Experimental Study of Multiple Scattering in X-Ray-Absorption Near-Edge Structure

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An experimental study of the magnitude of multiple scattering of the photoelectron in the x-ray-absorption near-edge structure is presented. Two types of multiple-scattering events are distinguished: type 1, in which the scattering atoms are approximately collinear with the center atom; and type 2, in which the various scattering atoms are far from collinear. Type 1, which is known to be important in the extended x-ray-absorption fine-structure range, has a similar importance in the x-ray-absorption near-edge structure range, while type 2 is important above the edge only when the bond distances are less than ~ 1.6 Å.

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Interest in using x-ray-absorption near-edge structure (XANES) determination has recently been stimulated by advances in calculating XANES spectra.[1-3] Over the last decade, the extended x-ray-absorption fine structure (EXAFS), which starts beyond the XANES, has provided information about the local structure of materials. The information that EXAFS can provide is limited when the coordination shells that surround the photoabsorbing atom are disordered or comprise atoms of low atomic number, because the fine structure decays rapidly past the edge; most of the information resides close to the edge, in the region that is currently designated the XANES region. We show in this experimental study on $KMnO_4$ and $K_3Mn(CN)_6$ that, in essence, the EXAFS region actually extends down through most of the XANES range.

XANES and EXAFS were originally distinguished[4] because the single scattering (SS), which is dominant in the EXAFS region, was thought to be inadequate in the XANES region. XANES has been thought to require multiple scattering (MS) corrections, and the recently developed techniques[1-3] for calculating XANES spectra explicitly account for all MS processes.

Recently, Muller and Schaich[5] have challenged the idea that MS dominates the XANES. They have shown that an SS XANES calculation for Cu metal that includes the spherical nature of the photoelectron wave agrees well with a band-structure calculation, which includes MS to all orders. Their SS theory is like EXAFS theory, but it does not make the plane-wave and short-wavelength approximations. On the other hand, Norman *et al.*[6] claim that SS theory is incapable of explaining the oxygen *K*-edge XANES spectra of NiO.

This controversy is of practical as well as fundamental interest. If SS dominates the XANES, then XANES provides the same sort of information as EXAFS. Conversely, if MS dominates the XANES, it may be possible to extract bond-angle information that is not accessible from the EXAFS region.[7,8]

We wish to distinguish two types of MS processes. The first, which we call type-1 MS, occurs when an intervening atom lies approximately collinearly with the central atom and a backscattering atom. The intervening atom focuses the photoelectron onto the backscattering atom and enhances scattering from it. Type-1 MS is the only MS effect that is important in the EXAFS region.

Type-2 MS comprises all MS processes that are not of type 1. For example, successive scattering from two atoms in the first coordination shell is of type 2, since any two first-shell atoms must be far from collinear with the central atom. Type-2 MS is negligible in the EXAFS region because large-angle scattering is weak there. Only type-2 MS has new bond-angle information, and it will be possible to extract this information only if the magnitude of type-2 MS is substantial.

$KMnO_4$ was obtained from a commercial supplier at > 99.5% purity; its x-ray powder pattern was measured and checked against a standard powder-pattern reference file. The sample was ground, sieved to 325 mesh, and brushed onto Scotch tape. About six layers of tape constituted the sample. Each layer appeared homogeneous and had an edge step $\Delta\mu x < 0.1$, so that thickness effects and particle size effects should be negligible.[9,10]

The measurements were performed at the Stanford Synchrotron Radiation Laboratory (SSRL) under dedicated running conditions. An Si(220) double crystal monochromator was used; the harmonic intensity was monitored and made negligible by detuning the monochromator. The sample was measured at 80, ~ 140, and 300 K. The energy resolution was < 1 eV, and the point density was 0.2 eV in the XANES region.

Figure 1(a) shows the XANES spectra for $KMnO_4$ at 80 and 300 K. The spectra are characterized by a large peak about 15 eV below the edge step and by a temperature-dependent fine structure at higher energies. The pre-edge peak has long been noted,[11] but the temperature-dependent structure is new. As in EXAFS analysis, we convert from E to k using $\hbar^2k^2/2m = E - E_0$, with $E_0 = 6552$ eV, and we subtract a smooth background in the region beyond the arrow in Fig. 1(a). The Fourier transform of the oscillatory structure over the range $k = 1.4$–11.8 Å^{-1} weighted with $k^5 \exp(-0.04k^2)$ window function is shown in Fig. 1(b).

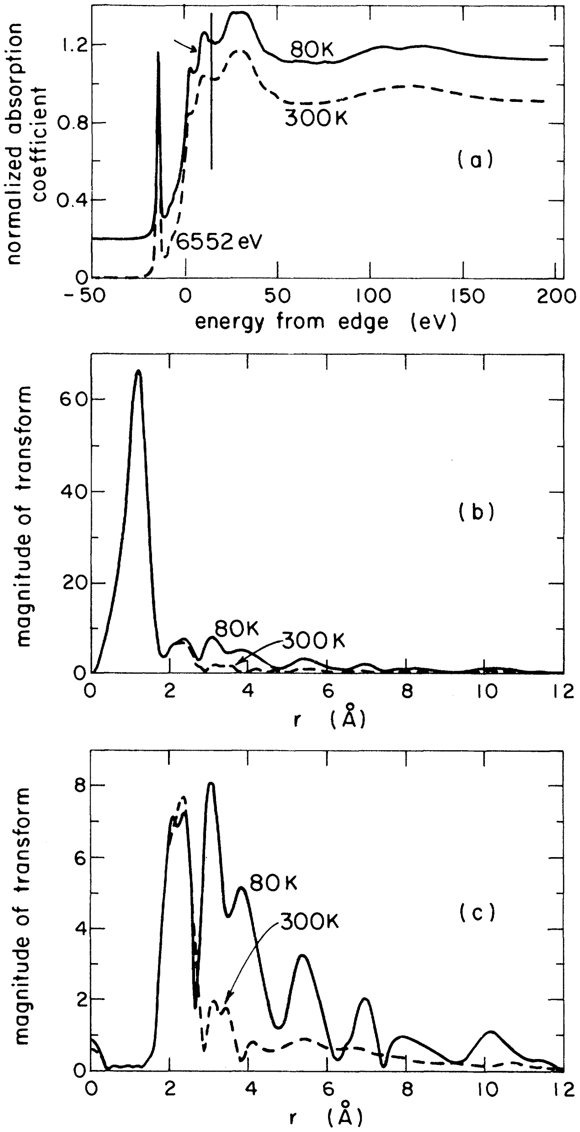

FIG. 1. (a) Absorption spectra of $KMnO_4$ near the K edge of Mn, measured at 80 and 300 K. The energy scale is relative to the K edge defined at 6552 eV. The arrow denotes the start of the Fourier transform range. The MS 2 effect is large to the left of the line. (b) Magnitude of the Fourier transform of $KMnO_4$ at 80 and 300 K, weighted with $k^5 \exp(-0.04k^2)$. (c) Magnitude of the Fourier transform of $KMnO_4$ at 80 and 300 K with the first shell removed. The noise level is ~ 0.5 unit.

The Fourier-transform peaks below ~ 2.7 Å are nearly independent of temperature, while the rest depend strongly on temperature. The former have their origin in the rigid tetrahedron of oxygen atoms that surround the Mn at a distance[12] of 1.63 Å; the latter are from the weakly bound atoms outside this central MnO_4^- ion. The largest peak in Fig. 1(b) is due to SS from the nearest-neighbor oxygens, as in EXAFS. The small peak immediately beyond it can only be explained as a type-2 MS effect. The lack of temperature dependence indicates that it originates from the rigid MnO_4^- ion; furthermore, the peak position does not correspond to any SS distance in the crystal which would be found beyond ~ 3.0 Å. It is not a sidelobe of the the first-shell peak, because its relative size is independent of the k-space window space; furthermore, it persists when the filtered first-shell signal is subtracted before transforming, as shown in Fig. 1(c).

Only one resolved temperature-independent MS peak is observed. This implies that the MS perturbation expansion[13] converges rapidly, because higher-order terms give peaks at larger distances in the Fourier transform. These, if present, are evidently small compared with the first term.

The position of the MS peak can be understood as a combination of the MS paths shown in Fig. 2(a), which have total path lengths (divided by 2) of 2.96 and 3.26 Å, respectively. Accounting for the expected phase shifts, these would peak around 2.4 Å, in agreement with experiment [Figs. 1(b) and 1(c)]. The next MS peaks would occur at ~ 2.7 Å and beyond.

We next determine the amplitude of the MS peak as a function of energy by inverse transforming the isolated peak from r space back to k space and then converting k back to E. The first-shell SS peak is then treated the same way, and the logarithm of their ratio is plotted versus energy in Fig. 2(b). The MS amplitude 13 eV beyond the edge is less than e^{-1} of the SS amplitude. In the conventional EXAFS region the MS amplitude is about e^{-2} of the SS amplitude. MS only becomes important within ~ 13 eV of the edge.

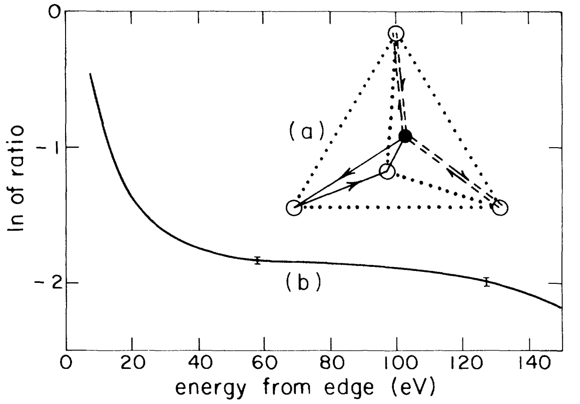

FIG. 2. (a) The two multiple-scattering paths that contribute to the second peak in the Fourier transform of $KMnO_4$, denoted by solid and dashed lines. The black dot is Mn, and the open dots are O atoms. (b) The logarithm of the ratio of the k dependence of the amplitudes of the first (SS) peak to the second (MS) peak of Fig. 1(b), plotted vs energy from the edge.

Over the range of analysis, which extends down to the arrow in Fig. 1(a), the SS signal is stronger than the MS signal. We cannot extend the analysis range to lower energy because it is not clear how the background should be subtracted. However, the large size of the peak below the edge indicates the presence of strong MS. This peak corresponds to transitions to an unfilled orbital of mainly Mn $3d$ symmetry, into which p character has been mixed. This mixing, which allows a dipole transition, can occur only if the Mn environment lacks inversion symmetry, which is the case for tetrahedral coordination. Such p-d mixing is a multiple-scattering effect. In SS theory, only the radial distance matters, and site symmetry has no effect.[14] Therefore, the large peak indicates strong MS effects, and it seems reasonable to assume that MS is strong everywhere to the left of the line drawn in Fig. 1(a).

The MS effect just described is type 2, as Fig. 2(a) confirms. We can investigate type-1 MS (the focusing effect) by studying the spectrum of $K_3Mn(CN)_6$. The sample was prepared and measured in the same way as the $KMnO_4$ sample. In $K_3Mn(CN)_6$ the Mn is octahedrally surrounded by six linear CN molecules. The first-shell carbon atoms are collinear with the Mn and the second-shell N, and so the latter are subject to type-2 MS enhancement. This effect is well established, and its energy dependence has been studied in the EXAFS region.[15,16] This analysis can be easily extended to the XANES region using the routine Fourier filtering methods as for $KMnO_4$.

After correction for the $1/r^2$ geometrical factor, we find that the type-1 MS enhanced the N scattering amplitude by the constant factor of 2.2 over the whole range. Therefore, type-1 MS is substantial at low as well as at high energies.

We have experimentally shown the importance of the two types of MS. Type 1 (the focusing effect) is important in both the XANES and the EXAFS region, whereas type 2 (large-angle MS) is only important within a few electronvolts of the edge in $KMnO_4$. The relation of the $KMnO_4$ results to other cases will now be considered. Theory[13] indicates that the nth-order scattering contribution scales as $a^{-(n+1)}$, where a is the length scale of the cluster of atoms. In the MnO_4^- ion, the bond length is unusually short for a metal at 1.63 Å, which enhances high-order MS contributions relative to SS contributions. If the bond length were the more common value of ~ 2.0 Å, the MS contribution would be even smaller relative to SS than is observed. Furthermore, tetrahedral coordination enhances the type-2 MS relative to octahedral coordination because of the presence of the factor $\cos\beta$ in powdered samples, where β is the angle between the first and last scattering paths.[17] In octahedral coordination $\cos\beta = 0$ for most of the MS paths. For all of the remaining paths $\beta = 0$ or π and there is a tendency for cancellation since $\cos 0 = -\cos\pi$. This tendency persists in any environment with inversion symmetry. We therefore expect that type-2 MS is generally important only within a few electronvolts of the edge for bond lengths greater than ~ 1.6 Å. On the other hand, when the bond length is less than 1.6 Å and there is no center of inversion symmetry, multiple scattering will become more important than in the $KMnO_4$ case. Such examples have been investigated by Stöhr *et al.*[18] recently where they found large multiple-scattering effects in the near-edge structure.

What remains to be explained are the calculations[6] that showed the existence of strong MS effects 30 (or more) eV above the oxygen K edge in NiO, where the NiO bond length is greater than 1.6 Å. NiO is of the NaCl structure, in which many atoms are collinear and type-1 MS can be substantial. The closest collinear atoms are oxygens, shadowed by Ni atoms. Since type-1 MS is strong from the edge through the EXAFS region, it can explain the calculated results.[6] In this case the type-1 enhancment should be particularly strong, because the oxygen backscattering amplitude is much larger than that of the nearest-neighbor Ni atoms over the range of calculation.

In conclusion, type-2 MS is important past the edge only for atoms surrounded by bond lengths less than 1.6 Å and lacking inversion symmetry. This limits the usefulness of XANES as a supplement to EXAFS. The type-1 MS (focusing) effect is large throughout the whole absorption fine-structure range suggesting that it is possible to approximate the absorption spectrum when type-2 MS is small by a relatively simple single-scattering calculation of the Müller and Schiach type[5] modified by the addition of the type-1 MS (focusing) effect. The general MS contribution could be a mixture of type-1 and type-2 MS, but XANES and EXAFS are physically distinct only when type-2 MS is large.

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