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Distortions of X-ray absorption spectra measured with fluorescence yield

F.M.F. de Groot[a,]*, M.A. Arrio[b], Ph. Sainctavit[a,b], Ch. Cartier[a], C.T. Chen[c]

[a] *LURE, Université Paris-Sud, Bâtiment 209D, 91405 Orsay, France*
[b] *Laboratoire de Mineralogie Cristallographie, Université Paris 6-7, 4 Place Jussieu, 75252 Paris, France*
[c] *AT&T Bell laboratories, Murray Hill, NJ 07974, USA*

Abstract

The 2p X-ray absorption spectra of 3d transition metal compounds measured with fluorescence yield (FY) appear distorted. It is shown that this distortion is intrinsic to FY detection and not due to self-absorption. It results from the final-state dependent variation of the fluorescence decay, which is more than 400%. The Auger decay is also final-state dependent but the variation is only 25%. In the approximation that the final states do not interfere with each other (which is shown to be approximately correct for Ni^{2+}), the FY spectral shape identifies with the X-ray absorption spectrum multiplied with its symmetry-dependent fluorescence decay. Results are given for the nickel 2p edge of $Cs[NiCr(CN)_6]\cdot 2H_2O$ measured synchronously with FY and electron yield.

1. Introduction

In the study of the metal 2p X-ray absorption spectra of 3d transition metals transmission measurements are in general not possible because of the strong X-ray absorption cross-section. The 2p hole decays for ~ 99% via Auger channels, used for Electron Yield (EY) detection, and for ~ 1% via fluorescence, used for Fluorescence Yield (FY). EY gives a good measure of the X-ray absorption cross-section because the penetration depth of soft X-rays is in general deeper than the escape depth of the (Auger) electrons. Given that the edge absorption is less than the background absorption FY is also a good measure of the X-ray absorption cross-section. One implicit assumption, both for EY and FY, is that the final state created in the absorption process decays equivalently via Auger and fluorescence. If this is not the case, the FY and EY signals are not identical.

2. Symmetry dependence of Auger and fluorescence decay

Using the crystal field multiplet model, which gives an accurate simulation of the 2p X-ray absorption spectral shape in case of ionic compounds [1,2], we will show that there is a difference between FY and EY. The ground state is given as $3d^n$ and the final states are formed by a series of $2p^5 3d^{n+1}$ excitonic configurations. The dominant Auger channels are the decay of the 2p-hole to $3p^2$, 3p3d and $3d^2$ [3]. The decay to $3p^2$ is independent of the symmetry of the 3d-states, hence constant. The variations in the lifetime broadening (Γ) in the decay to 3p3d and $3d^2$ is discussed in detail in Ref. [4]. It is found that the states at low energy have a smaller lifetime broadening both for the L_3 and the L_2 edge. The variation of the total Γ is from 0.20 to 0.25 eV. The Coster–Kronig decay of the $2p_{1/2}$-states causes an additional broadening to the L_2 edge.

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*Corresponding author.

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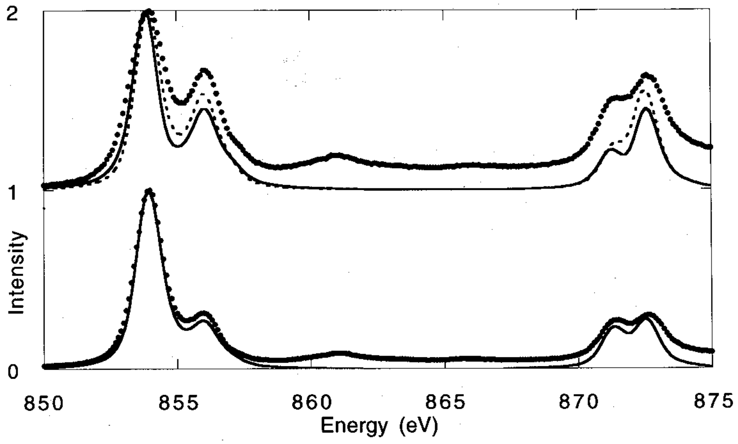

Fig. 1. Experimental TEY spectrum (bottom, points) and the FY spectrum (top, points) of $Cs[NiCr(CN)_6] \cdot 2H_2O$, compared with crystal field multiplet calculations. In the top spectrum both the coupled (solid) and de-coupled (dashed) calculations are included. The solid line in the bottom spectrum is a crystal field multiplet calculation. In the experimental spectra a constant background has been subtracted.

The dominating fluorescence channel is the decay of a 3d electron back to the 2p hole. Because the excitation and decay process are coherent, one describes it as an (in)elastic scattering process [5]. The intensity of the FY signal (I_{FY}) is given as

$$I_{FY}(\omega) = \sum_i \left| \sum_f \frac{\langle i|r_q|f\rangle\langle f|r_q|i_0\rangle}{E_{i0} + \omega - E_f - i\Gamma} \right|^2 . \qquad (1)$$

i is a $3d^n$ state with i_0 the ground state and f is a $2p^5 3d^{n+1}$ final state. r_q is the dipole operator and ω the excitation energy. If the separation of the $2p^5 3d^9$ final states of identical symmetry is larger than their lifetime broadening one can approximate this process as consisting of a separate X-ray absorption and fluorescence step. As a consequence, the FY is given as the product of the X-ray absorption and the fluorescence processes. For divalent nickel the fluorescence decay variation is about 400% [4], much larger than the 25% variation of the Auger decay.

Fig. 1 shows the experimental TEY (bottom, points) and FY spectrum (top, points). The FY and TEY spectra of $Cs[NiCr(CN)_6] \cdot 2H_2O$ (a molecular based magnet in which Ni^{2+} is surrounded octahedrally by six nitrogen atoms) were measured synchronously at the U4B beam line at NSLS [6]. The experiments are compared with the crystal field multiplet calculations for X-ray absorption (bottom, solid) and for, respectively, the coupled (top, solid) and the de-coupled (top, dashed) calculation. Atomic Slater integrals [2] and a cubic crystal field of 1.2 eV have been used in the calculations, which have been broadened with a lifetime broadening of 0.25 eV and a Gaussian of 0.3 eV to simulate the experimental resolution.

The EY spectrum is 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 is not reproduced. The FY is clearly different. The shape of the FY spectrum can be reproduced with the use of the symmetry-dependent fluorescence decay. The coupled and the de-coupled descriptions are similar and predict the correct change of the spectral shape. The additional broadening of the main peak is not reproduced.

From these observations we conclude that the FY detected spectrum does not identify directly with the 2p X-ray absorption spectrum. Instead it can be simulated satisfactory with a coherent description of the coupled X-ray absorption and fluorescence processes. This phenomenon is expected to be general for all systems with large multiplet effects. It is noted that this analysis is also valid for circularly polarized X-ray and in complete analogy one can describe the FY detection of the X-MCD spectral shape. For X-MCD the angular dependent effects, not discussed in this paper, will be more important.

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