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An angle-dependent magnetic circular x-ray dichroism study of Co/Cu(100): experiment versus theory

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Abstract. Values for the magnetic moments of 3d transition metals have been calculated from magnetic circular x-ray dichroism measurements using sum rules. In this work we reveal that these calculations are sensitive to a damping effect resulting from a decrease in photon penetration at the $L_{3,2}$ peaks. Known as *saturation effects*, we present a simple correction to compensate for this phenomenon. We also show that the magnetic moments, as determined using sum rules, are relatively insensitive to the step function fitted to the absorption spectra. The magnetic moments derived from our data differ from the known ground-state moments. The corresponding corrective factors appear to be transferable between cobalt and nickel.

1. Introduction

Measurements of the photoabsorption coefficient at the $L_{3,2}$ absorption edges in magnetic materials have been used to yield information on element specific magnetic properties [1, 2]. In particular by applying sum rules [3] to the dichroic absorption spectra element specific magnetic moments were determined [2, 3]. Similar results have been obtained from the integrated dichroic response of the photoabsorption spectra combined with theory [1]. However, despite considerable effort to understand the magnetic circular x-ray dichroism (MCXD) of bulk and multilayer samples [1–3] few MCXD measurements have been performed on thin films, grown *in situ* under UHV conditions.

In this paper we focus our study on the 3d transition metal Co where the MCXD sum rules have already been applied to bulk and multilayer samples [2, 3]. We concentrate on the 'simple' case of one metal–metal interface and one metal–vacuum interface. In particular, we investigate the magnetic properties of thin Co films grown on a Cu(100) substrate that allows for a well defined growth, in a tetragonal phase, up to a thickness of some 30 ML [4–6]. Such samples are shown to exhibit a homogeneous, mostly single domain, response based on resonance [7], Kerr [8, 9] and MCXD measurements [10, 11]. A systematic study of the $L_{3,2}$ edges of Co thin films as a function of angle is presented as well as their MCXD response. Saturation effects are clearly identified as has already been shown in the case of bulk Ni [12]. We have also measured the MCXD response for Ni and Fe films and present these as a comparison.

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2. Experiment

The experiments were performed using SX700 monochromator beamlines at the BESSY synchrotron facility in Berlin [10, 11]. The films were prepared using electron bombardment heating [10, 11]. The evaporation rate was calibrated using a quartz microbalance and by comparing the relative peak heights of the Cu substrate with the Fe, Co or Ni film in the Auger electron spectra. The chamber pressure during evaporation was below 8×10^{-10} mbar. After evaporation the films were characterized by means of *in situ* low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The critical temperatures (T_c) of the transition from the ferromagnetic to the paramagnetic phase of our films were obtained from the MCXD signal in a temperature range between 40 and 400 K [10, 11]. This critical property is a sensitive parameter related to the film growth. As such it was used as an independent check of the thickness calibration and film morphology. For non-layer-by-layer growth, yielding films with a rough surface, a poorly defined ferromagnetic to paramagnetic transition is observed: the MCXD signal versus temperature shows considerable broadening at T_c while the susceptibility signal shows no divergence. These magnetic quality checks confirm that our films grow in a layer-by-layer manner and exhibit good surface structure. Furthermore, the quality of surface topography was confirmed using adsorption measurements. O_2 molecules physisorbed at 40 K on the film surface were found to exhibit the same degree of orientation as on the clean Cu(100) surface [13]. No evidence for molecular adsorption on steps could be identified indicating the high quality of the film surface. During the measurements contamination from adsorbed impurities remained less than 0.2%. The films were magnetized in their easy magnetization direction (in plane for Co and Fe, perpendicular for Ni) using a pulsed power supply and then turned to the various measuring angles. Magnetizing the films with several field strengths confirmed that the applied magnetic field magnetically saturated the films. All experiments were performed well below the film critical temperature, T_c. Typically the reduced temperature, T/T_c, was of the order of 0.2 during measurements. The energy resolution of the photon beam was determined and gave a $\Delta E \approx 1.7$ eV at the Ni L_3 edge and better than 1.5 eV for the Co L_3 edge. Comparing our results with similar studies [2] reveals no substantial broadening due to the experimental resolution, the resonance peaks being dominated by the natural line width. The experimental set-up, shown in the inset to figure 1, used a rigidly mounted solenoid on the axis of the light. Keeping the helicity of the light constant eliminated background differences that can arise from asymmetries in the beamline geometry for σ^+ and σ^- light. The degree of circular polarization was 0.5(1) [10] and was accounted for when the sum rules were applied. With the channel plate detector below the sample the acceptance angle is kept relatively constant for all measuring angles. Only the sample need be rotated with respect to the incident photons for the different measuring angles, ensuring a high degree of reproducibility. Also illustrated is the photon penetration depth, λ, and effective electron escape depth, d.

Figure 1 shows typical absorption spectra from a 23 (ML) Co film measured at 12, 50 and 90°. We have complied with the accepted hypothesis that the size of the continuum jump above the Co L_2 edge is proportional to the number of atoms and hence scaled the spectra such that the edge jump is equal to 100 arbitrary units. The result is spectra that yield information on a 'per atom' basis. The normalized spectra coincide in the pre- and post-edge regions indicating that any differences in the background are negligible for the different magnetization directions, confirming the quality of our data. With a retarding voltage of 130 V, to maintain a degree of surface sensitivity, the *effective* electron escape depth, d, was 17 Å. This value has been derived experimentally from our library of more

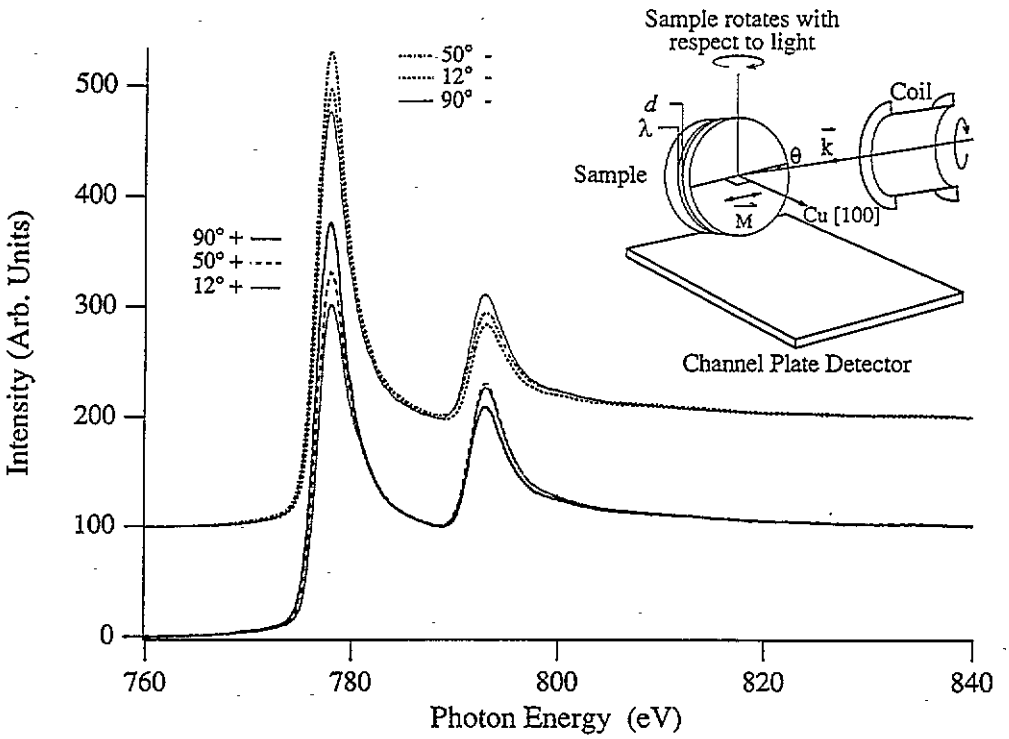

Figure 1. Typical photoabsorption spectra of a 23 ML Co film showing anomalous angular dependence in the $L_{3,2}$ peak heights (see the text). The minority (-) and majority (+) spectra are displayed with an offset of 100 units to aid inspection. Inset, the experimental set-up *d*, the effective electron escape depth, and λ, the photon penetration depth, are found to be of the same order of magnitude for grazing x-ray incidence angles.

than 30 films, ranging from 0.16 ML to 30.0 ML, and is thus appropriate for our measuring geometry. It has not been corrected for the channel plate acceptance angle or the fact that we used a retarding voltage.

3. Saturation effects

From simple geometric considerations, ignoring anisotropies due to spin–orbit interaction and crystal field effects [3, 14] and assuming only E1 transitions, one would expect the $L_{3,2}$ peak height maxima to vary with the cosine of the measuring angle, Θ. (Θ is measured relative to the sample surface, as shown in the inset to figure 1.) For our Co films, with the magnetization direction in the plane, the maximum signal was expected for measurements taken at grazing incidence to the sample surface ($\Theta = 12°$). An anomalous distribution is apparent from figure 2(a). The peak heights appear to have a random intensity distribution for measurements with photon spin antiparallel to the magnetization direction (the minority case). This effect is not so noticeable when the photon spin and magnetization direction are parallel (the majority case) since the damping simply enhances the expected peak intensity distribution. Analysis of our angle-dependent MCXD spectra revealed a dramatic damping for both the $L_{3,2}$ peak heights for measuring angles up to 45°. For normal measuring

angles ($\Theta = 90°$) the penetration depth of the photons, λ, exceeds the electron escape depth, d, by more than an order of magnitude, ensuring that, to a first-order approximation, the photons 'saturate' all of the potential 'donor' Co atoms. This is the case even at the $L_{3,2}$ peaks, where the photon penetration depth is reduced due to the effective increase of the cross-section of the Co atoms. However, measuring at grazing angles compounds the problem to the extent that the resonant peaks become artificially damped as observed and shown in figure 2(b). These angle-dependent saturation effects have been reported for photoabsorption and photoemission from the 3d core states in rare earths [15, 16], bulk Ni [12] and NiO [17].

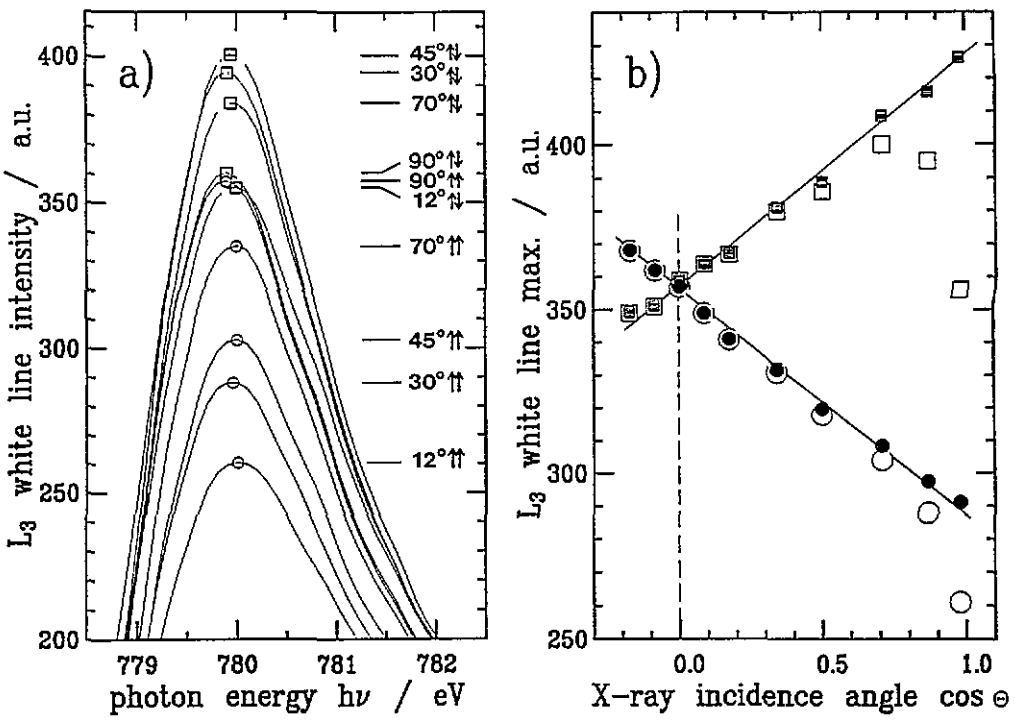

Figure 2. (a) The angular dependence of the L_3 peak height from a 23 ML Co film. The minority ($\uparrow\downarrow$) and majority ($\uparrow\uparrow$) spectra are indicated. (b) The saturation effect uncorrected (open symbols) and corrected (filled symbols) L_3 peak height distribution as a function of cos Θ for minority (squares) and majority (circles) spectra. The experimental error is indicated by the symbol size.

A correction was devised to compensate for these saturation effects based on the model presented by Van der Laan and Thole [18]. The electron yield can be described by the equation

$$Y_{\mathrm{th}}(E) = \mu(E)/[\mu(E) + (1/d)\sin\Theta]. \tag{1}$$

$Y_{\mathrm{th}}(E)$ is the electron yield, $\mu(E) = 1/\lambda$ the photoabsorption coefficient, d the electron escape depth and Θ the measuring angle taken relative to the sample surface. If the photon penetration depth is much larger than the electron escape depth ($\lambda \gg d \approx 17$ Å) then the yield is proportional to the photoabsorption coefficient, $\mu(E)$. For grazing measurements

at (or near) the $L_{3,2}$ peaks this is not the case. The photon penetration depth is of the same order as the electron escape depth ($\lambda \sin \Theta \approx d$) and the yield tends to unity. That is to say, the measured yield is no longer a true representation of the photoabsorption coefficient. Consequently, the raw absorption signal is not a satisfactory basis from which to derive magnetic moments. This fact can be seen directly in figure 2(b). The correction consists of calculating the theoretical yield for the pre- and post-edge region using (1). The photoabsorption coefficients for this were taken from tables [19]. The calculated yield is scaled to the experimental yield using the relation

$$Y_{\text{th}} = a + bY_{\text{exp}}. \tag{2}$$

From (2), we can construct two equations: one for the pre- and one for the post-edge region. The former is set to zero and the latter to 100 since the pre- and post-edge yield for the normalized experimental spectra is necessarily zero and 100 respectively. Thus, we have two equations and the constants a and b can be determined. We now focus our attention on the L_3 maxima and use (2) again to define a value for the yield scaled to (1). Note that this value is *still* damped by saturation effects. However, (1) can now be solved for the photoabsorption coefficient at the L_3 maxima. This $\mu(E)$ value is independent of saturation effects and hence can be substituted back into (1) to determine a value for the yield, free from saturation effects using $\Theta = 90°$. This new yield can be scaled to a meaningful value in terms of our experimental data using new constants, a and b, derived from the 90° data. The results of this correction procedure are shown in table 1 along with the derived values of the photoabsorption coefficient for thin films of Fe, Co and Ni.

Table 1. The L_3 peak maxima as measured and as corrected for Fe, Co, and Ni films, the experimental intensities were obtained using a 30° grazing geometry and the photoabsorption coefficient, μ, as derived for the L_3 white line using the correction procedure outlined in the text.

Element	Fe (30 ML BCC)		Co (23 ML FCC)		Ni (28 ML FCC)	
Magnetic anisotropy	In plane		In plane		Perpendicular	
Polarity	↑↑	↑↓	↑↑	↑↓	↑↑	↑↓
Experimental intensity	416	513	288	395	261	272
Corrected intensity	439	551	298	416	268	280
Relative correction	0.056	0.075	0.033	0.053	0.027	0.029
μ (cm^{-1})	566 000	720 000	384 000	541 000	332 000	347 000

The corrected and uncorrected L_3 resonance maxima are displayed in figure 2(b) as a function of cos Θ. The corrected data convincingly fall on a straight line, confirming a cosine dependence of the L_3 (and L_2) peak heights. It is also striking that the slope of the corrected data is identical for both majority and minority measurements. The amount of damping can now be seen directly and is considerable for grazing angles but still significant for measuring angles up to 45°. It is probable that a capping layer [2, 20] often used to prevent oxidation of multilayer samples measured *ex situ*, would further contribute to these saturation effects, because the magnetic system under investigation is buried within the sample.

In practice the correction procedure is performed on each point of the absorption spectra. The result is a curve modified only where the photoabsorption coefficient is large enough to prevent all the potential 'donor' Co atoms from being excited.

4. Determination of magnetic moments

Having corrected our spectra we used the now established sum rules [3] to determine values of the magnetic moments. Simple subtraction of the minority from the majority spectra yields the MCXD difference spectra from which the M_L/M_S ratio can be determined as in previous publications [10, 11]. However, to determine absolute values of M_L and M_S a step function must be fitted, and subsequently subtracted from the spectra, isolating the intensity relating to the final d states in the absence of magnetism. One has considerable latitude in the design of a step. Several parameters must be considered, notably, step width, the relative heights of each step component and their positions relative to the resonance peaks. The area under the d-state isolated spectra, shown in figure 3(b), changes by less than 5% for combinations of small variations, ± 2 eV, in the energy of the step inflection points and step widths, while different branching ratios produced changes of the order of 7%. We applied a step that is in keeping with those used in the literature. Following the work of Fink *et al* [21] and Zaanen *et al* [22] we have not deliberately obeyed the statistical 2:1 branching ratio for the $L_{3,2}$ peaks as advocated by some [12, 23]. Rather, our step was tailored empirically, using an error function, to fit the π-light spectra. Allowing for the fact that the $L_{3,2}$ peaks overlap due to their intrinsically asymmetric shape, step heights of 70 and 30 (yielding the normalized total function height of 100 arbitrary units) was used for the $L_{3,2}$ peaks respectively. This resulted in an L_3:L_2 step height ratio of 2.3:1. A half width of 1.25 eV was used for both edges with the inflection point 1 eV below the resonance maxima. The same step parameters were used consistently for spectra of all angles and are shown in figure 3(a) with the 45° π-light data. Having subtracted the step function the area under the d-state isolated spectra, shown in figure 3(b), is representative of the number of d holes. The sum rules yield magnetic information 'per hole'. Hence, meaningful values for the orbit and spin moments are limited by how well we can define the number of d holes for the system under study. In the case of Co we used the currently accepted value of 2.8 d holes per atom and for Ni, 1.8 [24, 25]. To yield magnetic moments consistent with previously published values [2, 26] it was necessary to fit the 'extreme' step (2.3:1 branching ratio but half width of 8 eV set 2 eV above the resonance maxima) shown as the dashed curve in figure 3(a). This had the effect of reducing the orbital moments by some 50% and thus the spin moment, determined using the difference spectra, approached the theoretical values. There is no apparent justification for using such an 'extreme' step to yield the theoretical value for M_S while enhancing M_L by 100% in the case of Co. We also examined the effect of different energy ranges to see if the background slope due to the continuum states, after the edges, affected the relative intensity of the resonant peaks when normalized to the 0–100 edge jump. Errors of this type affected the M_L:M_S ratio by less than 6%. Finally, before the sum rules can be applied, it is necessary to define some limits of integration for the areas under the white lines for both the difference spectra and the isolated d-state spectra. In our case this was straightforward since the spectra lay on the zero axis in the pre- and post-edge regions. Having dealt with these considerations applying the sum rules is relatively simple. Our results are presented in table 2.

The values of the orbital and spin magnetic moments as determined from our data are at variance with the theory by the same factors (3.3 and 1.8 respectively) for both Co and Ni atoms. Obviously the application of the sum rules fails, in the present case, to provide ground-state magnetic information. However, it does appear that the discrepancies are transferable between Co and Ni. Applying a corrective factor, as shown in table 2, appears to yield meaningful magnetic information. A similar observation was made recently for multilayer samples where only relative magnetic information using the sum rules was

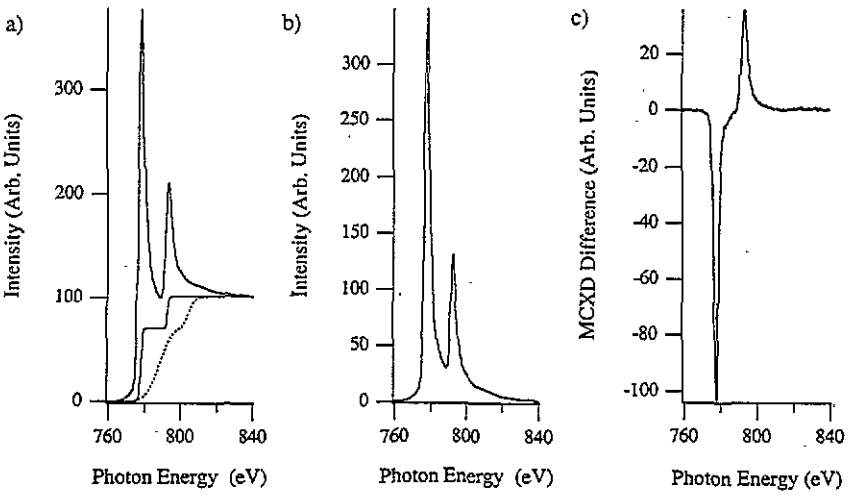

Figure 3. (a) Prior to applying the sum rules a step is fitted to the π-light absorption spectra from a 23 ML Co film. (b) Subtracted spectra isolating the d-state transitions. (The full width of the step components as used was 2.5 eV, while the for wide step (dashed curve) it was 8 eV.) (c) The MCXD difference spectra from the Co film.

obtained based on a comparison to a bulk sample [2]. Whether or not saturation effects constitute the entire reason why previous applications of the sum rules, with no corrective factor, have yielded magnetic moments for these systems significantly less than the values presented above remains to be seen. The departure from the theoretical values could stem from a number of factors. For example, it is plausible that the final states contributing to the $L_{3,2}$ resonances posses some s character. Equally, it is possible for the d states to extend far into the continuum. Our step function therefore fails to account for this mixing of s and d states. It should also be noted that the presence of core holes could influence the L-edge intensity distribution to such an extent that the difference and the d-state isolated spectra are not the appropriate input for the sum rules. It is also possible that other phenomena such as anisotropies due to spin–orbit interaction and crystal field effects are manifest in spectra of this type due to the strained growth phases of thin films. This might contribute to the fact that the corrective factors are different for M_L and M_S since the sum rule defining M_S contains an extra term related to local anisotropy fields. Though small in comparison to saturation effects, at grazing photon incidence, they limit our precision in determining magnetic moments. Another practical limitation in the application of sum rules is the overlap of the $L_{3,2}$ lines. Finally, the ambiguity surrounding the experimental definition of a base line may also introduce errors.

5. Conclusion

We have shown that saturation effects can significantly alter the relative intensities of the resonance peaks in photoabsorption spectra and thus influence calculations based on the sum rules. It is possible that this type of effect is present in many published spectra where a grazing geometry has been used. In variance with previous publications we observe that this application of the sum rules does not yield ground-state magnetic moments without the use of corrective factors. Further measurements appear to be needed for Co and Ni

Table 2. The magnetic moments for Co and Ni films as calculated using the sum rules on data corrected for saturation effects are compared with theoretical values, and in the last line the required corrective factor to bring our derived values into agreement with the theory. Using the 'extreme' step function (see the text) had the effect of yielding spin magnetic moments approaching the theory.

	Co (FCC)		Ni (FCC)	
	M_S	M_L	M_S	M_L
Present data on Cu(100)	2.7(5)	0.43(8)	1.2(2)	0.20(4)
Theoretical bulk values [24]	1.60	0.11	0.62	0.07
Corrective factor	1.7(3)	3.9(5)	1.9(3)	2.8(6)

films grown under different strain conditions to clarify the role of anisotropy fields when determining local magnetic moments.

After completing the present work similar experiments came to our attention [27]. The authors of the latter also determine M_L and M_S. The problem of a step function is also faced but the largest source of uncertainty in determination of magnetic moments is due to the assumptions concerning the number of d holes. It ranges from 2.1 [27] through 2.55 [25] to 2.8 [24] for Co and from 1.0 [27] through 1.66 [25] to 1.8 [24] for Ni. As long as these quantities cannot be obtained independently, the MCXD technique may be of limited practical use in the determination of magnetic moments.

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References

[1] Schütz G, Knülle M and Ebert H 1993 *Phys. Scr.* T **49** 302 and references therein
[2] Samant M, Stöhr J, Parkin S, Held G, Hermsmeier B, F, Herman, van Schilfgaarde M, Duda L, Mancini D, *Wassdahl N and Nakajima R 1994 Phys. Rev. Lett. 72 1112 and references therein*
[3] Carra P, Thole B, Altarelli M and Wang X 1993 *Phys. Rev. Lett.* **70** 694
[4] Li H and Tonner B 1990 *Surf. Sci.* **237** 141
[5] Zhang J, Han Z, Varma S and Tonner B 1993 *Surf. Sci.* **298** 351
[6] Idzerda Y and Prinz G 1993 *Surf. Sci.* **284** L394
[7] Schulz B, Schwarzwald R and Baberschke K 1993 *Surf. Sci.* **307–309** 1102
[8] Schneider C, Bressler P, Schuster P, Kirschner J, de Miguel J and Miranda R 1990 *Phys. Rev. Lett.* **64** 1059
[9] Huang F, Kief M, Mankey G and Willis R 1994 *Phys. Rev.* B **49** 3962
[10] Tischer M, Arvanitis D, Yokoyama T, Lederer T, Tröger L and Baberschke K 1994 *Surf. Sci.* **307** 1096
[11] Tischer M, Arvanitis D, Aspelmeier A, Russo M, Lederer T and Baberschke K 1994 *J. Magn. Magn. Mater.* **135** L1
[12] Vogel J and Sacchi M 1994 *Phys. Rev.* B **49** 3230
[13] Yokoyama T, Arvanitis D, Lederer T, Tischer M, Tröger L and K Baberschke 1993 *Phys. Rev* B **48** 15405
Tischer M, Arvanitis D, Aspelmeier A, Russo M, May F, Dunn J H and Baberschke K 1993 *Proc. IV Eur. Vacuum Conf.; Vacuum* at press
[14] Carra P 1992 *Synchrotron Radiat. News* **5**
[15] Sakho O, Sacchi M, Sirotti F and Rossi G 1993 *Phys. Rev.* B **47** 3797
[16] van der Laan G and Thole B 1983 *J. Electron Spectrosc. Relat. Phenom.* **31** 1
[17] Tröger L, Arvanitis D, Baberschke K, Michaelis H, Grimm U and Zschech E 1992 *Phys. Rev.* B **46** 3283

[18] van der Laan G and Thole B 1988 *J. Electron Spectrosc. Relat. Phenom.* **46** 123
[19] Robinson J 1974 *CRC Handbook of Spectroscopy* vol I (Boca Raton, FL: Chemical Rubber Company) p 59
[20] Weller D, Wu Y, Stöhr J, Samant M, Hermsmeier B and Chappert C 1994 *Phys. Rev* B **49** 12888
[21] Fink J, Muller-Heinzerling Th, Scheerer B, Speier W, Hillebrecht F, Fuggle J, Zaanen J and Sawatzky G 1985 *Phys. Rev.* B **32** 4899
[22] Zaanen J, Sawatzky G, Fink J, Speier W and Fuggle J 1985 *Phys. Rev.* B **32** 4905
[23] Böske T, Clemens W, Carbone C and Eberhardt W 1994 *Phys. Rev.* B **49** 4003
[24] Söderlind P, Eriksson O, Johansson B, Albers R and Boring A 1992 *Phys. Rev.* B **45** 12911
Eriksson O private communication
[25] Wu Ruqian and Freeman A J 1994 *Phys. Rev. Lett.* **73** 1994
[26] Wu Y, Stöhr J, Hermsmeier B, Samant M and Weller D 1992 *Phys. Rev. Lett.* **69** 2307
[27] O'Brien W and Tonner B *Preprint*