Magnetic dichroism in reflectivity and photoemission using linearly polarized light: 3*p* core level of Ni(110)

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We performed magnetic dichroism measurements on a Ni(110) single crystal, combining the techniques of resonant reflectivity and photoemission at the Ni 3*p* edges using linearly polarized synchrotron radiation. The experimental Ni 3*p* core-level spectra are compared to calculated results obtained using an Anderson impurity model. Resonant-reflectivity data show a magnetic dichroism well beyond the edge, in agreement with the calculations, giving the expected angular dependence. Calculated and experimental dichroism spectra agree well in terms of line shape for both reflectivity and photoemission, while discrepancies are observed in terms of absolute intensities. [S0163-1829(98)03931-9]

I. INTRODUCTION

One of the main needs of surface magneticians is to explore, in an element-specific and sensitive way, the surface vs bulk magnetic properties, where the understanding of the low-dimensionality magnetic systems is of both technological and fundamental importance. For this reason, 3*d* transition metals (TM's) have been widely investigated, following two principal approaches. The first one is the study of TM interfaces, alloys, and multilayers, which often give rise to peculiar features, such as giant magnetoresistance, and magnetocrystalline anisotropy, together with a different magnetic coupling between overlayers and bulk.[1,2] A second experimental effort has arisen in connection with the theoretically predicted strong variations in the magnitude of the orbital and spin-magnetic moments at the surface, not only for heterogenous interfaces but also for the surfaces of bulk magnetic materials, such as Fe(100) and Ni(110).[3,4] The latter is still a subject of intense research,[5] due to the difficulty to set up an experiment that is at the same time surface sensitive, element specific, and magnetometric.

Core-level spectroscopies based on the use of polarized x rays provide good opportunities to investigate magnetic phenomena, and the number of dedicated synchrotron radiation devices is steadily increasing. For 3*d* TM's, one usually relies on the use of circularly polarized light: two nonequivalent experimental geometries are obtained when the photon helicity is oriented parallel or antiparallel to the magnetization vector, resulting in polarization-dependent spectra (dichroism). This method has been exploited extensively for different spectroscopic techniques, such as absorption, resonant x-ray scattering, x-ray emission, and photoemission.[6–9] In addition, chirality can also be obtained using *linearly polarized light*. Kao *et al.*[10] measured the dichroism in resonant reflectivity at the 2*p* edges of Fe using *p*-polarized light, and more recently Roth *et al.* reported magnetic linear dichroism in the angular dependence (MLDAD) of photoemission from the Fe 3*p* core level.[11,12] Common to these techniques are three noncoplanar vectors that define the handedness of the experiment: the incoming light polarization (in the scattering plane), the magnetization direction (perpendicular to the scattering plane), and the direction of either the outgoing photon polarization in the case of reflectivity, or the outgoing photoelectron in the case of MLDAD. All three techniques give direct information about the alignment and magnitude of the elemental magnetic moment.[13–15] MLDAD and reflectivity represent in many aspects complementary techniques: (a) reflectivity is a photon-in photon-out process, allowing us to measure in the presence of applied magnetic fields (e.g., for element-specific hysteresis curves); (b) the probing depth of photoemission is ideally suited to detect the contributions of the top few atomic layers near the surface; and (c) reflectivity can still give information about buried layers. Moreover, the interpretational framework gives an interesting example for the relation between optical constants and electronic structure.

The analogy in the geometry is such that it appears natural to combine both photoemission and reflectivity experiments in a single setup. The use of linearly polarized light is also based on practical considerations: the most intense photon sources, such as undulators and wigglers, usually deliver linearly polarized light, allowing better statistics, and experiments based on elliptically polarized light often contain the degree of circular polarization as an ill-defined parameter,

which is difficult to quantify to better than 10% accuracy.

We present in this paper results from a combined MLDAD and resonant-reflectivity experiment, performed at the Ni $3p$ edge of a Ni(110) single crystal. The choice of the sample deserves some comments: photoemission from Ni presents, among the TM, the strongest satellite features. Concerning magnetic dichroism in photoemission, MLDAD from core levels has been reported extensively for the $3p$ and $2p$ edges of Fe, with magnetic asymmetries up to 12% of the total photoemission intensity (30% if one subtracts the background);[16] several examples have also been given for Co, whereas MLDAD from Ni single crystal is almost absent. To the best of our knowledge, the only Ni $3p$ MLDAD has been measured by Rossi *et al.*, for a thick polycrystalline layer grown onto Fe(100), with a dichroism that amounts to only a few percent asymmetry.[17,18] Ni also presents interesting magnetic properties in the bcc phase (which does not exist in the bulk form) obtained at the Ni/Fe(100) interface:[19] photoemission studies would certainly help to understand this metastable phase, but it is not straightforward to perform analysis on interfaces or thin films systems without reference values obtained from a crystalline sample, where structural disorder is absent. Finally, dichroism experiments on nickel mainly rely on absorption spectroscopy, and there is a need for independent information in order to refine the interpretational models currently under development.

II. EXPERIMENT

Experiments were carried out on the Swiss-French SU3 undulator beamline on the SuperACO storage ring at LURE (Orsay, France). The overall energy resolution and angular acceptance for the photoemission experiments were ~ 100 meV and $\pm 2°$, respectively. The Ni(110) single crystal was cleaned with repeated Ar^+ sputtering-annealing (800 °C) cycles. By means of a horseshoe electromagnet a magnetic field was applied along the $[1\bar{1}1]$ direction, which is an easy magnetization axis in the (110) plane. The crystal showed a squared hysteresis loop in *ex situ* Kerr effect measurements. Both reflectivity and photoemission measurements were done in remanence, reversing the magnetization at each data point of the spectrum. The base pressure was 8×10^{-11} mbar. The surface contamination was periodically checked by measuring the valence-band photoemission: we noticed that a rapid but mild annealing up to 600 °C allowed us to maintain the surface clean for several hours. Details about the experimental setup and the chiral geometry used can be found in Refs. 14, 20, and 21. Here we mention only that experiments were performed using two mirror geometries obtained by reversing the direction of the applied magnetic field, perpendicular to the scattering plane; the MLDAD asymmetry is defined as $A_{MLDAD}=(I_{up}-I_{down})/(I_{up}+I_{down})$, where $I_{up(down)}$ are photoemission intensities measured for the up (down) direction of the magnetization. Using the same chiral geometry, magnetic effects can be observed in the resonant elastic scattering of x rays. Examples have been reported in the past for specular reflectivity, Bragg diffraction, and diffuse scattering. We performed reflectivity measurements as a function of the photon energy over the range comprising the $3p$ edge of Ni, for different values of θ, where θ is the angle of the incoming beam with respect to its projection on the sample surface. The $0-10°$ range in 2θ was covered using a photodiode array mounted perpendicular to the light propagation direction. In addition, spectra were also recorded at $2\theta=45°$ using a single diode; the diodes were used in current mode. The asymmetry ratio R in the reflectivity experiment was defined in the same way as for photoemission, $R=(I_\uparrow-I_\downarrow)/(I_\uparrow+I_\downarrow)$. Due to the spectral function of the undulator source, the incoming light intensity was strongly energy dependent so that the spectra were difficult to correct for the I_0. Nevertheless, we were able to measure the asymmetry ratio R with high precision (10^{-4}) by switching the magnetization direction at each photon energy.

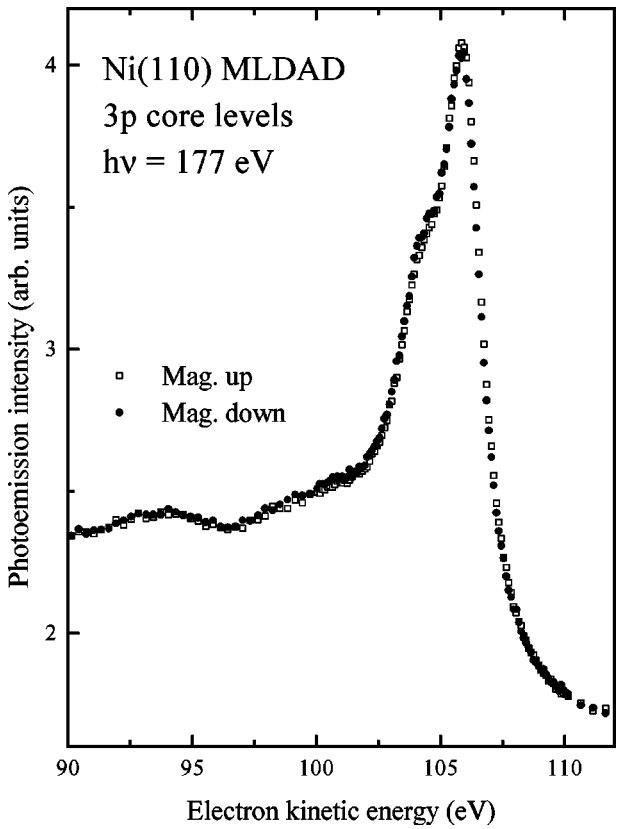

FIG. 1. Ni(110) $3p$ core-level photoemission spectra for opposite alignments of the magnetization along the $[1\bar{1}1]$ direction at a photon energy of 177 eV. The light was incident at 45° to the surface normal.

III. RESULTS

A. Photoemission

Figure 1 shows the raw spectra of Ni $3p$ core-level photoemission obtained in the two mirror experimental geometries, for a photon energy of 177 eV. At increasing photoelectron kinetic energy three satellite features are easily discernible. The measured spectra were compared to calculated results obtained using an Anderson impurity model, where a particular site in Ni metal is described with a basis set d^8, d^9, and d^{10} together with a matching number of electrons on adjacent sides.[22] The energy is determined by the charge-transfer, Coulomb interaction, hybridization, and crystal-field parameters with values that can be found in Ref.

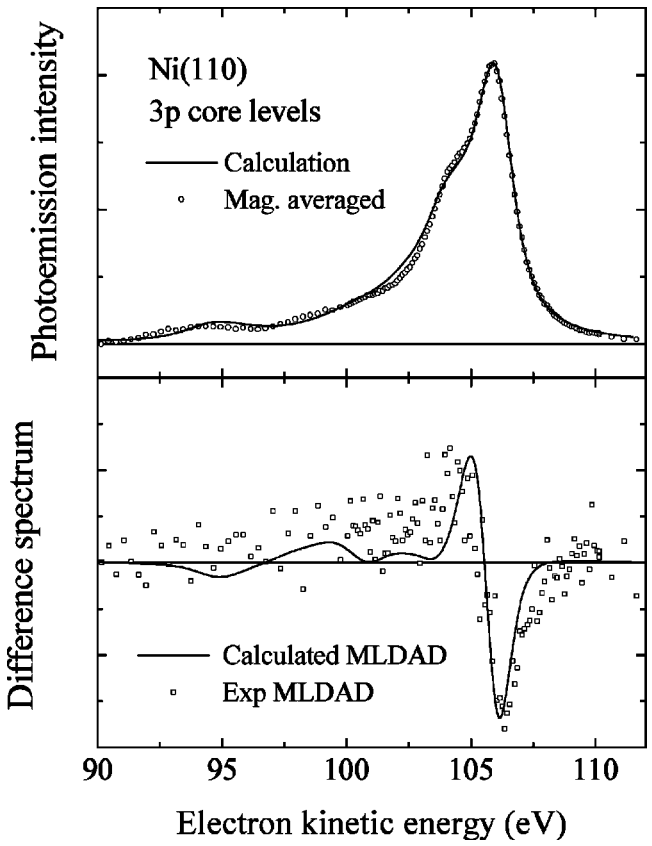

FIG. 2. Comparison between experimental and calculated Ni $3p$ photoelectron spectra of Ni(110). Top: Experimental photoemission spectrum (open circles) averaged over the two magnetization directions after an integral background subtraction. Bottom: MLDAD spectrum. Experimental curve (open squares) gives raw data. The calculated spectrum has been normalized to the peak maximum of the measured signal. The main negative feature in the spectrum corresponds to an asymmetry of 1.25% of the total photoemission intensity.

[23]. The final states after photoemission are a mixture of $3p^5d^8$, $3p^5d^9$, and $3p^5d^{10}$ configurations. The 6- and 14-eV satellites can be assigned to the $3p^5d^9$ final-state configuration with the main line associated with the $3p^5d^{10}$ configuration. In Fig. 2 we compare the calculation with the experimental data, for both the magnetically averaged photoemission signal (top panel) and the MLDAD (bottom). The averaged spectrum was obtained after an integral background subtraction, while the experimental MLDAD represents directly the raw data. The absolute size of the calculated Ni $3p$ MLDAD was about one order of magnitude larger than the experimental result. Since the origin of the reduced MLDAD is unknown, we scale the calculated magnitude down to the experimentally observed signal and compare only the spectral shapes. The experimental MLDAD agrees with the calculation around the region of the main line; however, our statistics is not good enough to make a detailed comparison with the rich dichroism structure in the satellite region. Results obtained at slightly different photon energy, i.e., $h\nu = 170$ eV, did not give any significantly different intensity of the dichroism. This suggests that the chosen photon energy does not correspond to a sharp minimum or maximum of the MLDAD signal, as might occur due to photoelectron diffraction effects.[24–27]

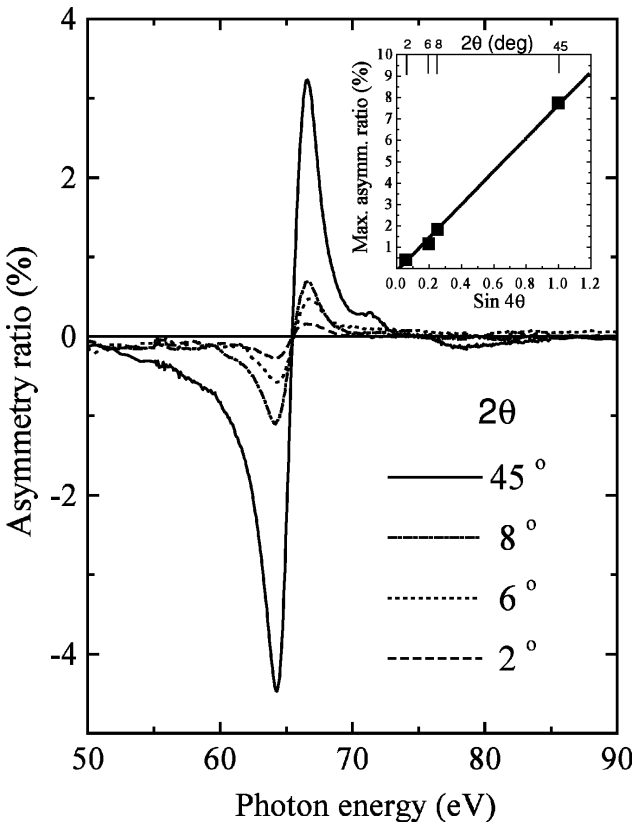

FIG. 3. Asymmetry ratio R of the resonant reflectivity vs photon energy at different 2θ angles. Inset: maximum of asymmetry ratio R vs 2θ fitted to $a \sin 4\theta/(1+b\cos 4\theta)$.

B. Reflectivity

The asymmetry curves for the reflectivity in the vicinity of the Ni $3p$ edge are shown in Fig. 3. A first remark concerns the angular dependence of R at a given photon energy: from the expression for the resonant-scattering amplitude given in Ref. 28, Eq. (1), one obtains for the asymmetry ratio the analytical form:

$$R = \frac{\mathrm{Im}\{\alpha\}\sin 4\theta}{1+\mathrm{Re}\{\alpha\}\cos 4\theta}, \tag{1}$$

where α contains the absorption cross sections for circularly polarized photons. The magnetic effects in the reflectivity of linearly polarized photons are a direct consequence of the presence of circular dichroism in absorption. The inset of Fig. 3 shows the peak-to-peak asymmetry ratio (64–66 eV) vs the scattering angle 2θ, where θ ranges from 1° to 22.5°. The line is a fit to the expression $a \sin 4\theta/(1+b\cos 4\theta)$. It is clear from the $\sin 4\theta$ dependence that strong magnetic signals are obtained by increasing the scattering angle; however at the same time the reflected intensity will drop rapidly with θ, and for p-polarized light it goes to zero at the Brewster angle. A scattering angle of 45° seems to be a good compromise between high intensity and strong magnetic signal: an asymmetry ratio of almost 8% peak-to-peak is obtained at the $3p$ edges of Ni with an excellent signal-to-noise ratio.

One can also observe that, contrary to absorption and photoemission, the magnetic signal in resonant reflectivity, influenced by the real part of the index, extends well beyond the resonance energy. Figure 3 shows that, for $2\theta = 45°$, the

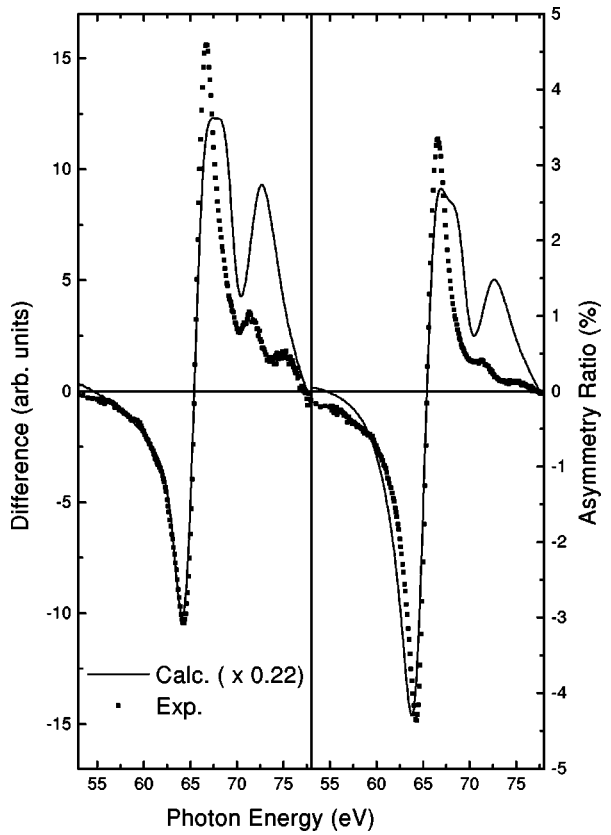

FIG. 4. Comparison between calculated and experimental curves for the magnetic dichroism in the reflectivity given as the difference between up and down magnetization (left panel) and as the asymmetry ratio R (right panel), at $2\theta = 45°$. Theoretical curves are multiplied by a factor 0.22 in order to match the experimental signal.

asymmetry ratio does not vanish over a range of almost 40 eV. Starting from the same parameters used in the MLDAD calculation, the absorption and the corresponding circular dichroism spectra of Ni were determined and inserted in the tabulated curve of k (dissipative part of the refractive index) for Ni (Ref. 29). The real part of the refractive index n and its magnetic dependence Δn were obtained by Kramers-Kronig transformation of k and Δk, respectively. The four real energy-dependent functions $n, k, \Delta n$, and Δk were used to build the two independent complex elements of the dielectric tensor ε, i.e., the diagonal term $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_{zz}$ (under the assumption of zero linear dichroism) as well as the off-diagonal term $\varepsilon_{xy} = -\varepsilon_{yx}$, which gives rise to the circular dichroism. The reflected intensity at the vacuum-Ni interface was subsequently calculated, solving directly Maxwell's equations, for a magnetization up or down with respect to the scattering plane. Figure 4 shows the comparison between the calculated and experimental curves for the magnetic signal in resonant reflectivity at $2\theta = 45°$. Also in this case, a multiplying factor has been introduced in order to match the absolute intensities.

IV. DISCUSSION AND CONCLUSIONS

We have measured MLDAD and resonant reflectivity at the Ni $3p$ core level of a Ni(110) single crystal, and we find a good qualitative agreement between experiment and theory. In the photoemission results of Fig. 2, the line shape of the magnetically averaged $3p$ photoemission intensity fits well the calculated results, taking into account the energy resolution of the experiment. Also, in the case of reflectivity, the general shape agrees fairly well, particularly when we consider that no additional parameters have been introduced and no further adjustments have been allowed in the model. From the comparison between experiment and theory, we note that both experimental asymmetry ratios R and A_{MLDAD} are smaller than the theoretical ones. Our experiment was performed at room temperature, and, according to the findings of magnetic x-ray circular dichroism in absorption,[30] any influence of temperature on the saturation value of the magnetic moment can be excluded. A comparison between our MLDAD results for Ni(110) and those for polycrystalline nickel on Fe(100) from Refs. 17 and 18 shows that the asymmetry ratios are equivalent on the main negative feature, i.e., $\sim 1.3\%$. We can compare our MLDAD results from Ni(110) to previous results from the literature. In the same range of photoelectron kinetic energies the maximum negative asymmetry value at $3p$ core levels, without any background subtraction, are (a) for Fe(100) single crystal about 10–12 %, and the same order of magnitude for polycrystalline Fe and disordered (quasiamorphous) Fe,[17] (b) about 9% for polycrystalline Co on Fe(100).[17] The Ni $3p$ MLDAD signal is thus about a factor of 10 smaller, and our results exclude both the influence of structural disorder, since the sample is a single crystal, and photoelectron diffraction effects, within the given range of kinetic energies. One should keep in mind, though, that the MLDAD signal is a function of several parameters (e.g., spin-orbit, photon energy, magnetic moments), implying that a quantitative cross comparison of the MLDAD for different elements is not straightforward. Our A_{MLDAD} value is, within the error bar, the same as the one measured on polycrystalline Ni on Fe(100), i.e. $\sim 1.3\%$, which means that structural disorder cannot be the reason for such a low value: it is still unclear why the observed Ni $3p$ MLDAD is so small compared to other $3d$ metals and to calculations, but our results suggest that it is consistently small for different surfaces of Ni. In resonant reflectivity, we observed magnetic effects for 2θ values between 2° and 45°, which follow the expected angular dependence. Model calculations, using the same parameters as for MLDAD, give a fairly good agreement for the line shape of the dichroism in reflectivity. Also in this case, though, the predicted values are larger than the experimental ones by almost a factor 5.

We do not have a clear explanation for this reduction in the dichroism, nor for its dependence on the specific technique (a factor 10 in photoemission, a factor 5 in reflectivity). One might invoke the different probing depths of the two techniques, but this would sound at the moment like pure speculation. The geometrical parameters of the experiment are all included in the calculations, and the chosen photoelectron energies (close to 100 eV) are in the range giving the maximum MLDAD effect. Photoelectron diffraction should not occur in this energy range, as confirmed by the comparison with our data at 170 eV photon energy. On the other hand, we are aware that it is not always straightforward, starting from a given model, to calculate consistently the results of different experiments, even when they should

trace back to the same fundamental parameters in the model. A couple of instructive examples can be found in recent literature, precisely about high-energy spectroscopies in nickel: (i) In Refs. 23 and 31 the same model was applied to describe the ground state of Ni in terms of admixture of $3d^8$, $3d^9$, and $3d^{10}$ configurations. In the former, the authors considered absorption and dichroism at the $2p$ and $3p$ edges plus isotropic $2p$ and $3p$ photoemission spectra in order to fit the adjustable parameters in the model (those used in the calculations presented here), and the same parameters were later also used to explain the resonant $2p$ photoemission.[32] The results were appreciably different from what was found in Ref. 31, where only $2p$ absorption and dichroism were considered as an experimental input. (ii) Menchero[33] successfully applied a cluster model to the interpretation of the $2p$ spin resolved photoemission data in Ni, but Manini *et al.*[34] showed that the same model was unable, using the same parameters, to interpret correctly the $2p$ absorption and dichroism data.

Finally, we showed that both MLDAD and reflectivity can be easily combined in a single experimental setup, exploiting the same geometry. Resonant reflectivity gives a magnetic signal whose magnitude is a function of the angle and can exceed that of MLDAD. On the other hand, MLDAD has an intrinsic sensitivity to the topmost atomic layers and is therefore more suited to study surfaces and thin films. The results obtained using these two spectroscopies are to be related to the same fundamental properties, and the combination of both techniques can facilitate the comparison between experiments and theory.

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[1] H. C. Siegman, J. Phys.: Condens. Matter **4**, 8395 (1992), and references therein.
[2] C. Turtur and G. Bayreuther, Phys. Rev. Lett. **72**, 1557 (1994).
[3] H. Krakauer, A. J. Freeman, and E. Wimmer, Phys. Rev. B **28**, 610 (1983).
[4] O. Eriksson, A. M. Boring, R. C. Albers, G. W. Fernando, and B. R. Cooper, Phys. Rev. B **45**, 2868 (1992); O. Eriksson, G. W. Fernando, R. C. Albers, and A. M. Boring, Solid State Commun. **78**, 801 (1991).
[5] G. van der Laan, M. A. Hoyland, M. Surman, C. F. J. Flipse, and B. T. Thole, Phys. Rev. Lett. **69**, 3827 (1992).
[6] C. T. Chen, F. Sette, Y. Ma, and S. Modesti, Phys. Rev. B **42**, 7262 (1990).
[7] C. C. Kao, C. T. Chen, E. D. Johnson, J. B. Hastings, H. J. Lin, G. H. Ho, G. Meigs, J.-M. Brot, S. L. Hubert, Y. U. Idzerda, and C. Vettier, Phys. Rev. B **50**, 9599 (1994).
[8] C. F. Hague, J.-M. Mariot, G. Y. Guo, K. Hrikovini, and G. Krill, Phys. Rev. B **51**, 1370 (1995).
[9] L. Baumgarten, C. M. Schneider, H. Petersen, F. Schäfers, and J. Kirschner, Phys. Rev. Lett. **65**, 492 (1990).
[10] C. C. Kao, J. B. Hastings, E. D. Johnson, D. P. Siddons, G. C. Smith, and G. A. Prinz, Phys. Rev. Lett. **65**, 373 (1990).
[11] Ch. Roth, F. U. Hillebrecht, H. Rose, and E. Kisker, Phys. Rev. Lett. **70**, 3479 (1993).
[12] Ch. Roth, H. Rose, F. U. Hillebrecht, and E. Kisker, Solid State Commun. **86**, 647 (1993).
[13] G. van der Laan, Phys. Rev. B **51**, 240 (1995), and references therein.
[14] F. Sirotti and G. Rossi, Phys. Rev. B **49**, 15 682 (1994).
[15] F. Sirotti, G. Panaccione, and G. Rossi, Phys. Rev. B **52**, R17 063 (1995).
[16] MLDAD asymmetry values can strongly vary, not only due to different background subtraction procedures, but also due to photoelectron diffraction effects (see, e.g., Ref. 24) and kinetic energy dependence. The value of 12% for Fe $3p$ core levels should be considered only as an average standard in the same photoelectron energy range as used in our experiment.
[17] G. Rossi, G. Panaccione, and F. Sirotti, in *Magnetic Ultrathin Films, Multilayers and Surfaces*, edited by A. Fert *et al.*, MRS Symposia Proceedings No. 384 (Materials Research Society, Pittsburgh, 1995), p. 447.
[18] J. C. Menchero, C. S. Fadley, G. Rossi, G. Panaccione, and F. Sirotti, Solid State Commun. **103**, 197 (1997).
[19] J. Vogel, G. Panaccione, and M. Sacchi, Phys. Rev. B **50**, 7157 (1994).
[20] G. Rossi, F. Sirotti, and G. Panaccione, in *Core Level Spectroscopies for Magnetic Phenomena: Theory and Experiment*, Vol. 345 of *NATO Advanced Study Institute, Series B: Physics*, edited by P. Bagus, G. Pacchioni, and F. Parmigiani (Plenum, New York, 1995).
[21] M. Sacchi, Surf. Rev. Lett. **4**, 343 (1997); M. Sacchi and A. Mirone, Phys. Rev. B **57**, 8408 (1998).
[22] G. van der Laan and B. T. Thole, Solid State Commun. **92**, 427 (1994); B. T. Thole and G. van der Laan, Phys. Rev. B **50**, 11 474 (1994).
[23] G. van der Laan and B. T. Thole, J. Phys.: Condens. Matter **4**, 4181 (1992).
[24] F. U. Hillebrecht, H. B. Rose, T. Kinoshita, Y. U. Idzerda, G. van der Laan, R. Denecke, and L. Ley, Phys. Rev. Lett. **75**, 2883 (1995).
[25] G. van der Laan, Phys. Rev. B **55**, 3656 (1997).
[26] G. Panaccione, Ph.D. thesis, Orsay, France 1995.
[27] W. Kuch, M. T. Lin, W. Steinhogl, C. M. Schneider, D. Venus, and J. Kirschner, Phys. Rev. B **51**, 609 (1995).
[28] J. P. Hannon, G. T. Trammell, M. Blume, and D. Gibbs, Phys. Rev. Lett. **61**, 1241 (1988).
[29] B. L. Henke, E. M. Gullikson, and J. C. Davis, At. Data Nucl. Data Tables **54**, 181 (1993).
[30] J. Vogel and M. Sacchi, Phys. Rev. B **53**, 3409 (1996).
[31] T. Jo and G. A. Sawatzky, Phys. Rev. B **43**, 8771 (1991).
[32] G. van der Laan, M. Surman, M. A. Hoyland, C. F. J. Flipse, B. T. Thole, Y. Seino, H. Ogasawara, and A. Kotani, Phys. Rev. B **46**, 9336 (1992).
[33] J. C. Menchero, Phys. Rev. Lett. **76**, 3208 (1996); Phys. Rev. B **55**, 5505 (1997).
[34] N. Manini, M. van Veenendaal, and M. Altarelli, Phys. Rev. Lett. **79**, 2594 (1997).