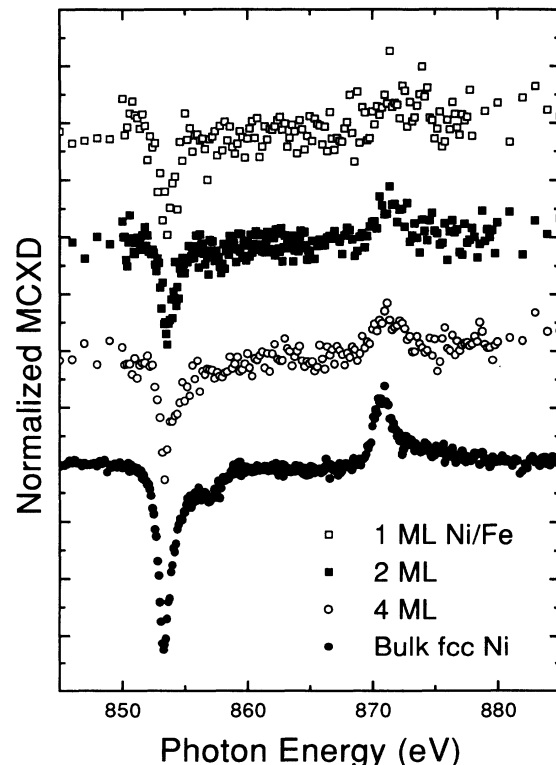


FIG. 2. Normalized MCXD curves for fcc Ni (filled circles) and 4 ML (open circles), 2 ML (filled squares), and 1 ML (open squares) Ni on Fe(100).

on Fe(100) (Refs. 25 and 26) and Ni on Cu(100).<sup>24</sup>

As we mentioned already, Moruzzi *et al.*<sup>9</sup> performed calculations for bulk bcc Ni as a function of the lattice constant. We extrapolated from their paper the magnetic moment per Ni atom when the lattice parameter equals that of the Fe substrate. The obtained value is about  $0.44\mu_B$ , i.e., quite close to our experimental estimates. Moreover, the growth of bcc Ni on Fe with the same lattice constant of the substrate was already inferred by the LEED analysis of Wang *et al.*<sup>3</sup>

In conclusion, we think that our results contribute to the discussion of the magnetic properties of bcc Ni layers on Fe(100). The occurrence of circular dichroism at the  $L$  edges is a direct and unquestionable proof that the layers are magnetically ordered.

In hypothesis of a negligible  $\langle T_z \rangle$  contribution, the

size of the moment per Ni atom is smaller than in bulk fcc Ni, contrary to the prediction of an increased value for the surface bcc layers. In particular we estimate for the total moment a value of  $0.35 \pm 0.10\mu_B$ , which does not vary, within the error, for the different thicknesses of the Ni layer that we considered. This value is quite close to the one calculated for bulk bcc Ni when the lattice parameter of Fe is assumed.

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