Measurements of Zn $L_{2,3}$ satellites using x-ray emission spectroscopy

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X-ray emission spectroscopy is a powerful experimental technique for studying the electronic structure of solids. Presently, the existence of X-ray emission satellite features originating from the decay of $L_{2,3}$ core holes in the presence of additional $3d$ vacancies have been studied. The satellites of the $L_{2,3}$ x-ray emission spectra of metals can be produced either directly in the ionization process or as a result of Coster-Kronig processes preceeding the core-hole decay. The vacancy satellites are traditionally referred to as Wentzel-Druyvesteyn satellites [1] and end up on the high energy side of the main line.

In a recent work [2], we presented X-ray emission spectra of Cu metal. For excitation energies passing the L_2 threshold, a sharp step of increasing satellite intensity was found at the Cu L_3 emission line, proving the importance of Coster-Kronig decay to the satellite contribution. Due to the grazing-incidence sample orientation, the spectra were found to be almost free of self-absorption effects. From a quantitative analysis of the spectra, the L_3/L_2 intensity ratio and the Auger contribution to the life-time broadening were extracted. In this contribution we have extracted the corresponding values for Zn metal using spectra excited at high resolution.

The experiments were carried out at the undulator beamline BW3 at Hasylab in Hamburg. A high-resolution, grazing-incidence spectrometer with a two-dimensional detector was used [3]. The Zn spectra were recorded using second order of diffraction of a 1200 lines/mm grating (radius 5 m). The base pressure in the experimental chamber was 5×10^{-9} Torr. In order to determine the excitation energies, x-ray absorption spectra in the threshold region were obtained by measuring the total electron yield from the sample with 0.5 eV resolution of the monochromator of the beamline. During the X-ray emission measurements the resolution of the monochromator of the beamline and the X-ray fluorescence spectrometer were 0.9 eV and 0.8 eV, respectively. The sample was of high purity (99.99 %) and oriented so that the photons were incident at an angle of 7° and with the polarization vector perpendicular to the surface plane. The emitted photons were recorded at an angle near normal to the sample surface, perpendicular to the incoming photons. The grazing-in normal-out setup was chosen to minimize self-absorption.

The Zn spectra were measured from excitation energies from 1021.8 eV, at the L_3 threshold, up to energies as high as 1200.8 eV, above both the L_2 (E_B=1044.9 eV) and the L_1 (E_B=1196.2 eV) thresholds. The X-ray emission process above the L_3 threshold is normally described as a "two-step" process. In the first step a photoelectron
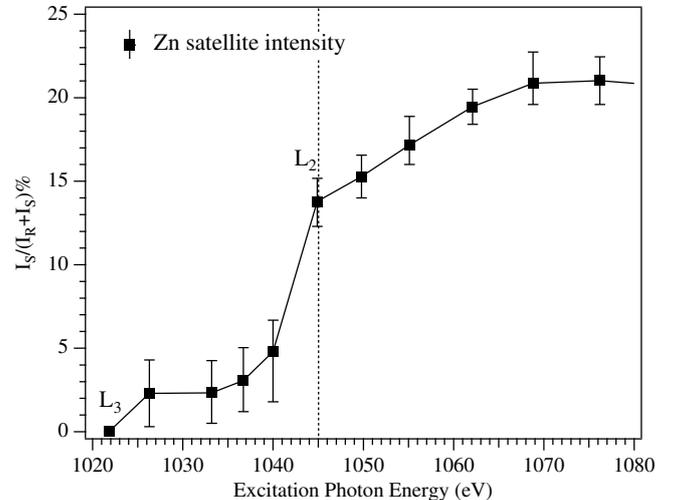

FIG. 1: (Color online) The relative x-ray emission satellite vs. the main line intensity ratio (in %) shown close to the L_3 and L_2 thresholds.

is excited from a core-orbital. In the decay step the core hole is filled by a valence electron and a photon is emitted. With separated excitation and emission steps, the satellite contribution can be separated from the main line by a proper subtraction procedure [4].

From a statistical point of view, the L_3 and L_2 core-level ionization ratio is 2:1 for Zn. With excitation energies above the L_1 threshold, the L_1 Coster-Kronig decay will also affect the initial core-hole population for X-ray emission of the L_2 and L_3 core levels. Just below the L_1 threshold, the L_3/L_2 emission intensity ratio was found to be 3.1, using the threshold spectra to subtract the satellite contribution. From this ratio, it is possible to obtain the Auger contribution to the life-time broadening Γ_A, using an experimental value of the Coster-Kronig width (0.39 eV) obtained by Nyholm *et al.* [5]. The Auger width Γ_A, for pure Zn metal is then found to be 0.71 eV by using the formula $\Gamma_A = 2\Gamma_{CK}/(I^{ratio} - 2)$ [5, 6], where I^{ratio} is the L_3/L_2 main-line intensity ratio (3.1). These values are in fairly good agreement with calculations by Yin *et al.*[7], where Γ_{CK} and Γ_A were found to be 0.75 eV and 0.65 eV, respectively.

Figure 1 shows the relative $I_S/(I_R+I_S)$ satellite intensity at the L_3 emission line (in percent), normalized to the satellite-free L_3 threshold spectrum excited at 1021.8 eV. The intensities were extracted after normalization by

subtracting the satellite-free threshold spectrum so that the intensities of the difference spectra were always positive. The error bars were obtained by varying the fit parameters.

For excitation energies below the L_2 threshold, the satellite has a slowly increasing intensity to less than 5 % of the total intensity, whereas for excitation energies closer to the L_2 threshold, a step of very rapid intensity increase is observed up to a new plateau at about 21 %.

To summarize, X-ray emission spectra of Zn metal have been measured close to the L_3, L_2, and L_1 excitation thresholds with monochromatic synchrotron radiation. From the quantitative analysis of the spectra, it is possible to extract the L_3/L_2 intensity ratio and the $L_{2,3}$ Auger-width. For excitation energies passing the L_2 threshold, a sharp step of increasing satellite intensity is found at the L_3 emission line, proving the importance of Coster-Kronig decay to the satellite contribution also for Zn metal.

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