

Spin-Polarized EXAFS Using $K\beta$ Detection

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Abstract: The first spin-polarized EXAFS of an anti-ferromagnetically coupled system using $K\beta$ detection is reported. The $K\beta$ SPEXAFS effect is much larger than the K-edge XMCD SPEXAFS, because of the greater spin polarization of the excited photoelectrons. This internally referenced technique is suited for antiferromagnetically coupled systems, as well as ferromagnetic and paramagnetic systems.

1. INTRODUCTION

Photoelectron spin polarization effects in the EXAFS region (SPEXAFS) have generated considerable interest recently, both in experiments [1,2,3] and theory [4,5]. The phenomenon was first observed in x-ray magnetic circular dichroism (XMCD) measurements with circularly polarized x-rays and an external magnetic field by Schütz [6]. In K edge absorption, the polarization of incoming photons is partially transferred to the spin polarization of the photoelectrons (about 10^{-2}), due to the influence of spin-orbit interaction on the transition dipole matrix element [7]. Because of the extra exchange terms in the scattering potentials of magnetic neighbors, only the metal-metal interactions will appear in the spectrum, while the diamagnetic neighbor contributions will be invisible.

Despite of the success of XMCD SPEXAFS, the technique is generally limited to concentrated ferromagnetic or paramagnetic systems. Also, K edge XMCD SPEXAFS effects are weak signals ($\Delta\mu/\mu \sim 10^{-4}$), and experimental observation of such a small effect is quite difficult, especially for dilute systems such as metalloproteins.

Recently, a new technique of spin-polarized X-ray absorption has been demonstrated by Hämäläinen and coworkers [8]. This method utilizes the separation of internally referenced spin-up and spin-down transitions by detecting different parts of $K\beta$ emission spectrum. The $K\beta$ X-ray emission spectra (XES) arise from $3p \rightarrow 1s$ transitions. The main peak ($K\beta_{1,3}$) and satellite ($K\beta'$) ultimately derive from the excitation of a $1s$ electron anti-parallel or parallel to the $3d$ spin direction. Simulations with ligand field multiplet theory [9] confirms the spin-polarization assignment.

Here we report the first SPEXAFS of an antiferromagnetically coupled binuclear complex $[\text{Fe}_2\text{O}(\text{OH})(6\text{TLA})_2](\text{ClO}_4)_3$. By detecting at $K\beta_{1,3}$ and $K\beta'$ emission energies, respectively, the spin polarization of photoelectrons can reach 85% and 100% for spin-down and spin-up electrons [10]. Besides this 100-fold increase in spin polarization, $K\beta$ detected SPEXAFS is internally referenced. It therefore requires no circular polarized light or external magnetic field, and it is also useful for antiferromagnetically coupled systems. The elemental specification and spin selectivity will greatly simplify the structure of complex proteins, and the sign of the effect could provide information on the nature of the magnetic coupling.

2. EXPERIMENTAL

A schematic description of the apparatus is shown in Figure 1. The incident beam is focused on the sample using the beamline optics. An array of spherically bent Ge(620) crystals on intersecting Rowland circles then diffracts fluorescence back to a common spot on the detector. Because the diffraction occurs in near-backscattering Johann geometry on an 850-mm-diameter Rowland circle, very high energy resolution (0.45 eV) can be obtained. An emission spectrum can be obtained by rotating the analyzer crystals while moving the detector to track the diffracted beam. Alternatively, a spin polarized excitation spectrum can be recorded by setting analyzer crystals at the main peak or the satellite of the emission spectrum and scanning the incident energy.

The SPEXAFS experiment was carried out at beamline 6-2 [11] in Stanford Synchrotron Research Laboratory using a pair of Si(111) beamline monochromator crystals. The spectrometer as described above [12] was used to collect the $K\beta$ XES and spin-polarized EXAFS spectra. $[\text{Fe}_2\text{O}(\text{OH})(6\text{TLA})_2](\text{ClO}_4)_3$ was synthesized by published procedure [13]. The sample was diluted with BN to 2% Fe by weight. All data were collected at 11K, and $(\text{NET}_4)[\text{FeCl}_4]$ was used for emission and edge calibrations [14].

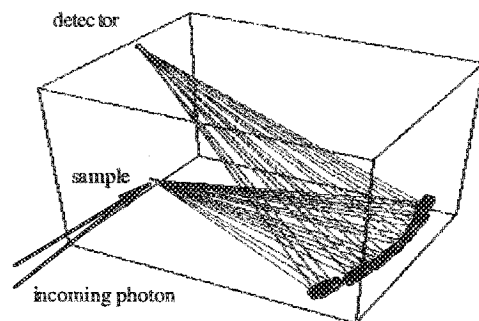
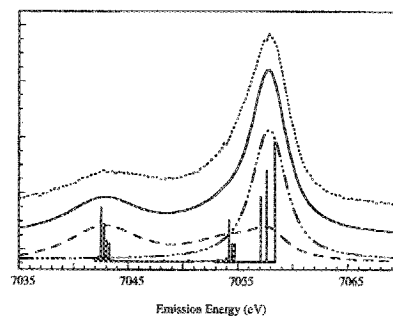


Figure 1. Experimental apparatus.

Figure 2. Experimental K β emission spectrum (top) vs. calculated spectra.

3. RESULTS AND DISCUSSIONS

Experimental (top, dotted lines) and theoretical K β XES of $[\text{Fe}_2\text{O}(\text{OH})(6\text{TfLA})_2](\text{ClO}_4)_3$ are shown in Figure 2. The emission spectrum is split into two parts, the main peak K $\beta_{1,3}$ at 7057.8 eV and at 14 eV lower energy the K β' satellite. A typical count rate at the K $\beta_{1,3}$ was 4200 c/s with background 4 c/s. A ligand field multiplet calculation was used to simulate the spectrum. The simulation involves a $1s^1 3d^5 \rightarrow 3p^5 3d^5$ transition in O_h symmetry, with the ligand field strength $10Dq=1.2$ eV. All the Slater integrals are reduced to 70% of their atomic values. Since the excitation of a 1s spin-down photoelectron partitions 6/7 of the fluorescence transition intensity to 7S symmetry, and the excitation of a 1s spin-up electron partitions 100% intensity of the 5S symmetry plus 1/7 of the 7S symmetry [10], it is possible to construct the spin-up and spin-down contributions separately by calculating transitions to 7S and 5S in K β XES. The final spin-up (dashed lines) and spin-down transitions (dotted dashed lines) are represented in the spectra. From the composition, it is clear that the satellite is 100% spin-up, while the main peak is around 85% spin-down.

By setting the analyzer crystals at the main peak and the satellite, we recorded spin polarized EXAFS. Figure 3 shows the k^3 -weighted spin-up and spin-down EXAFS as well as their Fourier transforms ($k=1-9\text{\AA}^{-1}$). The EXAFS data was calibrated and deglitched in each raw data set before spline was taken, then weighted by its signal counts, and finally smoothed over a $k=0.2 \text{\AA}^{-1}$ interval. There are some distinct differences in the spin polarized EXAFS data, which is most easily interpreted in the Fourier transforms. There are two major well-resolved peaks in the transforms. The feature at $r < 2.0 \text{\AA}$ corresponds to the first shell coordination sphere, including O and N atoms, and that at $r \sim 2.3 \text{\AA}$ corresponds to the Fe-Fe component. There is almost no difference in the backscattering amplitude of the first coordination contributions in both spin-up and spin-down EXAFS. The somewhat different amplitude at $r \sim 1.1 \text{\AA}$ is due to background subtraction. For the Fe-Fe component, however, the amplitude of the spin-down EXAFS is larger than that of spin-up. This result was reproduced in data from several different experiments.

The difference in backscattering amplitude for SPEXAFS derives from spin-up and spin-down electrons scattering with different probabilities from magnetic neighbors. From theoretical calculations [7], it can be predicted that parallel electrons have larger backscattering amplitudes than antiparallel ones. In the case of an antiferromagnetically coupled system, the spin-down EXAFS detects scattering by photoelectrons with opposite spins as the valence electrons of the x-ray absorber, i.e. the interaction with the magnetic neighbor is parallel. So the spin-down EXAFS will have larger backscattering amplitude, as we observed in our experiment.

In order to estimate the size of the effect, we performed EXCURVE fits on the spin-up and spin-down EXAFS using spin-independent potentials and phase shifts. Including multiple scattering paths, the best fit for spin-up EXAFS gives 2 O at 1.85 \AA , 4 N at 2.21 \AA and 1 Fe at 2.96(1) \AA . For spin-down EXAFS, all the other fitting parameters are the same except we find 1.1 Fe at 2.96(5) \AA . The different coordination number of Fe-Fe component reflects the difference in backscattering amplitudes with spin-up and spin-down electrons - spin-down EXAFS has 10% more intensity. This 10% effect is about 2 order of magnitude bigger than the K-edge XMCD SPEXAFS.



Figure 2. Experimental $K\beta$ emission and absorption spectra.

are shown in Figure 2. The 1 eV lower energy the $K\beta'$ field multiplet calculation in O_h symmetry, with the atomic values. Since the intensity to $7S$ symmetry, symmetry plus $1/7$ of the $7S$ separately by calculating positions (dotted dashed lines) spin-up, while the main

polarized EXAFS. Figure 3 shows ($k=1-9\text{\AA}^{-1}$). The EXAFS obtained by its signal counts, the spin polarized EXAFS well-resolved peaks in the leading O and N atoms, and backscattering amplitude of that different amplitude at amplitude of the spin-down experiment.

and spin-down electrons [7], it can be predicted. In the case of an atom with opposite neighbor is parallel. So the

spin-up and spin-down EXAFS, the best fit for spin-up EXAFS, all the other fitting number of Fe-Fe component spin-down EXAFS has XMCD SPEXAFS.

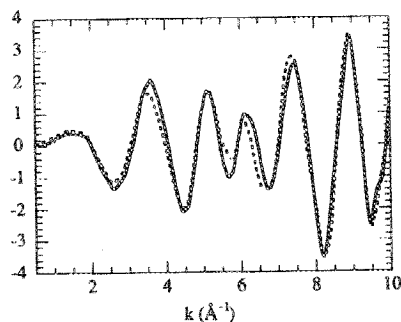


Figure 3a. k^3 -weighted spin-up (dotted lines) and spin-down (solid lines) EXAFS.

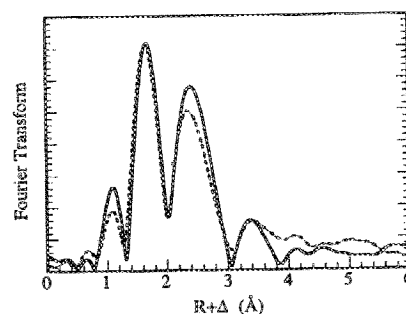


Figure 3b. Fourier Transform of spin-up (dotted lines) and spin-down (solid lines) EXAFS.

4. CONCLUSIONS

SPEXAFS by $K\beta$ detection should have broad applications in materials and biological science. The extra information should simplify EXAFS analysis of complex systems, and the sign of the effect could provide information on the magnetic coupling. At this stage, the low efficiency of this type of experiment is the main obstacle for practical use. With the development of third generation synchrotron sources, where incoming photon current can be expected to increase 2 order of magnitude, and the increasing efficiency of the fluorescence spectroscopy optics, spin-polarized x-ray absorption by $K\beta$ detection will have a bright future.

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