Extended X-Ray Absorption Fine Structure in Photoelectron Emission

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We report the first definitive measurements of extended x-ray absorption fine structure (EXAFS) made by monitoring the direct photoelectron emission as a function of photon energy. We have measured EXAFS associated with the Mn $3p$ and F $2s$ core levels in evaporated films of MnF_2 and found good agreement with bulk transmission EXAFS associated with the Mn $1s$ level. Photoelectron EXAFS makes possible surface-sensitive structural determinations using vacuum uv radiation on a virtually unlimited range of systems.

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Extended x-ray absorption fine structure (EXAFS) has become an important and widely used probe of short-range order in a variety of bulk solids.[1] By exploiting the short mean free path of electrons in solids it has become possible to apply the technique to surface problems as well. This has been done by monitoring either the total or partial electron yield[2] or the Auger yield[3] as a function of incident photon energy. These applications have been limited by several factors, including the profusion of shallow core levels, which interfere with the measurements, the frequent necessity of using high-energy x rays, and the limited number of elements with suitable core levels. An alternative technique which uses electrons as the excitation medium, extended appearance-potential fine structure,[4] suffers from related problems; however, a promising recent development, Auger-monitored extended fine structure,[5] apparently does not.

We report here the first definitive measurements of extended x-ray absorption fine structure made by monitoring the photoelectrons emitted from core levels as a function of photon energy. We have measured EXAFS from the $3p$ level of Mn and the $2s$ level of F in the compound MnF_2, compared the results to transmission EXAFS of the Mn $1s$ level, and found good agreement. This important development largely removes the previous limitations of surface EXAFS and allows the technique to be applied to virtually any surface system of interest. Almost all elements have suitable core levels in the low–binding-energy region. A major advantage is that photopeaks from adjacent core levels do not cross as the photon energy is varied. Finally, these measurements can be made with vacuum uv radiation, a significant extension of the usable range of photon energies.

It was pointed out previously[6] that the angle-resolved photoemission of crystalline materials is dominated by diffraction effects other than EXAFS. Indeed, these effects are used in the technique of photoelectron diffraction[7] to measure surface structure of single crystals in a manner much like low-energy electron diffraction. It was shown also that by averaging over all directions of emission of the photoelectrons all diffraction effects are eliminated except the backscattering that gives rise to EXAFS.[6] In our method of photoemission EXAFS this averaging is achieved by using polycrystalline samples and making use of the 2π azimuthal angle of acceptance of a cylindrical-mirror analyzer to detect the electrons. Margaritondo and co-workers[8] previously observed EXAFS-like oscillations in photoelectron peaks as a function of photon energy;

however, their data did not extend over a sufficient photon energy range to prove conclusively that EXAFS was involved.

In this Letter we compare the photoelectron EXAFS of MnF_2 to conventional bulk transmission EXAFS measured on the $1s$ level of Mn in the same compound. The latter was carried out at the Stanford Synchrotron Radiation Laboratory in the photon energy range of 6400 to 7500 eV. The photoelectron measurements were performed at the National Synchrotron Light Source at Brookhaven National Laboratory. We used beam line U14A on the vacuum-uv storage ring operating at 750 MeV. This line is equipped with a plane grating monochromator, which we used in the photon energy range of 90 to 280 eV to avoid complications due to absorption in the monochromator at the carbon K edge. At an energy resolution of about 1 eV, the photon flux on the sample at 175 eV, the maximum of the monochromator output, was about 3×10^8 photons/s$\cdot$mA; a typical storage ring current was 50 mA. The photoelectrons were detected with a double-pass cylindrical-mirror analyzer operated in the fixed-retarding-ratio mode, i.e., the ratio of pass energy to electron energy was held constant.[9]

The measurements were made in the constant-initial-state mode in which the photon energy and the electron energy are varied simultaneously so as to measure emission from the same initial state, taken here as the maximum of the photopeak. Because Auger electrons have a fixed kinetic energy they can move through the analyzer window in a constant-initial-state measurement. The likelihood of this occurrence is greatly reduced, however, because to be in the EXAFS region the photoelectrons have kinetic energies greater than about 50 eV, whereas the Auger electrons from these outer core levels will generally have lower energies. In fact, we took a number of energy distribution curves, i.e., electron intensity versus kinetic energy at a fixed photon energy, to verify that no Auger peaks were passing through the photopeak. Photoemission from deep core levels would generate more Auger transitions. In many cases these Auger electrons would have energies too low or too high to affect photoemission EXAFS and these deep core levels could also be used.

It is important to monitor the incident photon flux accurately to eliminate time- and energy-dependent variations due to the monochromator, beam movements, etc. We used a channel electron multiplier to measure the total electron yield of an 80%-transmission stainless-steel grid.[10] This was coated with evaporated LiF, chosen as it has no absorption edges in the energy region of interest. Both the incident flux I_0 and the photoelectron yield I were measured under computer control as the monochromator was scanned from 90 to 280 eV in 1-eV steps; the ratio I/I_0 is taken for the EXAFS analysis. For these measurements we used photopeaks which are two to three times as large as the inelastic electron background; several 10-min scans for each peak then sufficed to obtain good statistics.

The MnF_2 samples were prepared by evaporation onto Al substrates in a separate preparation chamber, which had a base pressure of 10^{-10} Torr; during evaporation the pressure rose to as much as 5×10^{-9} Torr. They were subsequently transferred under vacuum into the measurement chamber. These films were polycrystalline, contributing to the angular averaging, and thin enough that charging was not a problem. They were decomposed rapidly by a 1-keV electron beam, but remarkably stable in the lower-energy photon beam, and remained uncontaminated for several days in the 1×10^{-10} Torr vacuum. All data were taken at room temperature.

Our primary results are presented in Fig. 1. The left-hand three panels in this figure show the EXAFS function[1] $\chi(k)$ weighted by k^3 for three different edges. Here $\chi(k)$ is the oscillating fraction of the photoabsorption caused by the interference between the outgoing photoelectron wave and that portion backscattered from nearby atoms, and k is the outgoing electron wave vector defined by

$$k=[(2m/\hbar^2)(E-E_0)]^{1/2},$$

where E is the incident photon energy and E_0 is a parameter approximately equal to the binding energy of the core level (see discussion below). Figure 1(a) is the result of a transmission EXAFS measurement on the Mn $1s$ level, for which the binding energy is 6537 eV. Figure 1(b) is the photoelectron EXAFS measurement of the ${}^7P$ component of the Mn $3p$ core-level multiplet with a binding energy of 48 eV relative to the valence-band edge, and Fig. 1(c) is the corresponding result for the F $2s$ level, which has a binding energy of only 28 eV relative to the valence-band edge. Note that because the F $1s$ level is at 686 eV, well below the kiloelectronvolt range accessible to x-ray experiments, it is impossible to do conventional EXAFS on both components of MnF_2. On the other hand, both, like almost all atomic species, have core levels in the vacuum. For all three sets of data $\chi(k)$ was obtained by subtracting fitted splines to approximate the background. For the transmission case the pre-edge absorption was removed first. The background in the photoemission case is a more complex function of

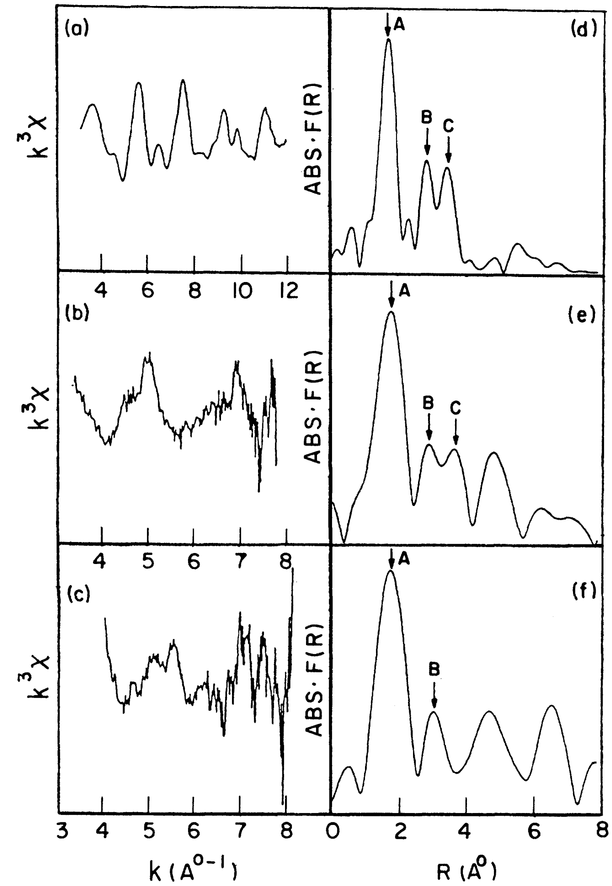

FIG. 1. EXAFS function $k^3\chi(k)$ vs electron wave vector k(Å^{-1}) and absolute value of Fourier transform $F(R)$ vs R(Å). (a),(d), Mn 1*s*. (b),(e), Mn 3*p*. (e),(f), F 2*s*.

energy and the range in k shorter in these preliminary data. We fitted three cubic splines to the full photoemission data range. Other choices of background do not seem to describe it as well. For photoemission no attempt was made to obtain the absolute amplitude of χ, although this is a refinement that we are pursuing.

The right-hand three panels of Fig. 1 show the corresponding magnitudes of the Fourier transform $F(R)$ of $k^3\chi(k)$, where R represents the distance from the absorbing atom. Consider first Figs. 1(d) and 1(e), which depict $F(R)$ for the Mn 1*s* transmission and 3*p* photoelectron results, respectively. All major features are the same. In particular, the first three prominent peaks, labeled *A, B,* and *C,* occur at 1.70, 2.82, and 3.41 Å and 1.72, 2.91, and 3.65 Å, respectively. The 3*p* peaks are about twice as wide because the data range in k is half as large. As no calculated phase shifts are available yet for 3*p* levels, we have performed preliminary analysis of these data using tabulated amplitude and phase functions of Teo and Lee[11] for 1*s* and 2*p* core levels, and optimized by using the procedure of Lee and Beni[12] on the first peak, varying E_0. This procedure produces peaks at 2.11, 3.19, and 3.85 Å for the 1*s* data, and 2.09, 3.38, and 3.80 Å for the 3*p* data. E_0 is shifted only a few volts. In MnF_2, which has the rutile structure,[13] the shortest Mn-F interatomic distances are 2.10, 2.13, 3.52, and 3.92 Å, and the shortest Mn-Mn distances are 3.31 and 3.82 Å. Thus each of the observed peaks in the transform arises from two closely spaced atomic shells. Particularly in view of the absence of suitable phase-shift calculations, the agreement both between the two measurements and with the known spacings is highly satisfactory.

Finally, we show in Fig. 1(f) the transform $F(R)$ for the F 2*s* EXAFS. Peaks are located at 1.76 and 3.00 Å, and go to 2.13 and 3.36 Å with use of the Teo-Lee calculated phase shifts for F 1*s* absorbers. The third peak is essentially absent. For an Mn absorber the third peak is due to eight Mn atoms at 3.82 Å and four F atoms at 3.92 Å, while for an F absorber only four Mn atoms at 3.92 Å contribute. The third peak will therefore be substantially smaller in the latter case.

On a speculative note, we wish to point out the presence in both the 3*p* and 2*s* photoelectron results of a prominent peak in the transform at 4.6 Å, or 5 Å including phase shifts. A similar peak, at the noise level, appears in the 1*s* transmission results, and its amplitude increases in data taken at 85 K. As it happens, both Mn and F are surrounded by shells of atoms at about this distance, 4.87 Å. We are studying further the apparent prominence of such distant shells in the photoelectron EXAFS.

In conclusion, these results demonstrate that, at least for polycrystalline samples, extended fine structure can be measured with photoelectron emission. This makes possible many interesting studies which would not otherwise be feasible.[14] As all photoelectron peaks are fixed relative to each other, they can never interfere by crossing, even when close in binding energy. Every element except hydrogen and helium has core levels in the vacuum, facilitating studies of virtually any interesting surface-absorbate system.

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