

Enhanced Orbital Magnetic Moment on Co Atoms in Co/Pd Multilayers: A Magnetic Circular X-Ray Dichroism Study

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Magnetic circular x-ray dichroism measurements at the Co L_3 and L_2 edges in Co/Pd multilayers give first experimental evidence for a greatly enhanced orbital moment compared to that in bulk Co, confirming recent theoretical predictions. Our results also show that, in general, there is no simple relationship between the dichroism signal and either the spin moment or the total moment. This is verified by a simple model calculation.

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The breaking of symmetry and/or the change in nearest-neighbor coordination near surfaces and interfaces introduces many interesting phenomena in magnetic materials. Among them, the existence of perpendicular magnetic anisotropy [1] and enhanced spin [2] and/or orbital magnetic moments [3–6] has attracted much attention. The understanding of magnetic anisotropy in thin films is an interesting scientific problem with great technological importance in areas like magnetic and magneto-optical recording. Since the microscopic origin of magnetocrystalline anisotropy is the spin-orbit interaction, which depends on both the spin and orbital angular momenta, direct, independent measurements of both quantities are highly desirable. Such measurements also allow direct comparison with theoretical predictions. The separation of orbital and spin moments is a difficult problem for most established techniques, e.g., neutron scattering. In principle, magnetic x-ray scattering is capable of separating the spin and orbital momentum densities [7], but a conclusive demonstration is still lacking. Here we demonstrate by application of a recently derived powerful sum rule [8] that magnetic circular x-ray dichroism (MCXD) measurements allow a quantitative determination of orbital magnetic moments. In particular, we determine the orbital moment of Co in Co/Pd multilayers, systems with great promise for use as future magneto-optical media.

The MCXD technique measures the difference in absorption between right- and left-handed circularly polarized x rays near a core absorption edge in magnetic materials [9, 10]. For transition metals dichroism measurements typically involve $p \rightarrow d$ core-to-valence excitations near L_3 and/or L_2 edges. Based on a simple one-electron picture it has generally been assumed that the so-measured MCXD signal is proportional to the difference in the spin-up and spin-down occupation in the empty d shell of the absorbing atom, i.e., to the local magnetic moment on the probed atom [9]. This led to the notion that MCXD can determine element specific magnetic moments [11, 12], assuming that the proportionality constant is transferable across different chemical and structural environments of a given atom. Recent

results for the pure $3d$ transition metals Fe, Co, and Ni [13, 14] suggested a more complicated situation however, in particular a breakdown of the one-electron picture [13, 15]. A particularly important development is the recent derivation of a sum rule by Thole *et al.* [8] which links the sum of the L_3 and L_2 dichroism intensities to the local orbital moment. Within an atomic or localized bonding picture the sum rule is valid in general, and holds even when effects of electron-electron correlations are included. It has been successfully applied to derive the small orbital magnetic moment ($0.05\mu_B$) of Ni metal [8].

In this Letter we present dichroism measurements at the Co L_3 and L_2 edges in the pure metal and Co/Pd multilayers. Application of the sum rule to our data reveals the existence of an enhanced orbital moment of Co in Co/Pd multilayers relative to Co metal. We also show experimentally and by a model calculation that, in general, the integrated dichroism signals at the individual edges or any linear combination is *not* proportional to the total magnetic moment on the probed atom. This result demonstrates the breakdown of the above-mentioned transferability concept.

The MCXD experiments were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline 8-2 which is equipped with a spherical grating monochromator. Circularly polarized x rays were obtained by moving the prefocusing mirror below the electron orbit plane yielding a degree of circular polarization of $(I^R - I^L)/(I^R + I^L) = (90 \pm 5)\%$, where I^R and I^L are the x-ray intensities with right- and left-handed circular polarization. The magnetization direction of the sample relative to the photon spin was then changed by alternately measuring two pieces of the same sample which were remanently magnetized in opposite directions. X-ray absorption was measured using total electron yield detection. The nominal structure of the multilayer sample used for the present study was Si(111)/(200 Å)Pd/[(10 Å)Pd/(4 Å)Co] $_N$ /(10 Å)Rh, where $N = 11$ is the number of periods. The sample was prepared by electron beam evaporation in a 10^{-8} -mbar base pressure system at a growth temperature below 50°C . X-ray diffraction measurements indicated that the crystal structure

of this multilayer is consistent with an fcc lattice with a strong [111] texture. The sample exhibited 100% remanence in the perpendicular direction and a large coercive field of ~ 2000 Oe. The hcp Co thin-film sample of 250 Å thickness was grown by dc sputtering as part of a Si(100)/(110 Å)NiFe/(100 Å)FeMn/(250 Å)Co/(10 Å)NiFe sandwich. Through exchange biasing by the antiferromagnet FeMn the so-grown Co film exhibited 100% in-plane magnetic remanence with a ~ 20 Oe coercive field.

Polarization-dependent x-ray absorption spectra at the Co L edges recorded with magnetization and photon spin parallel (I^{+1}) and antiparallel (I^{-1}) to each other and their differences, the dichroism spectra ($I^{+1} - I^{-1}$), are shown in Fig. 1 for the Co thin film and the Co(4 Å)/Pd(10 Å) multilayer. The spectra shown are normalized to the incident photon flux and rescaled to a constant step height far above the Co L edges. Our dichroism difference spectra for Co metal look similar to those recorded by Sette *et al.* [14] but the effect is significantly larger in our spectra. For the multilayer sample the L_3 resonance intensity is enhanced relative to that in Co metal and so is the L_3/L_2 dichroism ratio, which varies from $-1.7:1$ for the Co thin film to $-2.6:1$ for the multilayer sample.

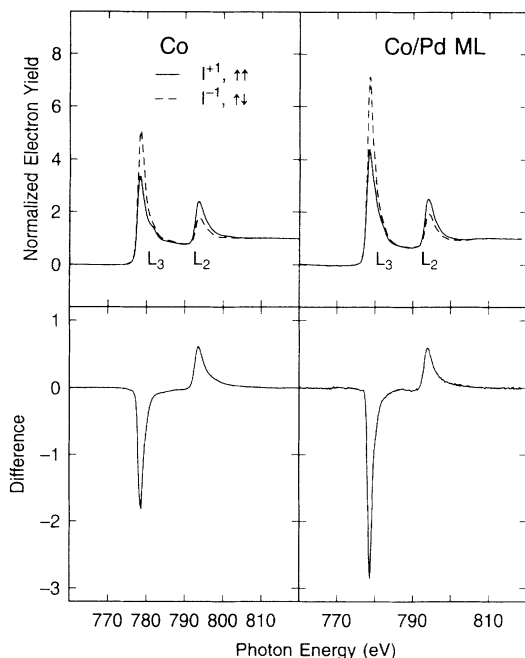


FIG. 1. Top panels: Co $L_{2,3}$ absorption spectra of Co thin film and Co/Pd multilayer samples recorded with parallel (I^{+1}) and antiparallel (I^{-1}) alignment of photon spin and magnetization vectors. The Co/Pd sample was measured at normal and the Co metal sample at 20° grazing x-ray incidence. The data were scaled so that the jump far above the edge is 1. Bottom panels: Dichroism spectra for the same samples obtained by taking the difference between the absorption spectra.

For the quantitative analysis of the data it is convenient to define $A_t = \int_{L_3+L_2} (I^{+1} + I^0 + I^{-1})dE$, $A_{L_3}^q = \int_{L_3} I^q dE$, $\Delta A_{L_3} = \int_{L_3} (I^{+1} - I^{-1})dE$ and similarly for the L_2 edge. Here the index $q = -1, 0, +1$ describes the orientation of the photon spin relative to the magnetization direction, in particular, I^0 denotes the x-ray absorption intensity when the two directions are orthogonal to each other. In terms of these definitions the sum rule [8] states

$$\frac{\Delta A_{L_3} + \Delta A_{L_2}}{A_t} = \frac{D_t}{A_t} = \frac{1}{2\hbar} \frac{c(c+1) - l(l+1) - 2}{l(l+1)n} \langle L_z \rangle. \quad (1)$$

Here, c and l are the orbital angular momentum quantum numbers for the core and valence shells and n is the number of holes in the d shell in the ground state. In practice, the integrals ΔA_{L_3} , ΔA_{L_2} , and A_t are determined from the polarization-dependent areas of the near edge resonances ("white lines"). For the determination of A_t we used the areas of the white lines above a step-like background. The step was placed at the white line peak position and we assumed $I^0 = \frac{1}{2}(I^{+1} + I^{-1})$. The uncertainties in the step positions and normalization of the spectra relative to each other account for most of the error estimates below. Taking into account the degree of circular polarization of the incident x rays, we derive from Eq. (1) a residual orbital moment per Co atom of $(0.17 \pm 0.04)\mu_B$ [orbital momentum of $(0.17 \pm 0.04)\hbar$], parallel to the spin moment, for the Co thin film and $(0.24 \pm 0.04)\mu_B$ for the Co/Pd multilayer sample. The results are summarized in Table I. Use of Eq. (1) requires the determination of A_t from the data and knowledge of n which, in practice, cause large uncertainties in the derived values for $\langle L_z \rangle$. A more accurate procedure is to determine $\langle L_z \rangle$ relative to a standard, assuming that the white line intensity A_t is proportional to n , the number of holes in the d shell for a given atom. Then $D_t = \text{const} \times \langle L_z \rangle$, and the relative hole momentum can simply be determined from the change in the dichroism signals D_t , which can be accurately derived from experimental difference spectra. Using this procedure we find that $\langle L_z \rangle$ for Co in the Co/Pd multilayer is larger by a factor of 1.9 than in Co metal.

These results give the first experimental confirmation of the suggestion that orbital moments can be greatly enhanced in multilayers relative to the pure metal. The first principle calculations by Daalderop, Kelly, and Schuurmans [6] quoted in Table I were carried out with and without an orbital polarization term [16]. Comparison with our experimental values suggests that the inclusion of such a term is essential. Although some care should be exercised in the comparison of experimental and theoretical results because the calculations used crystal structures that may differ from those of our polycrystalline samples, the general agreement in Table I is indeed

TABLE I. Comparison of measured and calculated Co orbital moment with (M_L) and without (M_{L_0}) orbital polarization in Co thin film and Co/Pd multilayer.

	Experiment				Theory		Comments	References
	D_t ^a	D_t/A_t	$\langle L_z \rangle / \hbar$ ^b (μ_B)	$\langle L'_z \rangle / \hbar$ ^c (μ_B)	M_L (μ_B)	M_{L_0} (μ_B)		
Co	-2.05	-0.042	0.17	0.13	0.13	0.08	hcp	This study
						0.09	hcp Co [0001], bulk	[6]
							hcp Co [0001], center of 5 layer slab	[5]
Co/Pd	-3.90	-0.061	0.24	0.25	0.28	0.14	Multilayer, [111] texture	This study
							Co ₁ /Pd ₂ multilayer	[6]

^a Corrected for x-ray incidence angle and degree of circular polarization.

^b Orbital moment per Co atom according to Eq. (1), assuming $n = 2$.

^c Assuming $\langle L_z \rangle / \hbar = 0.13 \mu_B$ per Co atom in Co metal and calculating the moment in Co/Pd according to the ratio in D_t .

very encouraging.

The question arises whether the measured L_3 and/or L_2 dichroism intensities can also be related to either the spin or the total Co moments in a simple way. The experimental results in Fig. 1 show that the L_3/L_2 dichroism ratio varies for the two samples such that it is unlikely that either signal by itself can be used as a measure of the total local moment on the Co atoms. In order to explore the general relationship between the L_3 and L_2 dichroism signals and the spin, orbital, and total moments we have carried out model calculations for a $3d$ transition metal ion with nine d electrons in the initial ground state. After photon excitation the final state contains one p -core hole and a filled $3d$ shell. Hence electron-electron and electron-hole exchange and correlation effects are absent. For our purpose the most important interactions in the ground state are the exchange interaction which polarizes the d shell into spin-up and spin-down states and the spin-orbit interaction within the d shell which gives rise to an orbital moment. Using the Hamiltonian

$$H = -e_J s_z + \xi_d l \cdot s, \quad (2)$$

we have calculated energy levels and wave functions of the d shell as a function of e_J and ξ_d and used a Boltzmann population at fixed temperature to vary the ground-state properties, i.e., the effective moments. For the final state we assumed that the $2p$ hole state is split by the core spin-orbit interaction, which of course is the origin of the L_3 - L_2 splitting in the observed spectra.

Figure 2 shows the results of a numerical calculation with e_J varying from 0 to 100 meV and $\xi_d=0$ (left panel) and $e_J = 100$ meV and ξ_d varying from 0 to -60 meV (right panel) while the temperature is fixed at 25 meV (300 K). In the absence of any d -shell spin-orbit interaction no orbital moment exists and the L_3 and L_2 dichroism intensities are of the same magnitude and have opposite sign, $\Delta A_{L_3} = -\Delta A_{L_2}$, and vary linearly with the spin moment as shown in Figs. 2(a) and 2(b). When the spin-orbit interaction is turned on [Fig. 2(c)] an orbital momentum arises in the d shell and the L_3 and L_2

dichroism signals become unequal and ΔA_{L_2} may in fact switch sign. As predicted by the sum rule [8] there is now a linear relationship between the orbital moment and the sum of the L_3 and L_2 dichroism intensities as shown in Fig. 2(d).

Although, for clarity, we only present here the results for a one-electron model, we have also carried out calculations for a two-electron atomic model. Our results confirm that both initial- (d - d) and final- (p - d) state correlation effects can change the relative "white line" intensities at the L_3 and L_2 edges, as pointed out before by others [17]. However, such multielectron effects cannot account for the anomalous L_3/L_2 dichroism ratios ob-

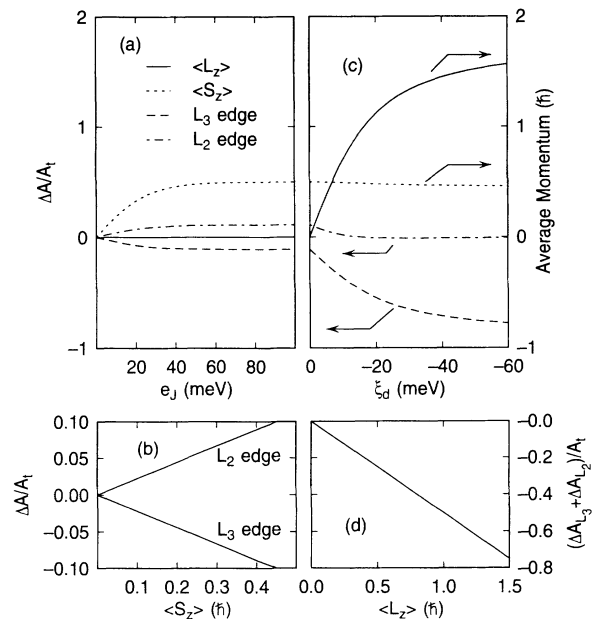


FIG. 2. (a),(c) Calculated dichroism signal and average spin ($\langle S_z \rangle$) and orbital ($\langle L_z \rangle$) momenta in a simple model (see text) as a function of exchange field (e_J) and the spin orbit interaction (ξ_d). (b),(d) Dichroism signal plotted as a function of spin and orbital momenta.

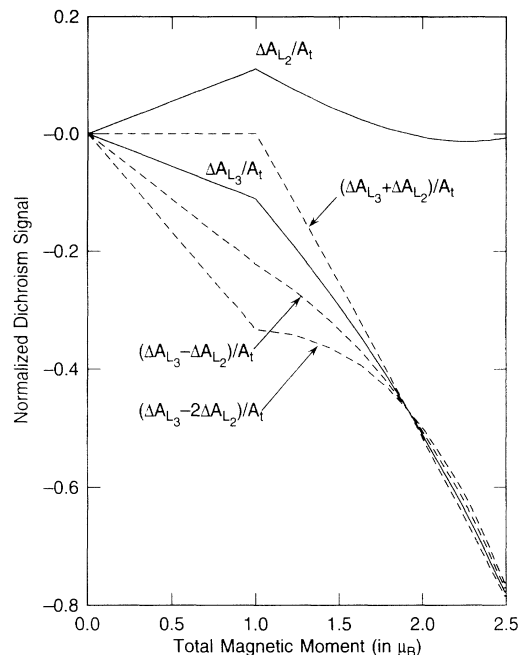


FIG. 3. Integrated dichroism signals at the L_2 and L_3 edges (solid) and various linear combinations (dashed) as a function of the absolute value of the total magnetic moment ($\mu_{\text{tot}} = \mu_B \langle 2S_z + L_z \rangle / \hbar$), using the results of Fig. 2. Note that only a spin moment exists for $\mu_{\text{tot}} \leq 1.0\mu_B$ while both a spin and orbital moment are present for $\mu_{\text{tot}} > 1.0\mu_B$.

served by us. For example, if only a spin moment exists in the electronic ground state, the *line shape* of the L_3 and L_2 dichroism spectra may change due to multiplet splitting but the L_3/L_2 dichroism ratio is always calculated to be $-1:1$, as in a one-electron model. In accord with the sum rule, deviations from this ratio are solely the result of the spin-orbit interaction in the d shell.

In order to explore whether a linear relationship can be established between the total moment μ_{tot} and the L_3 and L_2 dichroism intensities we can replot the dichroism signals calculated in Fig. 2 as a function of $\mu_{\text{tot}} = (2\langle S_z \rangle + \langle L_z \rangle)\mu_B/\hbar$. This is done in Fig. 3. For $\mu_{\text{tot}} \leq 1.0\mu_B$ the total moment is equal to the spin moment and there is a linear relationship between the normalized L_2 and L_3 dichroism intensities and μ_{tot} . For $\mu_{\text{tot}} > 1.0\mu_B$, both a spin and an orbital moment are present. In general, no simple linear relationship exists between the total moment and the measured quantities as indicated by the plots for various linear combinations of ΔA_{L_3} and ΔA_{L_2} in Fig. 3. This leads to the conclusion that, in the case of both spin and orbital contributions to the magnetic moment, it is difficult if not impossible to determine total magnetic moments by means of MCXD. Rather, our results emphasize that the strength of MCXD spectroscopy lies in its ability to determine orbital magnetic moments.

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- [1] L. Néel, *J. Phys. Radium* **15**, 225 (1954).
- [2] For an overview of surface, interface, and thin-film magnetism, see L. M. Falicov, D. T. Pierce, S. D. Bader, R. Gronsky, K. B. Hathaway, H. J. Hopster, D. N. Lambeth, S. S. P. Parkin, G. Prinz, M. Salamon, I. K. Schuller, and R. H. Victora, *J. Mater. Res.* **5**, 1299 (1990).
- [3] P. Bruno, *Phys. Rev. B* **39**, 865 (1989).
- [4] J. G. Gay and R. Richter, *J. Magn. Magn. Mater.* **93**, 315 (1991).
- [5] O. Eriksson, G. W. Fernando, R. C. Albers, and A. M. Boring, *Solid State Commun.* **78**, 801 (1991).
- [6] G. H. O. Daalderop, P. J. Kelly, and M. F. H. Schuurmans, *Phys. Rev. B* **44**, 12054 (1991); G. H. O. Daalderop (private communication).
- [7] D. Gibbs, D. R. Harshman, E. D. Isaacs, D. B. McWhan, D. Mills, and C. Vettier, *Phys. Rev. Lett.* **61**, 1241 (1988).
- [8] B. T. Thole, P. Carra, F. Sette, and G. van der Laan, *Phys. Rev. Lett.* **68**, 1943 (1992).
- [9] G. Schütz, W. Wagner, W. Wilhelm, P. Kienle, R. Zeller, R. Frahm, and G. Materlik, *Phys. Rev. Lett.* **58**, 737 (1987); G. Schütz, M. Knülle, R. Wienke, W. Wilhelm, W. Wagner, P. Kienle, and R. Frahm, *Z. Phys. B* **73**, 67 (1988); G. Schütz, R. Frahm, P. Mautner, R. Wienke, W. Wagner, W. Wilhelm, and P. Kienle, *Phys. Rev. Lett.* **62**, 2620 (1989).
- [10] G. T. Chen, F. Sette, Y. Ma, and S. Modesti, *Phys. Rev. B* **42**, 7262 (1990).
- [11] G. Schütz, R. Wienke, W. Wilhelm, W. Wagner, P. Kienle, R. Zeller, and R. Frahm, *Z. Phys. B* **75**, 495 (1989).
- [12] G. Schütz, H. Ebert, P. Fischer, S. Rüegg, and W. B. Zeper, *Mater. Res. Soc. Symp. Proc.* **231**, 77 (1992).
- [13] C. T. Chen, N. V. Smith, and F. Sette, *Phys. Rev. B* **43**, 6785 (1991).
- [14] F. Sette, C. T. Chen, Y. Ma, S. Modesti, and N. V. Smith, in *X-Ray Absorption Fine Structure*, edited by S. S. Hasnain (Ellis Horwood Limited, Chichester, England, 1991), p. 96.
- [15] T. Jo and G. Sawatzky, *Phys. Rev. B* **43**, 8771 (1991).
- [16] M. S. S. Brooks, *Physica (Amsterdam)* **130B**, 6 (1985).
- [17] J. Zaanen, G. A. Sawatzky, J. Fink, W. Speier, and J. C. Fuggle, *Phys. Rev. B* **32**, 4905 (1985); G. van der Laan and B. T. Thole, *Phys. Rev. Lett.* **60**, 1977 (1988); *Phys. Rev. B* **42**, 6670 (1990); **43**, 13401 (1991).