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Spin-dependent x-ray absorption of MnO and MnF_2

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A method to measure spin-dependent x-ray-absorption spectra that does not require long-range magnetic order is presented. It is based on the spin dependence of the emission spectrum. Using a high-resolution spectrometer to separate and select the different spin-polarized final states in the $K\beta$ fluorescence spectrum of MnO and MnF_2, spin-dependent absorption spectra in the vicinity of the Mn K edge were measured. Since this method uses the direction of the local magnetic moment as a reference it can be applied to paramagnetic and antiferromagnetic systems as well as to ferromagnetic.

Only recently, when dedicated and intense synchrotron radiation (SR) sources have become readily available has it been possible to observe the weak magnetic interactions between photons and solids. The polarization characteristics and tunability of the photon energy of SR has made possible several spectroscopic methods to study different spin related interaction phenomena and to probe the spin resolved density of states, which should lead to insights into the magnetic behavior of solids. In the x-ray region magnetic Compton scattering,[1] magnetic resonance scattering,[2] Faraday rotation,[3] and magnetic circular dichroism[4] (MCD) have shown promise in the study of magnetism. In particular, MCD near atomic core-level thresholds have recently attracted a great deal of interest.[5–8] 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.

In this paper we present a spectroscopic method to measure spin-dependent x-ray absorption which utilizes the local magnetic moment as the reference direction.[9] Therefore, it does not require long-range magnetic order and can be applied to paramagnetic and antiferromagnetic as well as ferromagnetic systems. Furthermore, it does not require the use of circularly polarized x rays or single crystals and the sample magnetization does not need to be oriented by an external field. This method provides a complementary technique to those where an ordered moment is needed. To demonstrate this technique we have measured spin resolved K-edge absorption spectra of MnO and MnF_2.

The experiment was carried out on the double focusing X25 hybrid wiggler beam line[10] at the National Synchrotron Light Source at the Brookhaven National Laboratory. The double crystal Si(220) monochromator gave an incident beam energy resolution of 0.7 eV. The analyzer, using a Rowland circle spectrometer based on a spherically bent Si(440) crystal, had an energy resolution of 0.3 eV at 6.5 keV.[11] The monochromatic flux at the sample was about 10^{11} photons/s.

A simple picture of the $K\beta$ fluorescence process is presented in Fig. 1. The incident photon ($\hbar\omega_1$) is absorbed, ejecting the spin up (or spin down) $1s$ electron to an unoccupied state. Since the spin is conserved in the fluorescence process, the intermediate $1s$ hole is then filled by a spin up (spin down) $3p$ electron leading to a fluorescence photon ($\hbar\omega_2$). The fluorescence photon energy is determined by the energy difference between the initial $1s^1 3p^6$ and the final $1s^2 3p^5$ states. If the final state energies, i.e., the fluorescence photon energies corresponding to the spin up and the spin down $3p$ holes are different, then with a high-energy resolution spectrometer one can resolve the various components of the $K\beta$ fluorescence radiation due to the different final states. By selectively monitoring one of the fluorescence components one is then able to choose the spin state of the photoelectron. Scanning the incident photon energy through the absorption edge one can then do spin selective near edge spectroscopy and gain information about unoccupied spin density of states.

To demonstrate the concept presented above, MnF_2 and MnO are used as examples. In an atomic picture the

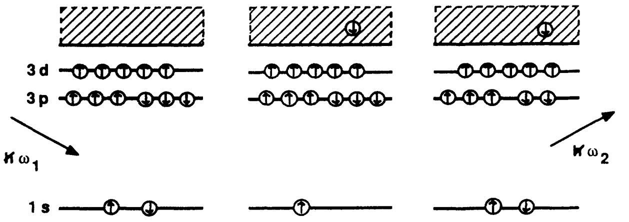

FIG. 1. Simple atomic picture of the MnO $K\beta$ fluorescence process where the photoelectron has minority spin character. The initial, intermediate, and the final states are shown from left to right, respectively.

final state of the Mn $K\beta$ fluorescence process is a single hole state with $1s^2 3p^5 3d^5$ configuration. As a result of the exchange interaction between the $3p$ and $3d$ electrons in the final state, the fluorescence spectrum shows pronounced satellite structure. Although there have been several studies of the Mn $K\beta$ fluorescence[12] spectra, to our knowledge, its spin properties have not been investigated. However, since the final state in the $K\beta$ fluorescence is the same as in the $3p$ photoemission one can expect the spin dependence to be similar to photoemission, which has been studied extensively.[13,14]

Figure 2 shows the $3p$ x-ray photoemission spectrum[15] (XPS) and our high-resolution $K\beta$ fluorescence spectrum from MnF_2. Clearly, both spectra show the same satellite structure: a well separated peak at 17 eV below the main peak and a shoulder at about -3 eV. The main peak of the fluorescence spectrum is somewhat wider than that of XPS because of the the K-shell lifetime broadening of about 1 eV which is not present in the XPS spectrum. The incident photon energy of 145 eV, used for the XPS, is not significantly larger than the Mn $3p$ binding energy of 47 eV and thus the validity of the sudden approximation is questionable; this may explain the different main/satellite peak ratio when compared with the fluorescence spectrum.[14] The origin of the satellite structures in $3s$ and $3p$ photoemission of Mn in solids has been interpreted as atomic multiplets due to the $3p^5 3d^5$ final-state configuration; this has recently been convincingly demonstrated for atomic Mn, MnO, and MnF_2.[14] Based on the spin assignments of the XPS spectra,[16] we have assumed that the main line in the fluorescence spectrum corresponds to $3p$ holes with minority spin (spin down), and the satellite structures to the majority spin (spin up) holes.

Given the spin dependence of the fluorescence spectrum and a high-resolution analyzer to resolve the various spin components in the spectrum as shown in Fig. 2, spin-dependent absorption can then be measured by accepting only one of the spin polarized components of the fluorescence spectrum. Spin polarization of the photoelectron in the absorption process is then achieved by spin conservation in the fluorescence process. Note that minority-majority spin is defined by the spin orientation of the $3d$ electrons, i.e., the direction of the local moment, thus no long-range magnetic order is needed.

To demonstrate that emission is spin resolved and to illustrate this technique we measured the K absorption spectra of two typical antiferromagnets, MnO [$T_N = 120$ K (Ref. 17)] and MnF_2 [$T_N = 75$ K (Ref. 18)] in the paramagnetic state at room temperature. The fine grid powder samples were layered on tape as thin as possible to minimize the self-absorption effects. The typical count rates at the Mn $K\beta$ fluorescence peak were of the order of 1000 cps. Figure 3 shows the comparison, when the incident energy is scanned through the Mn K absorption edge, between the high resolution fluorescence and conventional transmission x-ray absorption near-edge structure (XANES) where the total absorption was measured with an ion chamber. The transmission spectrum includes both spin contributions, while the high-resolution spectrum, recorded by monitoring a 0.3 eV bandwidth at the main fluorescence peak (see Fig. 2), is predominantly of minority spin character. The transmission spectrum is also broadened by the K-shell lifetime (about 1 eV), which in the case of our high-resolution XANES is suppressed.[11]

Figure 4 shows the spin sensitive XANES spectra from MnO and MnF_2. The spectra corresponding to majority and minority spin character XANES are normalized to be the same well above the absorption edge. The preedge peak below the absorption edge corresponds to a transition to unoccupied $3d$ states. For MnF_2, in particular, this prepeak almost totally disappears in the majority

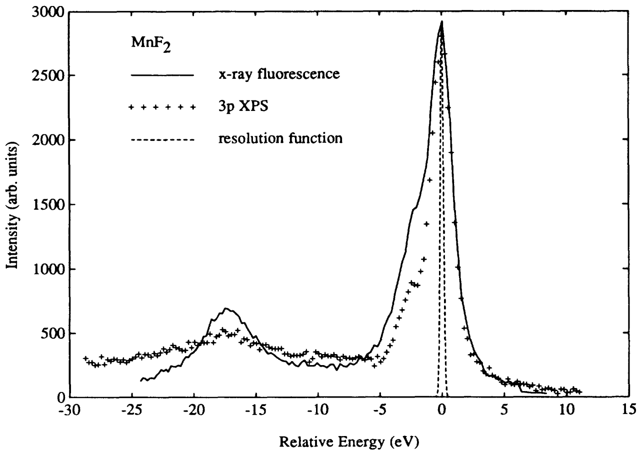

FIG. 2. Comparison between a high-resolution Mn $K\beta$ x-ray fluorescence spectrum and a Mn $3p$ x-ray photoemission spectrum (XPS). Negative relative energies correspond to lower fluorescence energies and higher binding energies for the XPS. The dashed line represents the analyzer resolution.

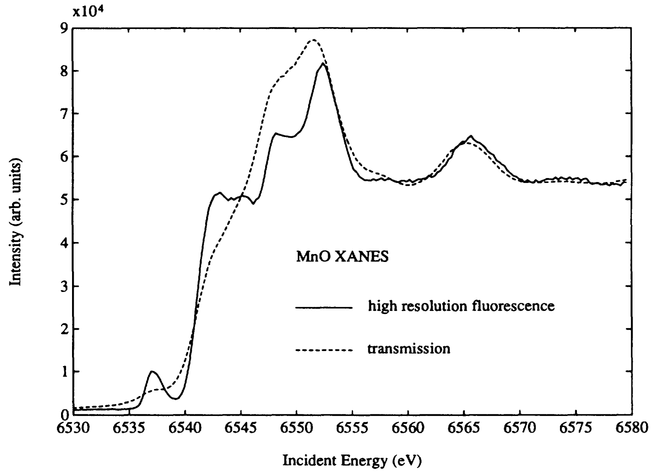

FIG. 3. A conventional transmission XANES spectrum compared with a high-resolution fluorescence XANES spectrum of MnO. The transmission spectrum includes both photoelectron final spin states while the high-resolution spectrum, measured by selectively monitoring only a 0.3 eV bandwidth at the main fluorescence peak in Fig. 2, includes only the minority spin states. The transmission XANES spectrum is additionally broadened by the K-shell lifetime width.

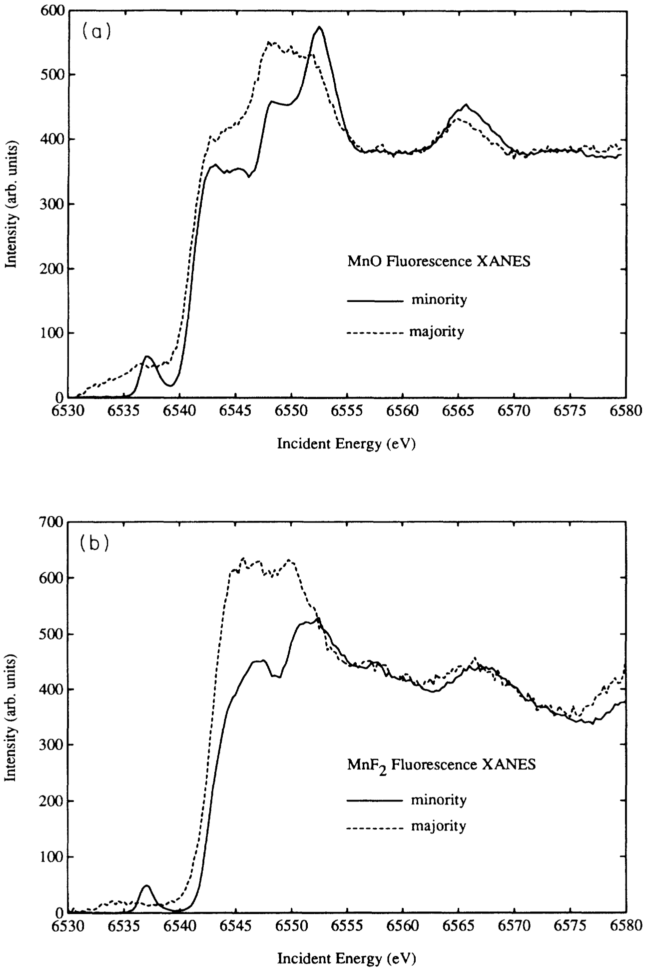

FIG. 4. High-resolution spin-dependent XANES spectra of (a) MnO and (b) MnF$_2$.

spin spectrum. This is understandable based upon the filling of the 3*d* band according to Hund's rule. All five available spin up 3*d* states are already occupied while all five remaining spin down states are empty. This behavior of the preedge 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 emission spectrum, which might explain the nonvanishing majority contribution at the preedge peak region in Fig. 4. It should also be noted that the measurements were carried out at room temperature, which is well above T_N of both compounds, indicating the viability of the technique even in the absence of long-range magnetic order.

Both in the case of MnO and MnF$_2$ the clear difference in the spin-dependent density of states (DOS) extends about 10 eV above the edge. Unfortunately, no theoretical calculations for these systems are available which extend far enough above the edge for a direct comparison. Also, the absorption edges have a slight energy shift between the different spin states (0.4 eV for MnO and 0.7 eV for MnF$_2$). This shift can be understood as an exchange splitting whereby the majority spin states have lower energy than the minority states. This splitting also contributes to the broadening of the conventional XANES spectrum (Fig. 3). If the minority spin spectra of MnO and MnF$_2$ are compared one can notice that the absolute position of the absorption edge is shifted by 1.5 eV while the preedge peak remains at the same position. This reflects the fact that *p* states are more sensitive to the change of chemical environment than the localized *d* states.

In summary, spin-polarized Mn *K*-edge absorption spectra were measured for MnO and MnF$_2$ in the paramagnetic state. This was possible because the method presented here does not require magnetically ordered samples or external magnetic fields but is purely an atomic probe. The spin resolution of this technique is limited only by the degree of spin purity of the emission spectrum. Similar to MCD, where good results have been achieved with a degree of circular polarization of as little as 0.7, with this technique good spin resolution can be obtained without completely resolved spin components in the emission spectrum. The spin sensitivity even in the paramagnetic state opens new possibilities for the study of the spin polarization of the unoccupied density of states with the evolution of magnetic order. Furthermore, the absorption measurement in the extended absorption edge region (EXAFS) should also reflect the spin dependence of the backscattering amplitude[5] and information about the local magnetic environment should be obtainable. Finally, although only measurements on Mn compounds have been carried out, many other magnetically interesting elements, for example, Fe and Ni, have similar fluorescence satellites and should also provide spin selectivity using this high-resolution XANES technique.

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