Chapter 6

Photoelectron Diffraction in Magnetic Dichroism: Theory

The effect of MD in photoemission from crystal surfaces can be separated into two parts of different physical origin: a free-atom part and a part that originates from diffraction of the outgoing photoelectron wave scattered by the atomic potentials at the crystal-lattice sites.

It was first shown for the example of MD signals from the Fe and Co 2p and 3p core-levels that, when the relative orientation between the vectors $\vec{M}$, $\vec{k}$, and $\vec{E}$ is fixed, photoelectron diffraction leads to a variation of the dichroic signal if the emission angle is changed with respect to the crystal lattice [72, 73]. The explanation of such a behavior goes beyond the atomic model and requires to take into account the diffraction of the outgoing photoelectron waves.

6.1 Single scattering in a two-atom cluster

The interference of the diffracted outgoing photoelectron waves and its influence on magnetic dichroism can be appreciated by using a simple two-atom cluster model within the single-scattering approach [73]. For reasons of transparency, we shall address photoemission from a p level into s and d final states. The model will show that the MD effect can originate solely from the interference of the outgoing photoelectron waves. When superimposed on the free-atom dichroism, this interference can lead to a complex angular dependence of the MD signal amplitude, which – in a single-atom picture – is exclusively determined by the vectors $\vec{M}$, $\vec{k}$, and $\vec{E}$ (see Chapter 4).

Let us start by considering the $p \rightarrow d$ excitation channel, with the scattering geometry given in Fig. 6.1. In the dipole approximation, p-polarized light yields photoelectron amplitudes for the core $\left|\frac{3}{2};\pm\frac{3}{2}\right\rangle$ states that are proportional to $1+3e^{\pm 2i\phi}$, with an electron-emission angle ϕ (see chapter 4.2). The primary waves derived from these states have the amplitude $1\pm 3i$ at the electron detector. The amplitude of the same primary wave at the scatterer, placed in the direction $\phi = 45^\circ + \alpha$, is $1 + 3ie^{\pm 2i\alpha}$. The scattered wave, arriving at the detector, has thus the amplitude

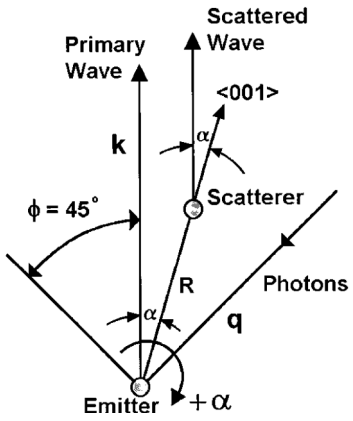

Figure 6.1: Photoemission and scattering geometry in the two-atom cluster model. The angles α and ϕ are defined by the propagation direction of the outgoing waves as rotations around the magnetization direction, which is oriented along the x-axis perpendicular to the plane of the figure; from Ref. [73].

$$\widetilde{A}_{\left|\frac{3}{2};\pm\frac{3}{2}\right\rangle} = 1 + 3ie^{\pm 2i\alpha}\,|f(\alpha)|\,e^{i\delta(\alpha)}, \tag{6.1}$$

with the scattering factor $|f(\alpha)|$ and the total phase shift $\delta(\alpha)$, due to scattering and a path-length difference.

The coherent sum of the primary and scattered waves reaches the detector. Magnetization reversal will exchange the states $\left|\frac{3}{2};\frac{3}{2}\right\rangle$ and $\left|\frac{3}{2};-\frac{3}{2}\right\rangle$. In an MD experiment, we measure the (incoherent) intensity difference given by expression

$$I_{\left|\frac{3}{2};\frac{3}{2}\right\rangle} - I_{\left|\frac{3}{2};-\frac{3}{2}\right\rangle} = 12\,|f(\alpha)|\sin\delta(\alpha)\,[1-\cos 2\alpha - 3\sin 2\alpha]\,. \tag{6.2}$$

The same calculation for the $m_j = \pm\frac{1}{2}$ magnetic sublevels yields

$$I_{\left|\frac{3}{2};\frac{1}{2}\right\rangle} - I_{\left|\frac{3}{2};-\frac{1}{2}\right\rangle} = 4\,|f(\alpha)|\sin\delta(\alpha)\,[1-\cos 2\alpha - 3\sin 2\alpha]\,. \tag{6.3}$$

The differences between the photoemission intensities from the levels with the same j, but opposite m_j values, give rise to the dichroism effect due to magnetization reversal (see 4.2 for detailed discussion).

In the framework of a single emitter and a single scatterer, the expressions 6.2 and 6.3 make it clear that sign reversal due to electron scattering and diffraction will arise when α passes from the left side (negative α) to the right side (positive α) of the emitter-scatterer direction (that defines $\alpha = 0$, see Fig. 6.1).

From the functional part depending on α in Eq. 6.2 and 6.3 it is clear that a periodic modulation of the MD signal with sign reversal should result. The term $|f(\alpha)|\sin\delta(\alpha)$ directly indicates that the magnetic linear dichroism for d-channel excitation originates solely from scattering and diffraction of the outgoing waves. In the absence of scattering, $|f(\alpha)|$ would be zero and no

dichroic effect could be observed. In particular for $\alpha = 0$, this diffraction dichroism vanishes.

The complete theory yields a MD effect caused by the combined influence of s- and d-channel interference and diffraction, even for $\alpha = 0$ [74]. If there is only the d channel, there would be an exact zero crossing of the MD asymmetry for $\alpha = 0$. If s-channel excitation is included, with interference between the s and d channels, a generalized expression for dichroism (difference in the $m_j = \frac{3}{2}$ intensities) is obtained [74]:

$$I_{\left|\frac{3}{2};\frac{3}{2}\right\rangle} - I_{\left|\frac{3}{2};-\frac{3}{2}\right\rangle} = D^{diff} + D^{atom} + D^{interf} \tag{6.4}$$

with

$$D^{diff} = 12\left(\left|f(\alpha)\right|/R\right) R_2^2 \sin\delta(\alpha)\left[1 - \cos 2\alpha - 3\sin 2\alpha\right], \tag{6.5}$$

$$D^{atom} = -24 R_0 R_2 \sin\Delta\left[1 + \left(\left|f(\alpha)\right|/R\right)^2 \cos 2\alpha\right], \tag{6.6}$$

$$D^{interf} = 48 R_0 R_2 \left(\left|f(\alpha)\right|/R\right)\left[\cos^2\alpha \sin\left(\delta - \Delta\right) - \cos\Delta\sin\delta\right]. \tag{6.7}$$

R_0 and R_2 are the radial matrix elements for the s and d channel, $\Delta = \delta_0 - \delta_2$ is the phase difference between the two channels. The first term, D^{diff}, is similar to Eq. 6.2 representing the diffraction dichroism. The second term, D^{atom}, is zero unless the interference between the two channels leads to atomic dichroism; the third term, D^{interf}, represents a more complex mixture of scattering and interference. Without excitation to the s channel (i.e. for $R_0 = 0$) only the first term would remain. On the other hand, excitation solely to the s channel (i.e. for $R_2 = 0$) results in zero dichroism, since it cannot be generated by an outgoing s wave. Equation 6.4 implies that the dichroism needs not to be zero for $\alpha = 0$. It also does not have to vanish when there is no scattering, i.e. when $|f(\alpha)| = 0$ because the term $-24 R_0 R_2 \sin\Delta$ remains, which is the limit for the purely atomic case.

It is instructive to expand Eq. 6.4 in a small region around $\alpha = 0$; the result to first order in α is then:

$$\begin{aligned} I_{\left|\frac{3}{2};\frac{3}{2}\right\rangle} - I_{\left|\frac{3}{2};-\frac{3}{2}\right\rangle} &= 72\left(\left|f(\alpha)\right|/R\right) R_2^2 \alpha \sin\delta(\alpha) \\ &\quad -24 R_0 R_2 \sin\Delta\left\{1 + 2\left(\left|f(\alpha)\right|/R\right)\cos\delta(\alpha)\right. \\ &\quad \left. + \left(\left|f(\alpha)\right|/R\right)^2\right\}. \end{aligned} \tag{6.8}$$

Eq. 6.8 shows that the MD is nonzero, but only slowly varying with α, so that the first term can give rise to the sign reversal MD when α changes sign. The second term, which also varies only slowly with α through $|f(\alpha)|$ and $\delta(\alpha)$, is proportional to $\sin\Delta$, and in this way results in a rigid shift of the angular dependence of the dichroic signal amplitude curve upward or downward (see Fig. 6.3). The model shows that both magnitude and sign of the dichroism signal depend on the emission angle with respect to the crystal lattice.

Including interference between two dipole-allowed excitation channels for PE in the model is not essential for the description of the periodic intensity variation

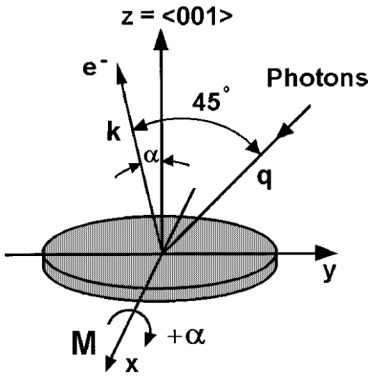

Figure 6.2: Photoemission geometry for dichroism experiments from the Fe $2p_{\frac{3}{2}}$ core level: p-polarized radiation impinges on the sample (cluster) in the yz plane at a fixed angle of 45° relative to the emission direction of the photoelectron. Dichroism is obtained by reversing the magnetization direction (from the +x to the -x direction). The dependence on the angle α is obtained by rotation of the sample around the x axis; from Ref. [73].

and sign reversal of the MD signal amplitude. Nevertheless, the interference between the s-d channels leads to a shift in the zero line of the curve describing the MD asymmetry variation as a function of emission angle α (see Fig. 6.3), which is very sensitive to the s-to-d partial-wave phase difference.

While this simple model is able to qualitatively account for the MD intensity modulation around the emitter-scatterer direction, including its sign reversal, a quantitative account of the full photoelectron diffraction (PD) intensity and the dichroism patterns in the low-kinetic-energy region (below 100 eV) requires model calculations using larger clusters, as well as an inclusion of multiple-scattering effects.

6.2 Specific case of the Fe $2p_{\frac{3}{2}}$ core level

The results derived in the previous section can be illustrated on the example of MD in photoemission from the Fe-$2p_{\frac{3}{2}}$ level [72, 73]. To model PE from the Fe(001) surface, a multiple-scattering approach was used as well as an atomic cluster of 100 atoms in 5 layers was considered. The results of the calculation are reproduced in Fig. 6.3, showing the strong intensity modulation in both total photoelectron intensity and MD signal amplitude.

Similar to the simple two-atom model, where the diffraction part of the MD signal reverses sign for $\alpha = 0$, these results also show a sign reversal of the MD signal around the direction defined by the maxima in the total intensity diffraction pattern, which corresponds to constructive interference in zero-order (forward scattering). These directions are in close relation to the low-index direction of the crystal lattice, as marked in Fig. 6.3.

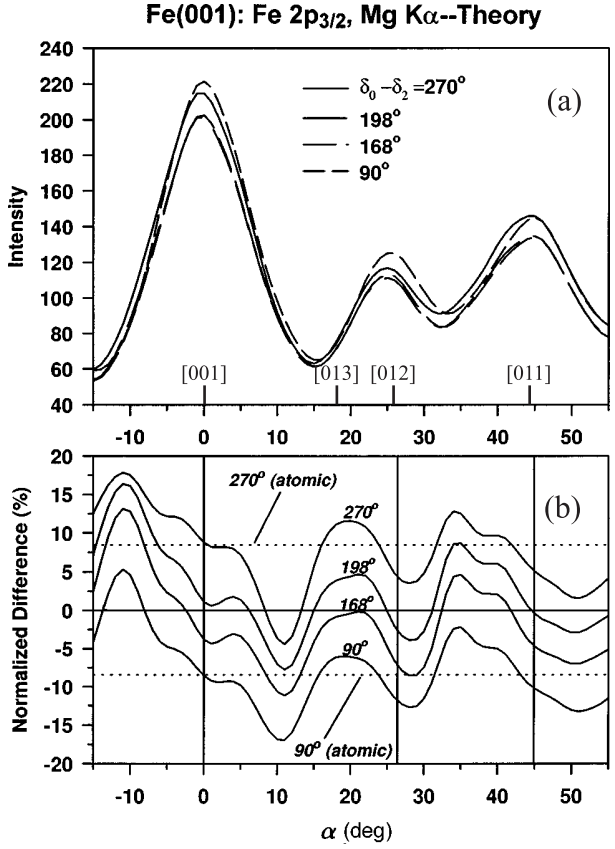

Figure 6.3: Angular dependences of (a) photoelectron intensities and (b) dichroic asymmetries calculated for the experimental geometries given in Fig. 6.2 for the Fe $2p_{\frac{3}{2}}$ core level, with Mg K_α x-ray excitation. Low-index directions are marked. The influence of the continuum-wave phase difference, $\Delta = \delta_0 - \delta_2$, is presented for the example of different D values ($\Delta = 90°$, 168°, 198°, 270°). Although the intensity changes little, the asymmetry shifts upward nearly uniformly as the phase shift difference increases from 90° to 270°. The dotted horizontal lines mark the two limiting cases of free-atom dichroism (with $\Delta = 90°$ and $\Delta = 270°$) which is independent of α; from Ref. [74].

An interesting aspect of these calculations is their sensitivity to the phase difference between the two excitation channels. The angular dependences of the MD signal intensity are presented for several values for Δ, starting from the free atom value of $\Delta = 168°$ [40]. Since the phase shift Δ in a solid can deviate from the one derived for an isolated atom [74, 75], a comparison of the experimental data with the results of the calculations is actually a way to determine the phase shift in the solid (through comparison of the experimental angular variations with model calculations).

The relative importance of the atomic and diffraction dichroism can be estimated. The maximum possible positive and negative values of the atomic

dichroism in the complete absence of diffraction occurs at $\Delta = 90°$ and $\Delta = 270°$ (as indicated by the dotted flat lines in Fig. 6.3. In the case of emission from the Fe $2p_{\frac{3}{2}}$ level it shows that MD due to diffraction can be about 1.5 times bigger than the free-atom dichroism. Because it is unlikely that Δ will be near these two extremes, the influence of diffraction is expected to be at least two times larger than the atomic effect. In addition, one can see that in the limiting cases of $\Delta = 90°$ and $\Delta = 270°$ the dichroism due to diffraction for $\alpha = 0$ is equal to that without diffraction for $\alpha = 0$. This further confirms the fact that the atomic contribution should dominate when emission is along a low-index direction.