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High resolution near edge x-ray spectroscopy

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Abstract

A technique to suppress the core-hole lifetime broadening in near edge x-ray spectroscopy is presented. A simple theoretical explanation based on total energy conservation in the fluorescence process is given to explain the improved resolution. The experimental arrangement is shown together with an application to the L_{III} edge of dysprosium. Furthermore, the application of high resolution fluorescence spectroscopy in the study of magnetism is presented. The spin-resolved absorption spectra from MnF_2 are shown as an example.

1. INTRODUCTION

Although the existence of variations in x-ray absorption with photon energy above the threshold has been known for more than 60 years the true value of these variations in understanding the local atomic structure and the unoccupied density of states at the absorbing atom were not fully realized until routine measurements using synchrotron radiation (SR) were possible. The variation of the absorption cross section is measured by scanning the energy of the incident photon beam while monitoring the transmitted beam, the fluorescence radiation or the nonradiative decay. The spectra observed within several tens of electron volts of the threshold can give information about the density of unoccupied states and hence provide information about the bonding, oxidation and coordination of the system. As the photon energy is increased the backscattering of the photoelectrons from neighboring atoms creates oscillatory structure and gives local structural information even in disordered systems [1].

As the number of SR facilities has grown so has the use of x-ray spectroscopy in the fields of chemistry, biology and material science. Although present as well as future dedicated sources have and will continue to provide increases in incident intensity they have not provided improved energy resolution beyond the limit of the natural lifetime broadening of the core hole. Attempts to overcome

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this limitation have been made previously by using coincidence techniques in photoemission spectroscopy [2] which probe the occupied levels and in x-ray emission spectroscopy [3] and in x-ray absorption spectroscopy by measuring the resonant Raman scattering (RRS) differential cross section [4]. In the present work we introduce a new method to overcome the lifetime broadening by monitoring the fluorescence photon energy with a high resolution spectrometer. Application to the L_{III} edge of dysprosium is presented [5].

Not only has the increased intensity at SR sources impacted x-ray spectroscopy studies but it has also made possible observations of the weak magnetic interactions between photons and solids. In particular, the polarization and tunability of SR has made possible several spectroscopic methods to study various aspects of the spin resolved density of states. In the x-ray region magnetic Compton scattering [6], magnetic resonance scattering [7], Faraday rotation [8] and magnetic circular dichroism [9-11] have shown promise in the study of magnetism. These methods, however are limited to the study of ordered systems and cannot probe the density of states in the paramagnetic state above the ordering temperature where differences between localized and itinerant systems may be important.

The high resolution technique presented here not only overcomes the lifetime broadening but it also permits spin resolved spectroscopy when well resolved spin states are present in the emission spectra [12]. In this case the local magnetic moment at the absorbing atom serves as the reference direction [13]. Therefore long range order is not necessary to measure the spin resolved absorption spectra. Thus the evolution of the spectra as a function of temperature can be studied as the long range order evolves. Spin resolved spectra are presented for MnF_2.

2. THEORY

In the x-ray absorption process the incident photon is annihilated and a photoelectron is ejected to an unoccupied state. The probability of finding the hole left by the electron decays exponentially as a function of time which gives rise to a Lorentzian energy broadening of the electron binding energy. Since the total energy is conserved in the absorption process the photoelectron energy ε in the case of K-shell absorption is

$$\varepsilon = \hbar\omega_1 - |E_K| \tag{1}$$

where $\hbar\omega_1$ is the incident photon energy and E_K the K-shell binding energy. In transmission experiments the incident photon energy is scanned through the K-shell binding energy while monitoring the beam attenuation of the sample. Near threshold, this gives information about the unoccupied density of states as the photoelectron energy is varied according to Equation (1). Thus the photoelectron is used as a probe whose energy can be controlled only indirectly and has an uncertainty of

$$\Delta\varepsilon = \Delta(\hbar\omega_1) + \Gamma_K \tag{2}$$

where Γ_K is the K-shell lifetime width. Therefore in this case Γ_K is the ultimate resolution limit and improving the incident beam resolution beyond the lifetime width is ineffective. For this reason standard two crystal monochromators with a bandwidth of the order of 10^{-4} are satisfactory. In particular for the heavier elements, with K-shell lifetime widths of more than 10 eV that almost totally smear the near edge structure, overcoming the lifetime broadening would be very beneficial.

Once the core hole is created in the absorption process it is eventually filled by another electron through various decay channels. The simple transmission measurement in principle integrates over all possible decay channels. In the KL-fluorescence process the K-shell hole is filled by an L-shell electron through a radiative decay and a fluorescence photon is created. The fluorescence process can be described using second order perturbation theory and arises from the $\mathbf{p}\cdot\mathbf{A}$ term in the interaction Hamiltonian. It involves an intermediate state with a lifetime proportional to Γ_K^{-1}. Again in this case the photoelectron energy is determined by the total energy conservation as

$$\varepsilon = \hbar\omega_1 - \hbar\omega_2 - |E_L| \tag{3}$$

where $\hbar\omega_2$ is the fluorescence photon energy and E_L the L-shell binding energy. The fluorescence photon energy is determined by the corresponding binding energies as $\hbar\omega_2 = |E_K| - |E_L|$ and has a natural linewidth of $\Gamma_K + \Gamma_L$ where the L-shell lifetime width, Γ_L, is normally much smaller than the corresponding K-shell width. Thus if the fluorescence photon is not energy analyzed the uncertainty of the photoelectron is still determined by equation (2).

However, with a fixed $\hbar\omega_1$ one can *measure* the fluorescence photon energy $\hbar\omega_2$ with a resolution better than its natural lifetime width. Uncertainty of the photoelectron energy in this case is

$$\Delta\varepsilon = \Delta(\hbar\omega_1) + \Delta(\hbar\omega_2) + \Gamma_L \tag{4}$$

which is limited only by the L-shell width Γ_L instead of the much larger Γ_K. Therefore by selectively monitoring, with a high resolution spectrometer, only a narrow energy window at the peak of the fluorescence line while scanning the incident energy through the K-shell absorption edge one can obtain an absorption spectra without K-shell lifetime broadening. The total energy resolution is limited only by the incident beam resolution together with the final state lifetime width and the fluorescence analyzer resolution. The photoelectron energies still have a natural spread of Γ_K but by fixing the fluorescence photon energy one can choose photoelectrons with a smaller energy spread.

Quantitatively, the improved resolution can be understood by looking at the KL-fluorescence cross section [14] as a function of incident energy

$$\sigma(\omega_1)=\left(\frac{\Gamma_{K,R}}{\Gamma_K}\right)\int_0^{\infty} d(\hbar\omega_2)\, B(\omega_2)\left(\frac{\omega_2}{\omega_1}\right)\frac{E_L-E_K+\hbar\omega_1-\hbar\omega_2}{E_L-E_K}\,\frac{\Gamma_K/2\pi}{(E_L-E_K-\hbar\omega_2)^2+\Gamma_K^2/4}$$
$$\times\int_0^{\infty} d\varepsilon\,\frac{\Gamma_L/2\pi}{(\hbar\omega_1+E_L-\hbar\omega_2-\varepsilon)^2+\Gamma_L^2/4}\,\sigma_K(-E_K+\varepsilon) \tag{5}$$

where Γ_K and $\Gamma_{K,R}$ are the K-shell total and radiative width, respectively, $B(\omega_2)$ the energy window of the fluorescence spectrometer and σ_K the K-shell photoabsorption cross section (the quantity of interest) which is proportional to the oscillator strength and to the density of unoccupied states.

Since the incident photon energy is the only directly controlled experimental parameter during the measurement one must integrate over all possible photoelectron and fluorescence photon energies according to equation (5). However, the second Lorentzian correlates the photoelectron and incident photon energies within the L-shell lifetime width and the first Lorentzian adds an uncertainty of Γ_K to the fluorescence photon energy. Therefore the resulting fluorescence line has a total width of $\Gamma_K+\Gamma_L$. Since the Lorentzians are sharply peaked normally having FWHM of the order of a few eV they naturally limit the uncertainty of the photoelectron energy. Thus a solid state detector with a resolution of several hundred eV can be used for fluorescence photon detection. However, if the spectrometer resolution $B(\omega_2)$ is better than the K-shell lifetime width, this suppresses the broader Lorentzian and absorption spectra with resolution better than lifetime width can be achieved.

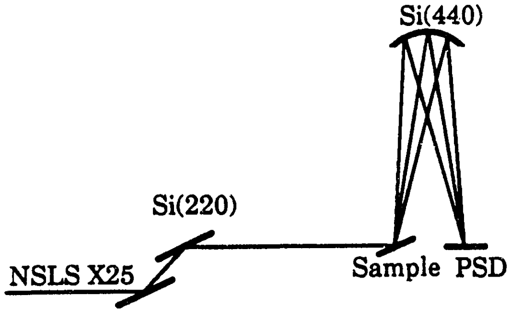

Figure 1. Experimental set-up.

3. EXPERIMENT

The experiment was carried out on the double focusing X25 wiggler beam line [15] at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. A two crystal Si (220) monochromator gave an incident beam resolution of 0.7 eV at 6.5 keV and a photon flux of the order of 10^{11} photons/s with spot size about 0.5 mm^2 at the sample. The experimental setup is shown in Figure 1. The fluorescence spectrometer was based on a spherically bent perfect Si (440) crystal sitting on the same Rowland circle as the sample and a position sensitive detector. A near-backscattering geometry (83^o-87^o) provided the necessary energy resolution which was limited by the source size to about 0.3 eV. A more detailed description of the instrument is given in Reference [16].

4 LIFETIME SUPPRESSION

Figure 2 shows the measured $L\alpha_1$-fluorescence spectrum from a Dy_20_3 sample when the incident energy was well above the absorption edge. The measured line width of about 9 eV is very large compared with the analyzer resolution of 0.3 eV. To show the effect of monitoring a small portion of this spectrum on the lifetime broadening, only the fluorescence radiation within a narrow band (see Figure 2) at the fluorescence peak was monitored while the incident energy was scanned through the L_{III} absorption edge. Figure 3 shows the resulting absorption spectrum from dysprosium nitrate (solid line). The improvement of the resolution is dramatic when compared with the transmission spectrum from the same sample with the same incident beam resolution (dashed line) where the resolution is limited by the L_{III} shell lifetime width of 4.2 eV [17]. The high resolution spectrum reveals a well separated true absorption edge followed by the white line

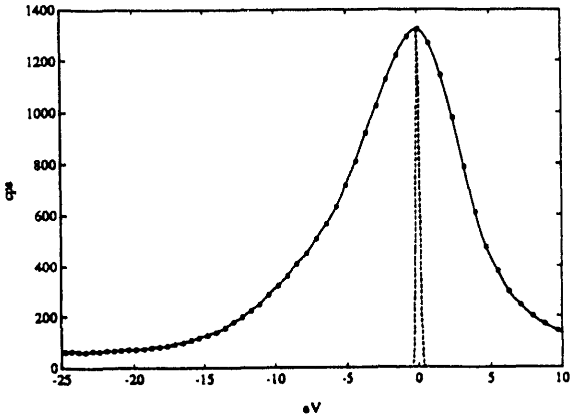

Figure 2. Experimental $L\alpha_1$ fluorescence spectrum from Dy_2O_3. The dashed line represents the analyzer resolution of 0.3 eV.

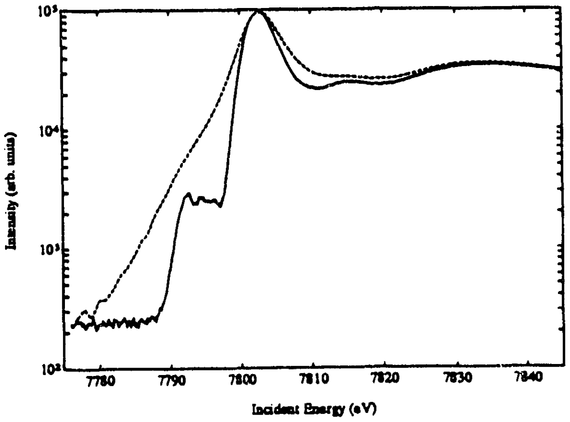

Figure 3. High resolution fluorescence absorption spectrum from dysprosium nitrate. The dashed line represents the conventional transmission spectrum.

corresponding to strong dipole allowed transitions to empty 5d states. The first edge is due to the quadrupole transitions to partially filled 4f states. A more detailed scan in this region is shown in Figure 4. Recently Tanaka et al. have been able to reproduce this structure theoretically using a multielectron atomic calculation [18]. All this structure is totally smeared in the transmission spectrum due to the L_{III}-shell lifetime broadening.

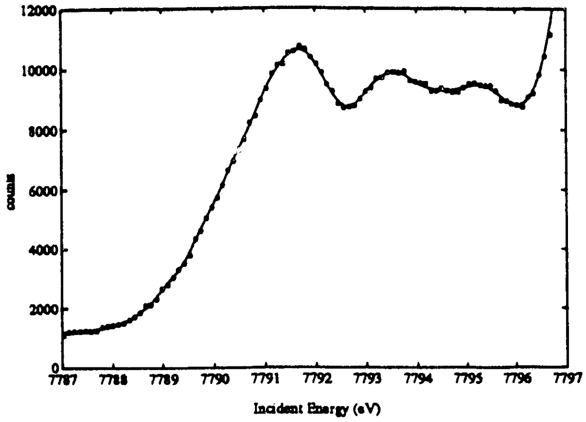

Figure 4. Inset of the absorption spectrum in Figure 3 around the absorption edge measured with a better statistical accuracy. The structure is related to the quadrupole transitions to the partly unoccupied 4f states.

5. MAGNETIC XANES

To date most studies of spin dependent near edge structure have utilized polarized light [7-11]. In this section a new technique for measuring spin dependent x-ray absorption spectra is presented which is based on the idea that fluorescence spectra of magnetic samples are often polarized. Thus, with a high resolution spectrometer capable of resolving different spin polarized final states in the fluorescence spectra, one can then select a particular final state to measure the partial absorption spectrum corresponding to a given spin polarization. In the following, the K-edge absorption spectra of MnF_2 will be used as an example to illustrate the spin sensitivity and other unique features of this new technique.

In the Kβ-fluorescence process the incident photon $\hbar\omega_1$ is absorbed, ejecting either the spin up or the spin down 1s electron to an unoccupied state. Assuming spin conservation in the fluorescence process, the intermediate 1s hole is then filled by a 3p electron with the same spin as the ejected 1s electron, and a fluorescence photon $\hbar\omega_2$ is emitted. The energy of the fluorescence photon is determined by the energy difference between the initial $1s^1 3p^6 3d^5$ and the final $1s^2 3p^5 3d^5$ states. If the final state energies corresponding to the spin up and the spin down 3p holes are different, then with a high energy resolution spectrometer one should be able to measure partial absorption spectra by selectively monitoring the fluorescence photons corresponding to one particular spin-polarized final state. In particular, one is then able to choose the spin orientation of the photoelectron involved in the absorption process, and obtain spin sensitivity in the absorption measurement. Another unique feature to be noted is that since this technique uses the direction of the majority spin of the ion as a reference it is no longer restricted to the study of ferro- and ferrimagnetic samples as is the case for magnetic circular dichroism, and can be applied to paramagnetic and antiferromagnetic samples as well.

Figure 5 shows a high resolution Kβ-fluorescence spectrum of MnF_2 which is similar to corresponding 3p x-ray photoemission spectrum. Since the final state of the Kβ-fluorescence is the same as the 3p photoemission process, we have based our assignment of the Kβ-fluorescence spectrum on the current interpretation of the 3p photoemission spectrum. Due to the strong exchange interaction between the 3d and 3p electrons, the main line is predominantly minority spin polarized, and the satellites are mostly majority polarized [19].

Partial absorption spectra were taken by monitoring the fluorescence intensity either at the main line or at the satellite in the fluorescence spectrum. Figure 6 shows the spin sensitive partial absorption spectra from MnF_2. The spectra corresponding to majority and minority spin are normalized to be the same well above the absorption edge. The first thing to be noted is that the pre-edge peak below the absorption edge, corresponding to a transition to unoccupied 3d states, almost totally disappears in the majority spin spectrum. This is consistent with the filling of the 3d shell in the Hund's rule ground state of Mn^{+2} ion, where all five 3d electrons have the majority spin. The behavior of the pre-edge peak confirms our assumption about the spin dependence of the fluorescence spectrum, and is direct evidence of the spin sensitivity of this method. However, configuration interaction, spin-orbit splitting, crystal field and other solid state effects can complicate the simple polarization dependence of the fluorescence spectrum, which might explain the non-vanishing majority contribution at the pre-edge peak region.

It should also be noted that the measurements were carried out at room

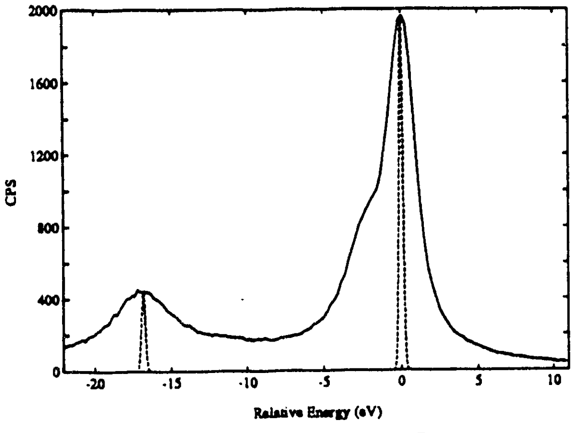

Figure 5. Measured $K\beta_1$-fluorescence spectrum from MnF_2 sample. The dashed lines represent the two different energy windows corresponding to two different spin polarized final states.

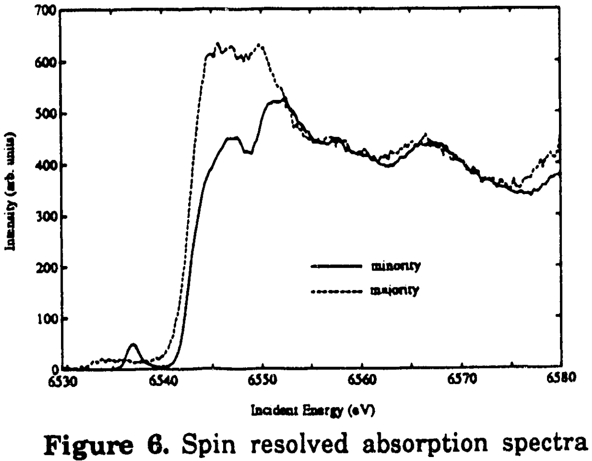

Figure 6. Spin resolved absorption spectra from MnF_2. The solid line corresponds to the minority spin (0 eV window in Figure 5) and the dashed line the majority spin contribution. (-17 eV window).

temperature, which is well above the Néel temperature (75 K) of MnF_2 [20], indicating the viability of the technique even in the absence of long range magnetic order. Furthermore, there exist clear differences in the spin dependent spectra around the absorption edge and well above the edge. The absorption edge has a small energy shift between the two spectra, 0.7 eV higher energy for the minority spin-polarized spectrum. This shift can be understood as an exchange splitting whereby the states with majority spin having lower energy than the states with minority spin. There is also significant difference in the spectra up to 15 eV above the edge. More detailed theoretical and experimental study is necessary to understand these differences.

6. CONCLUSIONS

In summary, a new technique has been presented that overcomes one of the limits to improved near-edge spectroscopy: core-hole lifetime broadening. The high resolution technique can also be used to select various parts of the emission spectra resulting from the decay of the core hole. This permits spin selectivity when the emission is spin resolved, as demonstrated here for the Mn Kβ-radiation. It is also inviting to think of valence selectivity when the emission from different oxidation states is resolved. In general, application of this technique will take full advantage of both dramatic flux increases and resolution provided by next generation sources.

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