Appendix B

Atomic Multiplet Theory of Photoemission from Gd-4f shell

An MD-in-PE (MDPE) experiment involves a measurement of the energy and, when compared to MD-in-XAS (XMCD), also of the emission direction of the electron. In addition, the crystal orientation becomes important (to describe diffraction effects). Detection of the photoelectron momentum allows one to observe MD in a wider range of experimental geometries. This advantage, however, renders an analysis of the experimental data significantly more demanding.

The theory of MD in angular-resolved photoemission was developed by Thole and van der Laan [32]. In particular, they derived a general expression for the core-level PE intensity in MDPE experiments:

$$J^a(\vec{q},\vec{k},\vec{M}) = \frac{1}{4\pi}\sum_x I^x \sum_{even\ b} U^{abx}(\vec{q},\vec{k},\vec{M}) \times \sum_{c\ c'} A^{cc'}_{abx} R^c R^{c'} e^{i(\delta_c-\delta_{c'})}. \quad \text{(B.1)}$$

Here, R^c denote radial dipole matrix elements, with phase shift δ_c for photoexcitation to continuum states with angular momentum $c = l \pm 1$. The sum includes interference terms between excitation channels $l-1$ and $l+1$. Coefficients $A^{cc'}_{abx}$ are tabulated in Ref. [32]. The experimental conditions are denoted by indices; light polarization: a; photoelectron angular distribution: b; atomic shell of the initial state: x. In particular, if one has circularly polarized light, a=1; linearly polarized light a=2; unpolarized light, a=0.

The so-called fundamental spectra, I^x, allow a description of the angle-resolved PE spectra by means of a linear combination of $2l+1$ fundamental spectra, giving the probability of removing an electron (with momentum x) from a core shell of orbital momentum l. For excitation from an f shell, e.g., there are seven different spectra I^x, with $x = 0, 1, ..6$. They contain ground-state information of the shell: fundamental spectra with odd values are connected with the oriented magnetic moments; dipole: I^1; octupole: I^3; fundamental spectra with even values represent aligned moments, e.g., quadrupole: I^2.

In magnetic dichroism, we are basically interested in the magnetic dipole moment. It was shown that the amplitude of the I^1 spectrum is proportional to magnetization [32]; that has been used to monitor the magnetization [43]. Intensity of the I^x spectra rapidly decreases with increasing x; nevertheless, the higher order spectra are always present. While the I^3 contributions are still considerably large, the I^5 intensities reach only a few percent of the I^0 intensities [32] and can be neglected.

The functions U^{abx} describe the characteristic angular distribution of photoelectrons ($\vec{k}$) of I^x for fixed $\vec{q}$ and $\vec{M}$. These functions are spherical in all three vectors and totally symmetric under rotation of the coordinate system, depending only on the relative angles between $\vec{q}$, $\vec{k}$, and $\vec{M}$. They are defined as:

$$U^{abx} = \sum_{\alpha\beta\xi} n^{-1}_{abx} \begin{pmatrix} a & b & x \\ -\alpha & -\beta & -\xi \end{pmatrix} C^{\alpha}_{a}(\vec{q}) C^{\beta}_{b}(\vec{k}) C^{\xi}_{x}(\vec{M}), \tag{B.2}$$

with

$$C^m_l(\theta,\varphi) = \sqrt{\frac{4\pi}{2l+1}} Y^m_l(\theta,\varphi) \tag{B.3}$$

and

$$\begin{aligned} n_{abx} &= i^g \left(\frac{(g-2a)!(g-2b)!(g-2x)!}{(g+1)!} \right)^{1/2} \\ &\times \frac{g!!}{(g-2a)!!(g-2b)!!(g-2x)!!}, \end{aligned} \tag{B.4}$$

where $g = a + b + x$. The sum over b in (B.1) is taken over even $b = |a-x|, ..., |a+x|$. The case $b = 0$ corresponds to angle-integrated PE; all other U^{abx} (with $b \neq 0$) vanish identically when integrated over 4π.

To get access to the magnetic dichroism spectrum I^1, both circularly-polarized (CP) and linearly-polarized (LP) light can be utilized in two different geometries: co-planar vectors $\vec{q}$, $\vec{k}$, and $\vec{M}$ for CP light with co-planar $\vec{q}, \vec{k}$, and orthogonal $\vec{M}$ for CP light.

Circularly-polarized light: In the CP case (a=1), the functions U^{abx} vanish identically for odd values of $a+b+x$. Eq. B.1 will give the following expression for excitation from f shells with CP light:

$$\begin{aligned} 4\pi J^1 &= I^1[\frac{3}{7}U^{101}(R^2R^2 - R^4R^4) \\ &\quad + \frac{6}{49}U^{121}(-2R^2R^2 - 3R^2R^4 cos\delta + 5R^4R^4)] \\ &+ I^3[\frac{2}{49}U^{123}(-9R^2R^2 + 4R^2R^4 cos\delta + 5R^4R^4) \\ &\quad + \frac{4}{49}U^{143}(R^2R^2 + 5R^2R^4 cos\delta - 6R^4R^4)] \end{aligned} \tag{B.5}$$

$$
\begin{aligned}
+ \quad & I^5[\frac{5}{49}U^{145}(R^2R^2 - \frac{8}{11}R^2R^4cos\delta - \frac{3}{11}R^4R^4) \\
& + \frac{10}{77}U^{165}(-R^2R^4cos\delta + R^4R^4)].
\end{aligned}
$$

For co-planar vectors $\vec{q}, \vec{k}, \vec{M}$ and with angles $\alpha = \angle(\vec{M}, \vec{q})$ and $\beta = \angle(-\vec{M}, \vec{k})$, the associated U^{abx} are linear combinations of trigonometric functions [10]:

$$
\begin{aligned}
U^{101} &= cos\alpha \\
U^{121} &= \frac{1}{4}[cos\alpha + 3cos(\alpha - 2\beta)] \\
U^{123} &= \frac{1}{8}[cos\alpha + cos(\alpha - 2\beta) + 5cos(\alpha + 2\beta)] \\
U^{143} &= \frac{1}{64}[9cos\alpha + 35cos(\alpha - 4\beta) + 15cos(\alpha - 2\beta) + 5cos(\alpha + 2\beta)] \quad \text{(B.6)} \\
U^{145} &= \frac{1}{128}[18cos\alpha + 7cos(\alpha - 4\beta) + 12cos(\alpha - 2\beta) + 28cos(\alpha + 2\beta) \\
& +63cos(\alpha + 4\beta)] \\
U^{165} &= \frac{1}{512}[50cos\alpha + 231cos(\alpha - 6\beta) + 105cos(\alpha - 4\beta) + 70cos(\alpha - 2\beta) \\
& +35cos(\alpha + 2\beta) + 21cos(\alpha + 4\beta)]
\end{aligned}
$$

Both the squared radial matrix elements and the interference term $cos\delta$ are present in the expression for $4\pi J^1$. At the photon energies used in the MDPE experiments of this work (40-100 eV), the probability to excite the f electron to g continuum states is much higher ($l+1$ transition) as compared to that for $f \rightarrow d$ excitation ($l-1$ transition).

The photon-energy dependence of the radial matrix elements, calculated by M. Martins (in Ref. [10]) with Cowan's code, is shown on Fig. B.1. The small R^2 leads to small R^2R^2 and $R^2R^4cos\delta$. For photon energies $h\nu > 60$ eV, one can neglect the interference term and the I^5 spectrum and the expression B.5 can be approximated by

$$
4\pi J^1 \approx I^1[(-\frac{3}{7}U^{101} + \frac{30}{49}U^{121}) + I^3(\frac{10}{49}U^{123} - \frac{24}{49}U^{143})]. \quad \text{(B.7)}
$$

The different angular characteristics of the various U^{abx} functions in Eq. B.7 allow one to vary the intensity ratio of I^1 to I^3 by special choices of $\vec{k}$ and $\vec{M}$ in the experiment.

Linearly-polarized light: With LP excitation, the expression for the measured intensity takes the form:

$$
\begin{aligned}
4\pi J^2 &= I^1U^{221}\left(\frac{45}{14}\right)R^2R^4sin\delta \\
&+ I^3\left[U^{223}\left(-\frac{5}{6}\right)R^2R^4sin\delta + U^{243}\left(-\frac{3}{2}\right)R^2R^4sin\delta\right] \quad \text{(B.8)} \\
&+ I^5\left[U^{245}\left(\frac{3}{14}\right)R^2R^4sin\delta + U^{265}\left(\frac{13}{42}\right)R^2R^4sin\delta\right].
\end{aligned}
$$

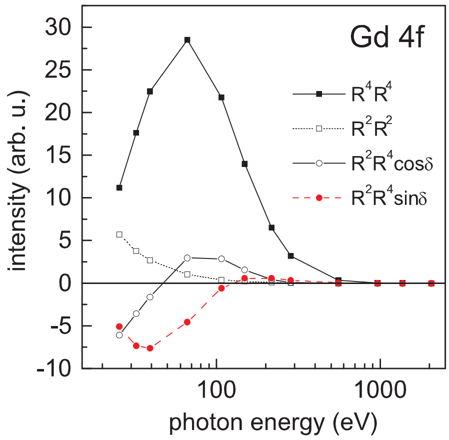

Figure B.1: Squared radial matrix element for a wide photon-energy range for PE from the 4f shell of Gd, calculated with Cowan's code by Martins (in Ref. [10]). Excitation into the g channel (R^4R^4) dominates over the d channel (R^2R^2). To obtain the given photon energy scale, $h\nu = E_{kin} + \Phi + E_B$ with $\Phi = 3.5\ eV$ and $E_B = 8.3\ eV$ were used.

For co-planar $\vec{E}$ and $\vec{k}$, orthogonal $\vec{M}$, and $\alpha = \angle(\vec{E}, \vec{k})$, the associated U^{abx} (odd $a+b+x$) can be calculated from B.2, B.3, and B.4. In the LP case, U^{abx} will have non-zero values only for odd values of $a+b+x$. Substitution in B.8 for LP light results in [10]:

$$4\pi J^2 = -(\frac{27}{14}I^1 + \frac{3}{4}I^3 + \frac{15}{112}I^5)R^2R^4 sin\delta\ sin2\alpha \tag{B.9}$$

It can be immediately seen that all fundamental spectra have the same angular dependence on the angle α. Therefore, their relative intensities ratio cannot be changed by the specific experimental geometry; in particular, the I^3/I^1-ratio is always about 0.4.