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LETTER TO THE EDITOR

What does the K-edge x-ray magnetic circular dichroism spectrum tell us?

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Abstract. Two rules which relate the magnetic circular dichroism (MCD) from the *s* core levels of a solid to the *p*-projected spin and orbital magnetization density of unoccupied states of the solid have been derived. Explicit calculations using the spin- and orbital-polarized relativistic multiple-scattering theory for bcc Fe, hcp Co and fcc Ni corroborate that the K-edge MCD spectrum probes the *p*-projected orbital magnetization density of unoccupied states.

In the past few years, we have witnessed significant developments and phenomenal interest worldwide in x-ray magnetic circular dichroism (MCD) experiments using intense, tunable, polarized synchrotron radiation sources [1]. On the theoretical front, the understanding of the origins of MCD and its connections with the magnetic moments has also been advanced. In particular, Thole *et al* and Carra *et al* [2] discovered recently that, within an atomic multiplet theory, the integrated MCD signals for given spin-orbit-split absorption edges are related to the local spin and orbital magnetic moments. These magnetization sum rules have made MCD an unique probe of the element specific and shell selective spin and orbital magnetic moments [3]. Nevertheless, the understanding of the relationship between the shape of the MCD spectrum and the magnetic aspects of the underlying electronic structure is still incomplete. For example, a clear interpretation of the K-edge MCD spectrum has yet to be found [4]. It is well known that, to a large extent, an x-ray absorption spectrum (XAS) measures the spectrum of an associated angular-momentum-projected charge density of unoccupied states. A MCD spectrum usually contains rich structures and one might expect that it provides information about some magnetization density of states (DOS). Angular-momentum-decomposed charge DOS spectra are important to understand, e.g., the chemical bonding and structural stability of the solid. Likewise, magnetization DOS spectra are important to explain the formation of the magnetic moments and other magnetic phenomena in the solid. Schütz *et al* [1] argued early on that, as a first-order approximation, the K-edge MCD is proportional to the *p*-projected spin density of states (SDOS). Indeed, they found that in the Fe systems the K-edge MCD spectrum is similar to the calculated *p*-projected SDOS spectrum. However, this interpretation fails for the Co and Ni systems [5]. More recently, Igarashi and Hirai [6] speculated that the shape of the MCD spectrum near the K edge is determined by the 3*d*-projected orbital magnetization density of states (ODOS).

In this paper, I will describe a derivation of two rules within the itinerant electron theory which allows us to interpret the relative MCD spectrum from the *s* core states of a solid in terms of the normalized *p*-projected ODOS and SDOS. The spin- and-orbital polarized relativistic multiple-scattering theoretical calculations of both the K-edge MCD spectrum and the ODOSs for bcc Fe, hcp Co and fcc Ni have been performed. I will use the results of these calculations to discuss the validity of these rules.

Within the itinerant one-electron theory, the absorption rate W^λ for an incident x-ray beam of polarization λ is given in terms of the retarded one-particle Green function $G^+(\mathbf{r}, \mathbf{r}, E)$ as [7]

$$W^\lambda(\hbar\omega) = -\frac{2}{\hbar} \sum_c \langle \Phi_c | \Pi_{q\lambda}^* \text{Im} G^+(\hbar\omega + E_c) \Pi_{q\lambda} | \Phi_c \rangle \theta(\hbar\omega + E_c - E_f) \quad (1)$$

where Φ_c and E_c are, respectively, the initial core state wavefunction and energy. E_f and Π_λ are the Fermi energy and electron–photon interaction operator, respectively. MCD is caused by the simultaneous occurrence of spin–orbit coupling and spin polarization in a magnet [8]. Therefore, we use the spin-polarized relativistic multiple-scattering theory (SPRMST) [9]. Then,

$$\text{Im} G^+(\mathbf{r}, \mathbf{r}', E) = \sum_{\Lambda, \Lambda'} Z_\Lambda(\mathbf{r}, E) \text{Im} \tau_{\Lambda, \Lambda'}(E) Z_{\Lambda'}^+(\mathbf{r}, E) \quad (2)$$

where Z_Λ ($\Lambda = \kappa, m$) are the single-site scattering solutions of the Dirac equation. $\tau(E)$ is the so-called scattering path matrix describing the multiple scatterings in the solid. The charge, spin and orbital magnetization DOSs are given, respectively, by

$$N(E) = -\frac{1}{\pi} \text{Im} \int \text{Tr} G^+(\mathbf{r}, \mathbf{r}, E) d\mathbf{r}^3 \quad (3)$$

$$S(E) = -\frac{1}{\pi} \text{Im} \int \text{Tr} \beta \sigma_z G^+(\mathbf{r}, \mathbf{r}, E) d\mathbf{r}^3 \quad (4)$$

$$O(E) \approx -\frac{1}{\pi} \text{Im} \int \text{Tr} \beta \hat{L}_z G^+(\mathbf{r}, \mathbf{r}, E) d\mathbf{r}^3. \quad (5)$$

The s core state wavefunctions $\Phi_c^\dagger(\mathbf{r})$ can be written as

$$[g_{\kappa_c}^{m_c}(r) \chi_{\kappa_c}^{m_c^\dagger}(\hat{\mathbf{r}}), -i f_{\kappa_c}^{m_c}(r) \chi_{-\kappa_c}^{m_c^\dagger}(\hat{\mathbf{r}})].$$

The scattering solutions $Z_\Lambda^+(\mathbf{r})$ are given by

$$\sum_{\kappa'=\kappa, -\kappa-1} [g_{\kappa, \kappa'}^m(r) \chi_{\kappa'}^{m^\dagger}(\hat{\mathbf{r}}), -i f_{\kappa, \kappa'}^m(r) \chi_{-\kappa'}^{m^\dagger}(\hat{\mathbf{r}})].$$

$\chi_\kappa^m(\hat{\mathbf{r}})$ are the usual spin angular functions.

Since the quadrupole transition is negligible [10, 6], we make the dipole approximation, i.e., $\Pi_{q\lambda} = -e\alpha \cdot a_\lambda$ [10]. To simplify the derivation, one can replace $-e\alpha \cdot a_\lambda$ with $-i(e\hbar/m_e c) \nabla \cdot a_\lambda$, thereby ignoring negligible spin-flip transitions [11]. Consequently, the radial matrix elements do not contain the coupled large and small radial wavefunction integrals (e.g., $(\int r^2 g_{\kappa, \kappa}^m(r) f_{\kappa, \kappa}^{m_c}(r) dr)$) [10] and, thus, one can keep only the large-component terms. We now assume that the coupling between $g_{\kappa, \kappa}^m(r)$ and $g_{\kappa, -\kappa-1}^m(r)$ is small, thus neglecting the off-diagonal component $g_{\kappa, -\kappa-1}^m(r)$. As a result, only the diagonal scattering path matrix elements $\text{Im} \tau_{\Lambda, \Lambda}(E)$ survive in equation (1). This is the most severe approximation made in the present derivation, especially for the systems where the spin polarization is large. We further assume that $g_{\kappa, \kappa}^m(r)$ is independent of m , i.e., $g_{\kappa, \kappa}^m(r) = g_\kappa(r)$. After some algebra, we obtain the following:

$$W^+(E) - W^-(E) = -\frac{4e^2\hbar}{9m_e^2c^2} \left[2R_{p_{1/2}}^2 \sum_{m=-1/2}^{1/2} m \tau_{1,m}^I + R_{p_{3/2}}^2 \sum_{m=-3/2}^{3/2} m \tau_{-2,m}^I \right] \quad (6)$$

$$W^+(E) + W^0(E) + W^-(E) = -\frac{6e^2\hbar}{9m_e^2c^2} \left[R_{p_{1/2}}^2 \sum_{m=-1/2}^{1/2} \tau_{1,m}^I + R_{p_{3/2}}^2 \sum_{m=-3/2}^{3/2} \tau_{-2,m}^I \right] \quad (7)$$

$$O_p(E) = -\frac{2}{3\pi} \left[2F_{p_{1/2}} \sum_{m=-1/2}^{1/2} m\tau_{1,m}^I + F_{p_{3/2}} \sum_{m=-3/2}^{3/2} m\tau_{-2,m}^I \right] \quad (8)$$

$$S_p(E) = \frac{2}{3\pi} \left[F_{p_{1/2}} \sum_{m=-1/2}^{1/2} m\tau_{1,m}^I - F_{p_{3/2}} \sum_{m=-3/2}^{3/2} m\tau_{-2,m}^I \right] = S_{p_{1/2}}(E) + S_{p_{3/2}}(E) \quad (9)$$

$$N_p(E) = -\frac{1}{\pi} \left[F_{p_{1/2}} \sum_{m=-1/2}^{1/2} \tau_{1,m}^I + F_{p_{3/2}} \sum_{m=-3/2}^{3/2} \tau_{-2,m}^I \right] \quad (10)$$

where $\tau_{\kappa,m}^I$ denotes $\text{Im}[\tau_{\kappa m, \kappa m}(E)]$, R_{p_j} denotes $\int r^2 dr g_{p_j}(r) dg_s(r)/dr$ and F_{p_j} , $\int r^2 dr g_{p_j}^2(r)$. Note that the x-ray absorption coefficient $\mu^\lambda(\hbar\omega)$ is given by $2\hbar c W^\lambda(\hbar\omega)/\omega\Omega$. Finally, by assuming $R_{p_{1/2}}(E) \approx R_{p_{3/2}}(E)$, $F_{p_{1/2}}(E) \approx F_{p_{3/2}}(E)$, and $\mu^0(E) \approx (\mu^+(E) + \mu^-(E))/2$, we arrive at the central results of this work,

$$\frac{\mu^+(E) - \mu^-(E)}{\mu^+(E) + \mu^-(E)} = \frac{\mu_c(E)}{\mu_0(E)} = \frac{3O_p(E)}{2N_p(E)} \quad (11)$$

$$\frac{\mu^+(E) - \mu^-(E)}{\mu^+(E) + \mu^-(E)} = \frac{3[S_{p_{3/2}}(E) - 2S_{p_{1/2}}(E)]}{2N_p(E)}. \quad (12)$$

Clearly, for each spin-orbit-split component of the p conduction band, one can obtain equation (11) without assuming the radial integrals for $p_{1/2}$ and $p_{3/2}$ to be equal. Furthermore, equations (8), (9), (11) and (12) show that $O_p(E) = S_{p_{3/2}}(E) - 2S_{p_{1/2}}(E)$. This interesting relation is a special case of the general formula

$$O_l(E) = lS_{l_j^+}(E) - (l+1)S_{l_j^-}(E) \quad (13)$$

where $j^\pm = l \pm 1/2$. This formula is valid if the approximations mentioned above are valid. Interestingly, equation (12) (equation (13)) clearly illustrates that the MCD ($O(E)$) would be zero either if there were no spin-orbit coupling since in this case $S_{p_{3/2}}(E) = 2S_{p_{1/2}}(E)$ [$lS_{l_j^+}(E) = (l+1)S_{l_j^-}(E)$] or if there were no spin polarization.

If we assume that the radial matrix elements (R_{p_j} , F_{p_j}) and the photon frequency (ω) near the K-edge are constant and integrate both sides of equations (6)–(8) and (10) from E_f to a cut-off energy E_c where MCD is zero, we obtain a sum rule

$$\frac{\int_{E_f}^{E_c} dE [\mu^+(E) - \mu^-(E)]}{\int_{E_f}^{E_c} dE [\mu^+(E) + \mu^0(E) + \mu^-(E)]} = -\frac{\langle L_z \rangle_p}{n_p^h} \quad (14)$$

where n_p^h is the number of p holes and $\langle L_z \rangle_p$ is the p-projected ground state orbital magnetic moment. Thus, we have just rederived from the itinerant electron theory the s core level orbital magnetization sum rule of Thole *et al* [2]. Note that the rules discussed above are applicable for any x-ray absorption spectra from the s core states such as the K- and L_1 -edges.

We now investigate the validity of the orbital magnetization density of states rule (equation (11)). We will not be concerned further with the spin magnetization density of states rule (equation (12)) since $[S_{p_{3/2}}(E) - 2S_{p_{1/2}}(E)]$ is perhaps not a useful quantity. I have performed explicit calculations of both the polarized x-ray absorptions and the charge and magnetization DOSs of bcc Fe, hcp Co and fcc Ni using the SPR-MST [9]. Note that, in these explicit calculations, none of the approximations (except the dipole approximation) introduced in the derivation of equations (6)–(14) was made. The underlying electronic structure was calculated self-consistently also using the SPR-MST. The so-called orbital polarization correction [12] has been included in both the electronic structure

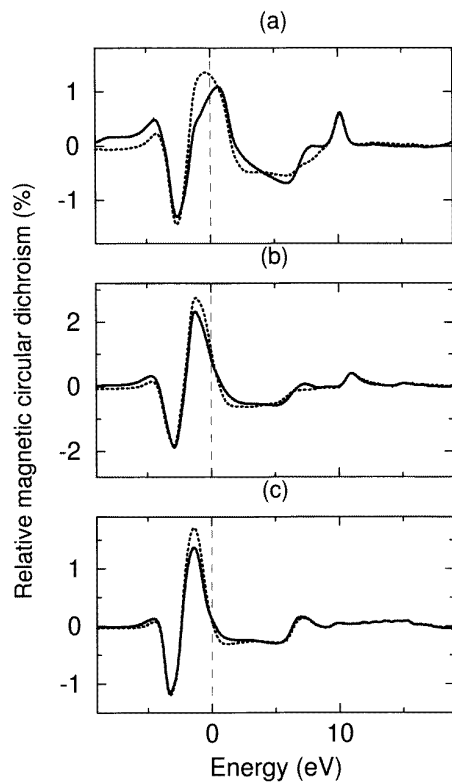


Figure 1. The relative K-edge magnetic circular dichroism ($\mu_c(E)/\mu_0(E)$) calculated from equation (1) (full curve) and normalized p-projected orbital magnetization density of states ($3O_p(E)/2N_p(E)$) calculated from equations (3) and (5) (dotted curve): (a) bcc Fe, (b) hcp Co and (c) fcc Ni. Zero energy is the Fermi level.

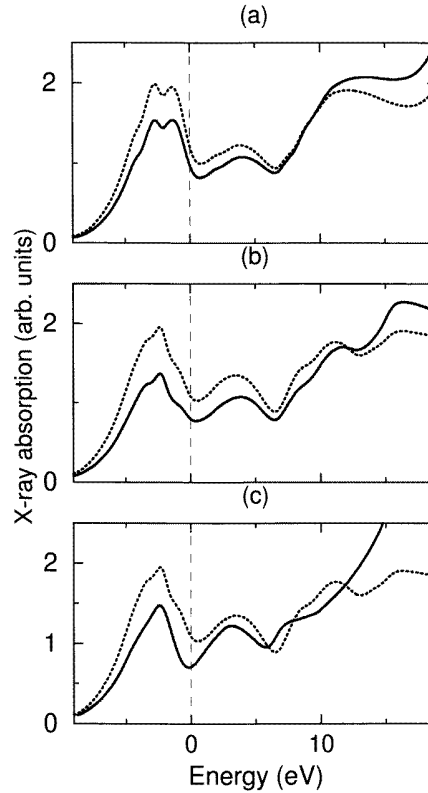


Figure 2. The K-edge x-ray absorption spectrum ($\mu_0(E)$) calculated from equation (1) (full curve) and p-projected density of states ($N_p(E)$) calculated from equation (3) (dotted curve): (a) bcc Fe, (b) hcp Co and (c) fcc Ni. Zero energy is the Fermi level.

and x-ray absorption calculations. Further details concerning these calculations are given elsewhere [13]. The calculated K-edge relative MCD ($\mu_c(E)/\mu_0(E)$) and normalized ODOS (defined as $3O_p(E)/2N_p(E)$) of bcc Fe, hcp Co and fcc Ni are plotted in figure 1. The spectra in figure 1 have been Lorentzian broadened with a width of 0.5 eV. Clearly, the normalized ODOS follows closely the relative MCD spectrum especially in hcp Co and fcc Ni. The experimental uncertainties for the K-edge MCD are often quite moderate perhaps because of the smallness of the MCD signals. Thus, one may say that the rule (equation (11)) holds quantitatively. As mentioned before, the most severe approximation is the neglecting of the small partner $g_{\kappa,-\kappa-1}^m(r)$ of the coupled scattering solutions of the Dirac equation. The errors due to this approximation may be expected to increase with the spin polarization. This is why the discrepancies in Fe are larger than in Co and Ni.

If the radial matrix elements were energy independent, the MCD (μ_c) would be exactly proportional to the ODOS and the XAS (μ_0) to the charge DOS. To see how much the radial matrix elements modify the p-projected DOS, I plotted the XAS and p-projected DOS in figure 2, and the MCD and p-projected ODOS in figure 3. The spectra in figures 2 and 3 have been Lorentzian broadened with a width of 0.5 eV. Figure 3 shows that there

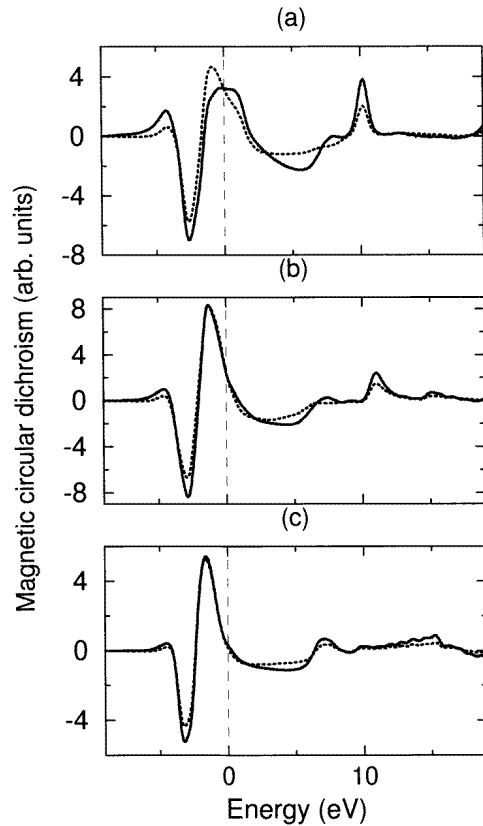


Figure 3. The K-edge magnetic circular dichroism ($\mu_c(E)$) calculated from equation (1) (full curve) and p-projected orbital magnetization density of states ($O_p(E)$) calculated from equation (5) (dotted curve): (a) bcc Fe, (b) hcp Co and (c) fcc Ni. Zero energy is the Fermi level.

is a good agreement between the MCD and the rescaled p-projected ODOS. Therefore, one may conclude that, at least for Fe, Co and Ni, the K-edge MCD measures the p-projected ODOS. There is also a good agreement between the rescaled p-projected DOS and the XAS within an energy range up to 12 eV above E_f . Beyond that, the energy dependence of the radial matrix elements appears to be important and some pronounced discrepancies can be seen (figure 2). These discrepancies do not occur in the MCD spectrum in figure 3 because the MCD signals and the p-projected ODOS are very small in this energy range. Finally, note that the conclusions concerning the validity of the ODOS rule of equation (11) made here do not depend on the orbital polarization correction being included in the present calculations, although including the orbital polarization correction gives rise to a better agreement between the theory and experiments [13]. A vigorous comparison between the theoretical and experimental K-edge MCD spectra is given elsewhere [13].

To summarize then, I have shown that the K-edge MCD spectrum probes the p-projected orbital magnetization density of unoccupied states.

References

- [1] See, e.g., van der Laan G *et al* 1986 *Phys. Rev. B* **34** 6529
Schütz G *et al* 1987 *Phys. Rev. Lett.* **58** 737
Chen C T *et al* 1990 *Phys. Rev. B* **42** 7262
- [2] Thole B T *et al* 1992 *Phys. Rev. Lett.* **68** 1943
Carra P *et al* 1993 *Phys. Rev. Lett.* **70** 694
- [3] Chen C T *et al* 1995 *Phys. Rev. Lett.* **75** 152
- [4] Schütz G and Fischer P 1996 *Europhys. News* **27** 101
- [5] Schütz G and Wienke R 1989 *Hyperfine Interact.* **50** 457
- [6] Igarashi J and Hirai K 1994 *Phys. Rev. B* **50** 17 820; 1996 *Phys. Rev. B* **53** 6442
- [7] Durham P J 1988 *X-ray Absorption* ed D C Koningsberger and R Prins (New York: Wiley)
- [8] Argyres P N 1955 *Phys. Rev.* **97** 334
- [9] See, e.g., Strange P, Ebert H, Staunton J B and Györfly B L 1989 *J. Phys.: Condens. Matter* **1** 2925
- [10] Ebert H, Strange P and Györfly B L 1988 *Z. Phys. B* **73** 77
- [11] Guo G Y and Ebert H 1995 *Phys. Rev. B* **51** 12 633
- [12] Brooks M S S 1985 *Physica B* **130** 6
- [13] Guo G Y 1996 *Phys. Rev. B* submitted; 1996 *J. Physique Coll. IV* at press