

X-Ray Absorption Spectroscopy Beyond the Core-hole Lifetime

BNL--47995

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A new technique to overcome the core-hole lifetime broadening in x-ray absorption spectroscopy is presented. It utilizes a high resolution fluorescence spectrometer which can be used to analyze the fluorescence photon energy with better resolution than the natural lifetime width. Furthermore, the high resolution spectrometer can also be used to select the final state in the fluorescence process which can offer spin selectivity even without long range magnetic order in the sample.

Keywords: x-ray absorption spectroscopy, lifetime, spin-resolved spectroscopy, dysprosium

1. Introduction and theory

In an x-ray absorption process the incident photon ejects an inner-shell electron to an unoccupied state, thus creating a core hole. The transition probability depends on the unoccupied density of states and the atomic environment. In x-ray absorption spectroscopy the photoelectron is used as an indirect probe whose energy ϵ can be controlled only through the total energy conservation requirement $\epsilon = E_i - E_k$, where E_i is the incident photon energy and E_k , for example, is the K-shell binding energy. However, due to the finite lifetime of the intermediate hole the binding energy is determined only within the natural lifetime width of the core hole. Therefore the effective uncertainty of the binding energy, the lifetime width Γ_k , results in an equivalent uncertainty of the photoelectron energy. Thus the unoccupied density of states recovered from an absorption measurement is smeared by the core-hole lifetime width. Existing two-crystal monochromators can easily deliver an incident beam resolution comparable to the lifetime width but improvement beyond this usually serves no purpose. Therefore using conventional techniques, even the third generation synchrotron sources will only yield quantitative improvements for transmission XANES.

However, the absorption spectra can be measured also by monitoring the various decay channels of the core hole. In the case of radiative decay the core hole is filled by one of the outer shell electrons and a fluorescence photon is created. The total energy is again conserved and in the case of KL-fluorescence, for example, the photoelectron energy is determined by equation $\epsilon = E_i - E_f - E_L$, where E_f is the fluorescence photon energy and E_L is the L-shell binding energy. The fluorescence photon energy is determined by the binding energy difference between the inner and the outer shells and its natural linewidth is $\Gamma_k + \Gamma_L$. However, one can measure the fluorescence photon energy with a resolution better than its natural linewidth¹⁾. By defining the fluorescence photon energy one can limit the uncertainty of the photoelectron energy according to the total energy conservation requirement. In this case the photoelectron uncertainty will be limited only by the incident photon energy resolution and by the final state lifetime width Γ_L . Therefore, by selectively monitoring only

a narrow energy window at the peak of the fluorescence line using a high resolution spectrometer, while scanning the incident energy through the absorption edge, one can obtain an absorption spectrum without the K-shell lifetime broadening. This will improve the energy resolution at the expense of reduced count rate since only a limited number of fluorescence photons are accepted by the high resolution analyzer.

2. Experiment

Typical lifetime widths are of the order of a few eV. However, it is well known that using perfect crystals sub-eV resolution can be achieved in a near-backscattering geometry when the source size problem can be overcome. The spectrometer used for this experiment was based on a spherically bent perfect Si (440) crystal sitting on the same Rowland circle as the sample and the position sensitive detector. The source size limited resolution of the spectrometer was about 0.3 eV²⁾. The experiments were carried out on the NSLS X25 wiggler beam line at the Brookhaven National Laboratory³⁾. A two-crystal Si (220) monochromator together with a doubly-focusing mirror delivered a photon flux of the order of 10^{11} photons/s with 0.7 eV bandwidth at the sample with a spot size of less than 1mm^2 .

In order to demonstrate the improved resolution, the LIII absorption edge of dysprosium was studied¹⁾. Figure 1 shows the measured Dy $L\alpha_1$ fluorescence spectrum from Dy_2O_3 when the incident energy is well above the LIII absorption edge. The measured linewidth is clearly larger than theoretical atomic calculations predict ($\Gamma_{LIII} = 4.2$ eV and $\Gamma_{MIV} = 1.4$ eV) and offers a favorable test case to see the improved resolution. To illustrate the improved resolution both conventional transmission XANES and high resolution fluorescence measurements were performed using the same sample and the same incident beam resolution. These are shown in Figure 2. The high resolution spectrum was achieved by monitoring only a 0.3 eV energy window at peak of the fluorescence line while the transmission spectrum was obtained using ionization chambers to measure the total absorption at the sample. The comparison shows the dramatically improved resolution in

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the high resolution fluorescence measurement when the LIII-shell lifetime width is suppressed. High resolution XANES reveals a well separated true absorption edge followed by the white line corresponding to strong dipole allowed transitions to empty 5d states. The first edge, clearly separated from the white line, is due to the quadrupole allowed transitions from 2p to the partially filled 4f states. A more detailed scan shows also structure between the two edges¹⁾. Recently, Tanaka et al. have been able to explain the structure in detail⁴⁾. All the fine structure is totally smeared in the transmission case due to the LIII-shell lifetime broadening.

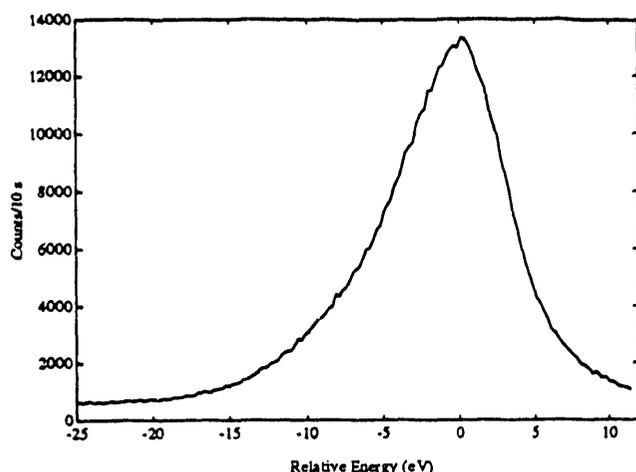


Fig. 1. Experimental Dy_2O_3 $L\alpha_1$ fluorescence spectrum. The energy is relative to the energy difference between the LIII and MV levels. Vertical scale is counts/10 s.

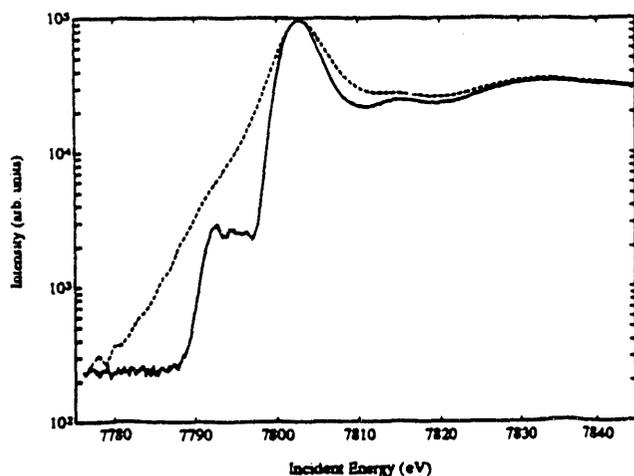


Fig. 2. High resolution fluorescence (solid line) and conventional transmission XANES spectra from dysprosium nitrate. The high resolution spectrum was collected by monitoring only a 0.3 eV energy bandwidth at the $L\alpha_1$ fluorescence peak.

The high resolution technique presented here not only reduce the influence of lifetime broadening but it can also be used to choose final states of slightly different energies⁵⁾. In the case of MnF_2 $K\beta$ -fluorescence, for example, the final state $1s^2 3p^3 3d^5$ has a very strong exchange interaction between the 3p and 3d electrons. Therefore the $K\beta$ -fluorescence spectrum has a pronounced satellite which can be seen in Fig. 3 at about -17 eV. The main and satellite lines correspond to predominantly spin down and spin up 3p holes, respectively. Since the spin is conserved in the fluorescence process, the photoelectron has the same spin character as the 3p hole. By selectively monitoring only the energy window at the main or the satellite peak in Figure 3, while scanning the incident photon through the absorption edge, one can obtain spin resolved absorption spectra.

Figure 4 shows spin resolved XANES spectra from MnF_2 . The pre-edge peak below the absorption edge corresponds to transitions to unoccupied 3d states. In the spectrum for the majority spin the pre-peak almost totally disappears. This is easily understood because all five available spin up 3d states are already occupied while all five remaining spin down states are empty. This obvious behavior confirms the assumption about the spin sensitivity.

3. Discussion

The potential of a new high resolution technique for XANES is demonstrated. It can be used to overcome the inner-shell lifetime broadening and limit the energy resolution to the final shell and incident beam energy broadening. The high resolution demands extremely high incident photon flux to get reasonable count rates. However, the next-generation synchrotron sources with higher flux and brightness should make this technique routine.

A promising technique to measure spin resolved density of states is presented. It utilizes the local magnetic moment as a reference direction. Therefore, it does not require long-range magnetic order (external magnetic field/single crystals) or a special incident beam polarization and it can also be applied to antiferromagnetic systems. To demonstrate the method we have measured the spin resolved XANES spectrum from MnF_2 in the paramagnetic state at room temperature. It can be applied to many other magnetically interesting elements, for example Fe and Ni, which have similar fluorescence satellites.

The authors would like to acknowledge S. P. Cramer, C.-C. Kao, B. Sincovic and V. Stojanoff. This work was supported by the U.S. department of Energy under Contract No. DE-AC02-76CH00016 and one of the authors (KH) is indebted to the Finnish Academy for financial support.

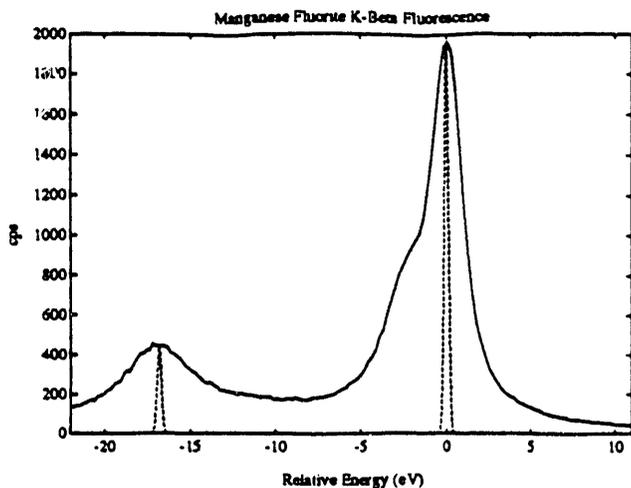


Fig. 3. Experimental MnF_2 $\text{K}\beta_1$ fluorescence spectrum. The satellite structure results from strong final state exchange interaction. The main peak corresponds to final states with predominantly spin down holes and the satellite peak at -17 eV to those with spin up hole final state. The dashed lines represent the two different energy windows used for the spin resolved absorption measurement.

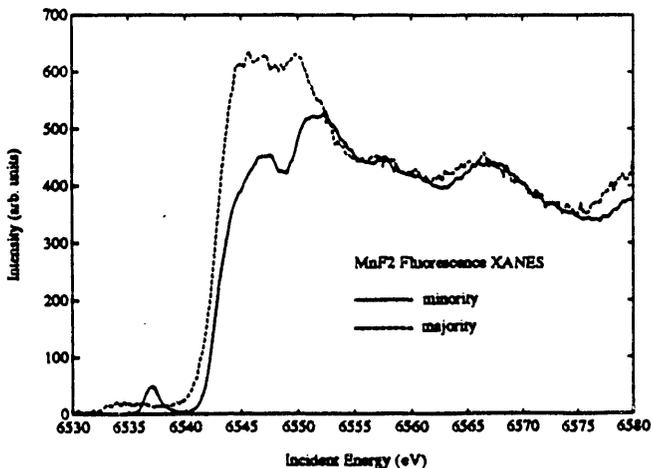


Fig. 4. Spin resolved XANES spectrum from MnF_2 . The solid line corresponds to the minority spin and the dashed line to the majority spin spectrum. They are measured by monitoring the narrow energy windows shown in Figure 3.

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