X-ray magnetic circular dichroism (XMCD) spectroscopy

A powerful spectroscopic procedure to determine magnetic moments makes use of x-ray magnetic circular dichroism (XMCD). As the radically different SQUID technology, the topic of Section 3.5, this method has been extensively employed to determine the magnetic moments of carbon nanostructures (see in particular chapter 12).

The chief idea underlying XMCD spectroscopy consists in making the x-ray absorption of a magnetic sample spin dependent. This succeeds by use of circularly polarized incident x-ray radiation. The magnetic moments of the analyzed sample are then obtained by recording *dichroism intensities*, defined as differences in the absorption intensity of x-rays with right and left circular polarization. The procedure is customarily illustrated by the example of $3d$ transition metals such iron, cobalt, and nickel. In these cases, x-ray absorption proceeds from the 2p core shell, involving the excitation of electrons from the spin-orbit split $3p_{\frac{3}{2}}$ $(= L_3)$ or $3p_{\frac{1}{2}}$ $(= L_2)$ levels into the 3d shell whose incomplete occupation is the origin of the magnetic moment [1, 2]

The procedure is sensitive to both the spin magnetic moment, m_S, and the orbital magnetic moment, m_{orb} . The former is given by the difference between the numbers $N_\uparrow$ and $N_\downarrow$ of d electrons with up and down spin orientation, respectively, according to

$$\mu_S = -2\mu_B \langle S_z \rangle = (N_\uparrow - N_\downarrow)\mu_B, \tag{1}$$

The physical cause for the appearance of this magnetic effect is the exchange interaction which induces an exchange splitting of about 1 eV in the d-shell. It thus dominates the spin-orbit splitting, which amounts to $\approx$ 50 meV, by a substantial margin.

The orbital magnetic moment is given by

$$\boldsymbol{\mu}_{orb} = -\mu_B \langle \hat{\mathbf{L}} \rangle \tag{2}$$

In the potentials defined by the ligand fields of the transition metal crystals, the $+m$ and the $-m$ levels of the d-shell orbtals are occupied with equal population. For instance, the d_{xz} and d_{yz} orbitals are represented in the following way:

$$
\begin{aligned}
d_{xz} &= \frac{1}{\sqrt{2}}(|2,-1\rangle - |2,+1\rangle), \\
d_{yz} &= \frac{i}{\sqrt{2}}(|2,-1\rangle + |2,+1\rangle)
\end{aligned}
\tag{3}
$$

In consequence, the orbital magnetic moment vanishes unless perturbations give rise to an imbalance between $|L, m\rangle$ and $|L, -m\rangle$ states. This imbalance arises as a result of spin-orbit coupling, giving rise to an orbital magnetic moment that is, as a rule, substantially smaller than the spin magnetic moment.

The essential features of XMCD spectroscopy are summarized in Figures 3.5 and 3.6. The incoming x-ray photons induce dipolar transitions. Depending on

their polarization which may be positive (q = -1, left circular polarization) or negative (q = +1, right circular polarization) they transfer an angular momentum of $+\hbar$ or of $-\hbar$ to the p electrons in the spin-orbit coupled core states. The transitions caused by the x-rays are subject to the selection rules operative for dipolar radiation, namely

$$\Delta L = \pm 1, \ \Delta$$
$$\Delta m_S = 0, \qquad (4)$$
$$\Delta m_L = q.$$

As implied by the spectra shown in Figure 3.6 and substantiated by the relative transition intensities indicated in Figure 3.7 for the case of $m_s = \frac{1}{2}$, the overall transition intensity from any given p level to the d shell changes with the circular polarization of the x-rays. The p multiplet with $J = \frac{3}{2}$ ($p_{3/2}$) gives rise to stronger absorption in case of right circular polarization, and weaker absorption for the left circular polarization alternative. As $J = \frac{1}{2}(p_{\frac{1}{2}})$, this order of intensities switches around (compare with the corresponding spectrum displayed in Figure 3.6). The reason for this difference lies in the change of the sign of the spin-orbit interaction as one goes from the $p_{\frac{3}{2}}$ to the $p_{\frac{1}{2}}$ multiplet, as reflected by the order of the energy levels with $m_J < 0$ and $m_J > 0$ for $J = \frac{3}{2}$ and $J = \frac{1}{2}$. [1]

Carra et al. [5] derived sum rules that relate the spectroscopically observable absorption intensities for both L_3 and L_2 edge electrons, and for left as well as right circular polarization to the magnetic moment of the analyzed sample. With respect to the spin moment, one obtains

$$[A - 2B]_\alpha = -\frac{C}{3}(2\langle S_\alpha \rangle + \langle T_\alpha \rangle), \qquad (5)$$

with $\alpha = x, y, z$. Here A(B) stand for the dichroism intensity for absorption by the L_3(L_2) edge, i.e. for $\Delta I_{L_3}(\Delta I_{L_2})$, and

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[1] Consider the sign switch of $2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} | J, L, S, m_J, m_L, m_S \rangle = (J(J+1) - L(L+1) - S(S+1)) | J, L, S, m_J, m_L, m_S \rangle$, as J changes from $\frac{3}{2}$ to $\frac{1}{2}$
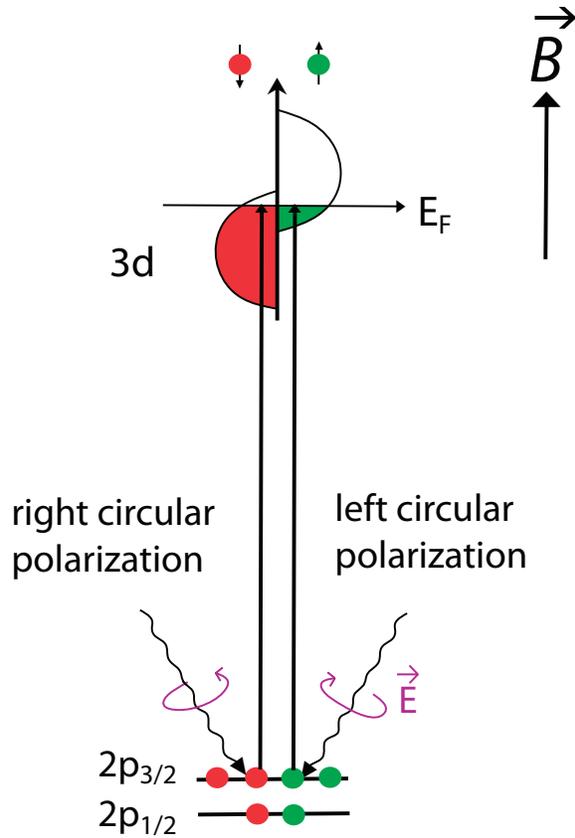
Figure 1: Determining the magnetic moment by use of the x-ray magnetic circular dichroism (XMCD) technique. Illustration of the XMCD mechanism by the example of a 3d transition metal [4].
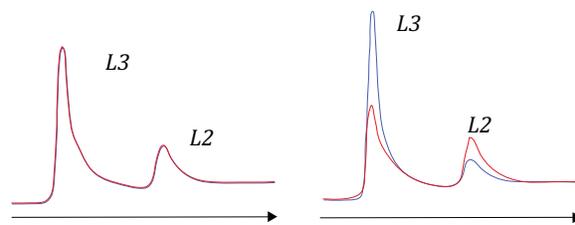
Figure 2: Determining the magnetic moment by use of the x-ray magnetic circular dichroism (XMCD) technique. Absorption spectrum for photoelectron transition from the p-shell into the d-shell for non-polarized (left) and circularly polarized (right) x-rays. The blue (red) line corresponds to a left-circular, $\Delta m_L = -1$ (right-circular, $\Delta m_L = +1$) transition [4]

Figure 3: Schematic representation of the possible transitions from a spin-orbit split p core states to d valence states with $m_s = +\frac{1}{2}$. The degeneracies of both levels are lifted by the exchange interaction. The transitions are induced by circularly polarized x-rays. The direction of incidence is parallel the z axis, chosen as the quantization axis. The number associated with the lines connecting the p and the d states are proportional to the respective transition intensities. The plus (minus) sign labels transitions with q = +1 (q = -1) [4]

$$\Delta I = I^+ - I^-, \tag{6}$$

where the superscript +(-) stands for right (left) circular polarization. The constant C in Eq. (5) is proportional to the square of the radial p $\rightarrow$ d transition matrix element [3], and $\hat{\mathbf{T}}$ denotes the *intra-atomic magnetic dipole operator*, defined as $\hat{\mathbf{S}} - 3\mathbf{r}(\mathbf{r} \cdot \hat{\mathbf{S}})/r^2$. Thus, the second term on the right hand side of Eq. (5) reflects the anisotropy of the spin density and therefore represents an angular correction to the isotropic contribution involving $\langle \hat{\mathbf{S}} \rangle$. Acknowledging this partition, one may rephrase Eq. (5) in terms of an effective magnetic moment $\boldsymbol{\mu}_{eff}$ which is composed of an *isotropic spin moment*, μ_S, and an *intra-atomic magnetic dipole moment*, $\boldsymbol{\mu}_D$, according to

$$[A - 2B]_\alpha = -\frac{C}{\mu_B}\mu_{eff}^\alpha = -\frac{C}{\mu_B}(\mu_S + \mu_D^\alpha), \tag{7}$$

By summing over all three axes, which amounts to an angular average over the expression on the right hand side of Eq. (5), one isolates the isotropic spin moment and arrives at [3]

$$\sum_\alpha [A - 2B]_\alpha = -\frac{C}{\mu_B}m_s. \tag{8}$$

The orbital moment, $\boldsymbol{\mu}_{orb}$, is derived from another sum rule, namely

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$$[A + B]_\alpha = -\frac{C}{2\mu_B}\mu_{orb}^\alpha. \tag{9}$$

We mention that, in a similar fashion, linearly polarized x-ray radiation may be used to determine the direction of the magnetic axis in antiferromagnetic samples. In this case, one exploits the dependence of the transition intensity on the direction of the electric vector with respect to this axis [6, 7].

Bibliography

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