FLUORESCENCE YIELD DETECTION: WHY IT DOES NOT MEASURE THE X-RAY ABSORPTION CROSS SECTION

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It is shown that fluorescence yield (FY) detection does not measure a pure X-ray absorption spectrum if multiplet effects are important. The reason is that while the Auger decay is approximately constant, the fluorescence decay shows a strong dependence on the final state. With a coherent description of the X-ray absorption and X-ray emission processes, the observed differences between TEY and FY detected nickel 2p edges can be reproduced accurately. In the approximate, incoherent description the FY spectral shape identifies with the X-ray absorption spectrum multiplied with its state dependent fluorescence decay. Self-absorption effects are calculated and the implications for X-ray Magnetic Circular Dichroism (X-MCD) and generalisations to other systems are discussed.

Keywords: E: X-ray spectroscopies; synchrotron radiation.

1. INTRODUCTION

In the study of the metal 2p X-ray absorption spectra of 3d transition metals both Total Electron Yield (TEY) and Fluorescence Yield (FY) are used. Transmission measurements are in general not possible because of the strong X-ray absorption cross section. The 2p hole decays for more than 99\% via Auger and less than 1\% via fluorescence [1]. The Auger electrons escape from the solid if they are created in about the top 10 nm of the sample. It has been found that in general Auger electron detection gives a correct measure of the X-ray absorption cross section, though some complications can arise [2]. Because the total number of secondary electrons per core hole is a constant, also TEY is a correct measure of X-ray absorption. Also FY detection is in general found to be a good measure of the X-ray absorption cross section if the edge absorption is less than the background absorption [3]. Thus, in case of impurities, FY is an ideal tool for detection [4]. However, for the use of FY one makes an implicit assumption that the fluorescence decay is equal for all states created in the X-ray absorption process. In other words one assumes that the final state dependence of fluorescence decay is proportional to the final state dependence of the Auger decay. In this case FY gives the same result as TEY. However, if there is a final state dependent fluorescence decay which differs from the Auger decay one probes something different from the pure X-ray absorption cross section. In the following we will argue that this is indeed the case.
The model we will use for the analysis of the 2p spectra of transition metal compounds is the crystal field multiplet model [5-7]. This model gives an accurate simulation of the 2p X-ray absorption spectral shape in case of ionic compounds. Charge transfer effects, which dominate the 2p XPS spectral shapes [8], give rise to satellites in the X-ray absorption spectrum [9,10]. We choose not to include charge transfer effects as they are not crucial for the analysis of the symmetry dependence of Auger and fluorescence decay. The crystal field multiplet model describes the ground state as a pure 3d\(^{\alpha}\) state. The final states are formed by a series of excitonic configurations of the type 2p\(^5\)3d\(^{\alpha+1}\), with a series of different symmetries as can be reached from the ground state with a dipole transition. For each final state 2p\(^5\)3d\(^{\alpha+1}\) the 2p X-ray absorption cross section is described as

\[ I_{XAS}(\omega) = |(f|\gamma_{\omega}|i_0)|^2 L_f G_E, \]

with

\[ L_f = \frac{\Gamma_f/\pi}{(E_f - E_{i0} - \omega)^2 + \Gamma_f^2}, \]

where \(i_0\) is the ground state and \(f\) are the 2p\(^5\)3d\(^\alpha\) final states, \(E\) gives their respective energies, \(r_q\) is the dipole operator and \(\omega\) is the energy of the incoming X-ray. The line spectrum is broadened by: (1) \(L_f\), a Lorentzian determined by the life time broadening \((\Gamma_f)\) of the 2p\(^5\)3d\(^{\alpha+1}\) states, and (2) \(G_E\), a Gaussian convolution given by the experimental broadening. Divalent nickel in an octahedral crystal field of 1.2 eV will be chosen as an example. Its ground state is 3d\(^{\alpha}[3A_2]\).

In the rest of the paper we describe in Section 2 the state dependent Auger and fluorescence decay. The consequences for FY detection are discussed using both a coherent and an incoherent description. Section 3 discusses the consequences of self-absorption effects.

2. SYMMETRY DEPENDENCE OF AUGER AND FLUORESCENCE DECAY

Once a 2p core hole is created it can decay via either Auger decay or fluorescence decay. The three dominant Auger channels are respectively the 2p3p3p-decay, the 2p3p3d-decay and the 2p3d3d-decay. Together they present more than 95% of the total decay. Weak channels, not discussed further, are those including a 3s-electron [11]. The single dominating fluorescence channel is the decay of a 3d electron to the 2p hole, the inverse process of the X-ray absorption process.

The Auger decay strength is given by the overlap of the wavefunctions of the participating electrons. For example 2p3p3p-decay can be described by the Auger matrix element \(R^{2p}(2p, 3p; 3p, \epsilon)\), where \(\epsilon\) is a free electron with symmetry \(p\) or \(f\) and its kinetic energy given by the difference of the three core states [11]. For each final state 2p\(^5\)3d\(^{\alpha+1}\) the decay to respectively 3p\(^4\)3d\(^{\beta}\)(ppp), 3p\(^5\)3d\(^{\beta}\)(ppd) and 3d\(^{\gamma}\)(pdd) is calculated. The result is given in Fig. 1. Only final states which have a cross section larger than 0.01 A\(^2\) are included. The three channels have each a life time broadening \((\Gamma)\) of the order of 0.8 eV. The 2p3p3p-decay is independent of the symmetry of the 3d-states, hence constant. One can observe that, with some exceptions, the states at low energy have a smaller life time broadening, both for the L\(_2\) and the L\(_3\) edge.

The variation of the Auger decay strength, in other words the life time broadening, is in between 0.20 and 0.25 eV. For the 2p X-ray absorption process also the Coster–Kronig decay channel of the 2p\(_{1/2}\) states is important. This 2p\(_{1/2}\)2p3p3d-channel is strong and causes an additional broadening to the L\(_2\) edge. We will see below (Fig. 2) that the variation of the fluorescence decay is considerably larger and to limit the complexity of the description of the fluorescence process we will assume a constant life time broadening of 0.25 eV.
The fluorescence, or X-ray emission, decay can be described by the inverse of the X-ray absorption process. The $2p^53d^9$ excitonic states decay back to $3d^8$ via a $3d \rightarrow 2p$ transition. The X-ray emission intensity is given as:

$$I_{XES}(\omega, \omega') = \sum_i \left| \sum_f \frac{\langle i|r_f|f \rangle \langle f|r_q|i_0 \rangle}{E_{i0} + \omega - E_f - i\Gamma} \right|^2 L_i(\omega, \omega') G_E,$$

where $i_0$ is the $3d^8^{3}A_2$ ground state, $f$ are the $2p^53d^9$ final states and $i$ the $3d^8$ states. $E$ gives their respective energies and $\omega$ and $\omega'$ are respectively the incoming and outgoing X-ray energies [12]. $L_i$ indicates a Lorentzian broadening given by the life time of the $3d^8$ states generated in the X-ray emission process. These life time broadenings are smaller than 0.01 eV. The total fluorescence decay is given by the integral over the outgoing energy $\omega'$. $L_i$ disappears and one obtains:

$$I_{FY}(\omega) = \sum_i \left| \sum_f \frac{\langle i|r_f|f \rangle \langle f|r_q|i_0 \rangle}{E_{i0} + \omega - E_f - i\Gamma} \right|^2 G_E. $$

If the separation of the $2p^53d^9$ final states (of identical symmetry) is larger than their life time broadening one can approximate this formula with an incoherent formulation [2].

$$I_{FY} \approx I_{FY}^i(\omega) = \sum_i \left| \langle i|r_q|f \rangle \right|^2 I_{XAS}. $$

In this incoherent approach the X-ray absorption and X-ray emission step are described separately. $I_{XAS}$ was given in equation (1). The FY is given as the product of the X-ray absorption and the X-ray emission processes and this line spectrum is broadened. It turns out to be the case that this incoherent approximation identifies, apart from a constant, with the expectation value of the $G$-exchange Slater integral of the $2p^53d^9$ final state [13].

Within the incoherent description one can determine the variation in fluorescence decay strength of each final state. Note, that in the coherent description this is not possible because the overall decay strength at a certain energy depends on all states close in energy. These states can interfere because, using equation (3), one takes the square of their sum. Figure 2 plots the fluorescence decay. One notices that while the total Auger decay varies by about 20%, the fluorescence decay varies much stronger (up to 400%). This large difference justifies the use of a constant Auger decay in the description of the fluorescence decay.

With both the coherent and the incoherent description we analyze the FY and TEY spectra the Ni 2p X-ray absorption spectrum of Cs[NiCr(CN)6] .2H2O. In this molecular magnet Ni$^{2+}$ is surrounded octahedrally by six nitrogen atoms. The FY and TEY measurement were carried out synchronously at the U4B beam line [14] of the National Synchrotron Light Source at the Brookhaven National Laboratory. Experimental details will be described elsewhere [15].

For the present analysis it is important to mention that the sample used was a powder pressed onto the sample plate. No angular dependence of the FY signal could be observed indicating small self absorption effects (see next section). Figure 3 shows the experimental TEY (bottom, points) and FY spectrum (top, points). The experiments are compared with the crystal field multiplet calculations for X-ray absorption (bottom, solid) and for respectively the coherent (top, solid) and the incoherent (top,
dashed) calculation. Atomic Slater integrals and a cubic crystal field of 1.2 eV have been used (see [7]). The calculations have been broadened with a life time broadening of 0.25 eV and the spectra are convoluted with a Gaussian of 0.3 eV to simulate the experimental resolution and additional broadening effects due to solid state effects not included in the crystal field multiplet model.

One can observe that the incoherent approximation to the FY spectrum gives a similar though not identical spectrum as the coherent model. The differences indicate that with the life time broadening of 0.3 eV there is some significant interference between final states of identical symmetry. Thus in the present case the incoherent approximation is not exactly valid. From Fig. 3 we further conclude that the main structures of the TEY-spectrum are correctly simulated by the crystal field multiplet calculations. The main peak and the shoulder of the $L_3$ edge and the two peaks of the $L_2$ edge are reproduced. The peak at 862 eV, which is caused by charge transfer effects [9], is not reproduced. The most prominent difference in the FY spectrum is the decrease of the main peak, which on first observation leads to the hypothesis that the spectrum is saturated. However, for the $L_2$ edge the first peak, of lower intensity in the X-ray absorption spectrum, loses intensity with respect to the second peak, which is incomprehensible with the saturation-hypothesis. The spectrum obtained with the coherent model simulates correctly the increase of the peaks at higher energy, both for the $L_2$ and the $L_2$ edge. That the incoherent spectrum looks even closer to experiment might indicate that because of a slightly different crystal field or due to charge transfer the amount of interference effects of the final states decreases. A discrepancy between theory and experiment is that the FY detection does not measure the X-ray absorption cross section spectrum and the related resonant X-ray emission spectra will be published elsewhere [16].

3.2. Consequences for X-MCD

X-MCD is normally measured with FY. Also the FY detection of the X-MCD spectral shape must be described with equation (3) or (4), that is as the X-ray absorption spectrum multiplied with its integrated X-ray emission spectrum, now separately for left and right circularly polarized X-rays. It is possible to include a magnetic field in the crystal field multiplet model. This has been exploited for X-ray absorption by van der Laan and Thole [17] and can be used also for the descriptions as given in this paper for the FY detected spectrum. The angular dependent effects of the X-ray emission decay, not discussed in this paper, will be more important due to the presence of the magnetic field.

3.3. Generalization to other systems

Similar discrepancies between TEY and FY have been observed for other nickel compounds [18]. In general we would like to notice that for all transition metal compounds where multiplets are important FY will not be related to the X-ray absorption cross section, but to equation (3) or, if there is no interference, to equation (4). Depending on the system and the measurement conditions self-absorption effects will further affect the spectral shape. Ni$^{2+}$ is somewhat special because its 3d-band is almost and both saturation and self absorption effects are absent. In the case that $\mu_B \approx \mu_{FY}$ there is saturation and also self absorption. To calculate the self absorption it is necessary to calculate the X-ray emission spectrum for each excitation energy. At each emitted X-ray energy one must calculate its absorption, hence the calculation of the self absorption is given as

$$I_{SA}(\omega) = \int_{\omega'} I_{XES}(\omega, \omega') I_{XAS}(\omega').$$

The resonant X-ray emission spectrum is given with equation (2), the X-ray absorption spectrum with equation (1). As 99% of the self absorbed X-rays decay via Auger their fluorescence can be neglected. Saturation will decrease the highest peak in intensity and effectively broaden the spectrum. Self absorption will, for the present case, only cause an additional broadening. As the $L_2$ edge has lower intensity the effects from saturation will be negligible. Its difference from the TEY spectrum is a clear indication that the symmetry dependent decay is indeed the cause that FY detection does not measure the X-ray absorption cross section. Details on the self absorption spectrum and the related resonant X-ray emission spectra will be published elsewhere [16].

3. DISCUSSION

3.1. Self absorption effects

We would like to distinguish between two effects: (1) the consequence if the edge absorption ($\mu_{FY}$) is larger than the background absorption ($\mu_B$) which we call saturation and (2) the consequences if the escaping X-ray is absorbed again by the nickel 2p excitation which we call self absorption ($\mu_{SA}$). The relation between the measured intensity ($I_{FY}$) and the FY absorption cross section is given as [3]: $I_{FY} = \mu_{FY}/(\mu_{FY} + \mu_{SA} + \mu_B)$. In the dilute limit $\mu_B \gg \mu_{FY}$
filled. This implies that the variations in the X-ray absorption and emission cross sections are large and also that there are relatively little final states.

All systems which can be described relatively accurate with the crystal field multiplet model, for example ionic transition metal compounds and molecular systems with metal centers, are expected to “suffer” from multiplet effects on their FY detected spectra. Charge transfer effects will not modify the results qualitatively though they will affect the analysis. In particular charge transfer effects tend to make differences in decay strengths smaller, essentially because it makes the states less pure in symmetry [19]. A systematic study of the trends through the 3d-series is in progress [16].

4. CONCLUDING REMARKS

We have shown, for the case of divalent nickel, that the FY detected spectrum does not relate to the 2p X-ray absorption spectrum. Instead it can be simulated satisfactorily with a coherent description of the coupled X-ray absorption and X-ray emission processes. This phenomenon that the FY spectrum does not identify with the X-ray absorption spectrum is expected to be general for all systems with large multiplet effects. Also their X-MCD spectra will be affected.

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