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Multiple scattering in the x-ray-absorption near-edge structure of tetrahedral Ge gases

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X-ray-absorption fine-structure (XAFS) measurements of $GeCl_4$, GeH_3Cl, and GeH_4 were made. We experimentally isolate the single- and multiple-scattering terms in the XAFS of $GeCl_4$ by comparison of the spectra of the three compounds. The multiple-scattering (MS) amplitude is comparable to the single-scattering (SS) amplitude only within 15 eV of the edge. Beyond 40 eV the MS to SS amplitude ratio is less than 0.06. Calculations are in qualitative agreement with experiment. Our results suggest that XAFS data in the range $1 < k < 3$ Å^{-1} can be analyzed in a SS picture in many cases.

INTRODUCTION AND BACKGROUND

Extended x-ray-absorption fine structure (EXAFS) (Ref. 1) yields information on distances to atoms in the first few coordination shells. Because EXAFS primarily involves only single scattering (SS) of the photoelectron, it provides little information about bond angles. An exception is the case of small-angle ("type-1") multiple scattering, which is strong at all energies, and can provide some limited information about bond angles. In this paper we are concerned with large-angle ($>30°$, "type-2") multiple scattering. In contrast to EXAFS, the x-ray-absorption near-edge structure (XANES), which is a result of both SS and multiple scattering (MS), does contain some information on three-dimensional structure, even for noncrystalline materials. The extent to which XANES provides information inaccessible by EXAFS depends critically on the size of the MS and the range in energy over which it extends. To date, the few experiments[2,3] that have been performed to answer this question have resulted in very different interpretations. At one extreme there are claims that complete three-body correlation functions are obtainable from the XANES;[3] the opposite extreme position is that the XANES is a simple linear sum of contributions from each backscatterer separately, i.e., that MS is totally negligible. If the latter point of view were correct, then XANES and EXAFS would contain essentially the same information, and could be analyzed in the same way. The point of the present paper is to *experimentally* determine where the reality lies between these two extremes.

A previous study[2] of MS in XANES was able to experimentally distinguish the MS contribution from the SS in the Mn *K*-edge spectrum of the MnO_4^- ion in $KMnO_4$, and showed that the type-2 MS among the first-neighbor oxygen atoms decays rapidly with energy above the edge.[4,5] Specifically, the ratio of the MS amplitude to the SS amplitude dropped to approximately 15% beyond about 40 eV above the edge. Another[3] recent experimental and theoretical study along similar lines reached very different conclusions. Here, large-angle MS was found to be important as high as 160 eV above the edge, well into the EXAFS region. These conclusions are based on the experimental observation that the spectra of MnO_4^- and Mn^{2+} ions in aqueous solution, when appropriately rescaled,[6] superimpose only for energies above ≈ 160 eV. However, other possible explanations were not ruled out, such as: the possible existence of a disordered second shell around the ions in water, differences between backscattering amplitudes or central atom absorption at low k for the two chemically very dissimilar systems (Mn^{7+} versus Mn^{2+} formal charge state), and breakdown of $1/r^2$ scaling because of spherical wave effects (1.63 Å versus 2.17-Å bond length).

Because of the uncertainties inherent in the previous studies, and the very different conclusions that were reached, we have attempted to clarify the problem by studying the Ge *K*-edge x-ray absorption spectra of the tetrahedrally coordinated Ge gases $GeCl_4$, GeH_3Cl, and GeH_4. These compounds permit one to isolate the MS signal and compare its magnitude with SS as a function of energy. The use of molecular gases eliminates interference from the SS of atoms beyond the nearest neighbors, and the gases are chemically and structurally similar, minimizing problems of "nontransferability" of scattering amplitudes. Since wide-angle scattering of the photoelectron from hydrogen can be neglected, the $GeCl_4$ spectrum contains contributions from both MS and SS, while the GeH_3Cl spectrum arises from SS alone, and the GeH_4 spectrum is that of an isolated Ge atom $\mu_0(E)$. Although, as we shall see below, SS from hydrogen *cannot* be totally neglected, the SS and MS from Cl can be readily separated. The structures of the gases are known[7–9] and there exists extensive theoretical and experimental literature on $GeCl_4$.[10–13]

In this paper we show that large-angle multiple scattering decreases rapidly with energy above the edge in $GeCl_4$: the MS to SS amplitude ratio decreases to less than 6% beyond 40 eV above the initial onset of the edge. In the vicinity of the "white line" (i.e., the peak at the top of the edge) MS is found to be comparable to SS. Theoretical simulations yield qualitatively similar spectra, but overestimate the size and range in energy of the MS. Our conclusions support the use of low-k data ($1 < k < 3$ Å^{-1}) for EXAFS analysis of the first shell in all cases, and often for higher shells, as long as good standard compounds are used. Finally, we find some experimental and theoretical evidence for scattering from hydrogen at low energies.

EXPERIMENTAL METHODS

The samples were prepared as follows. Samples were handled in a vacuum system composed of only glass and Teflon valves. Sample cells were glass with 3-mil (1 mil $\equiv 10^{-3}$ in) polyimide (Kapton) windows. The $GeCl_4$ and GeH_4 were high-purity gases obtained from commercial suppliers. The $GeClH_3$ sample was synthesized from GeH_4 and $SnCl_4$, and fractionated[14] to obtain pure $GeClH_3$. Infrared (ir) absorption spectra from 4000 to 400 cm^{-1} were taken on all samples less than 24 h before and after the EXAFS measurements were made and compared with published data, in order to ensure sample purity. We also compared the Cl EXAFS amplitude of $GeClH_3$ to that of $GeCl_4$. The Cl coordination numbers of these two compounds should be in a 4:1 ratio; the actual ratio is 3.9±0.10. From these checks we are certain of our sample integrity.

EXAFS measurements were conducted in transmission mode on the National Biostructures Participating Research Team (PRT) beamline X9A at National Synchrotron Light Source (NSLS). The experimental setup was standard: ionization chamber detectors and a double crystal Si(111) monochromator were used. Harmonics were eliminated by detuning the monochromator. The experimental energy resolution was estimated to be about 3.5 eV by comparison with previously published high-resolution spectra.[15] Compared with earlier work, we find that the white line in our $GeCl_4$ spectra is reduced in magnitude about 20%. As discussed below, this will lead to about a 20% underestimate of the MS contribution within ≈ 15 eV of the edge. However, farther above the edge, the experimental resolution should have little effect on the amplitude of the MS signal.

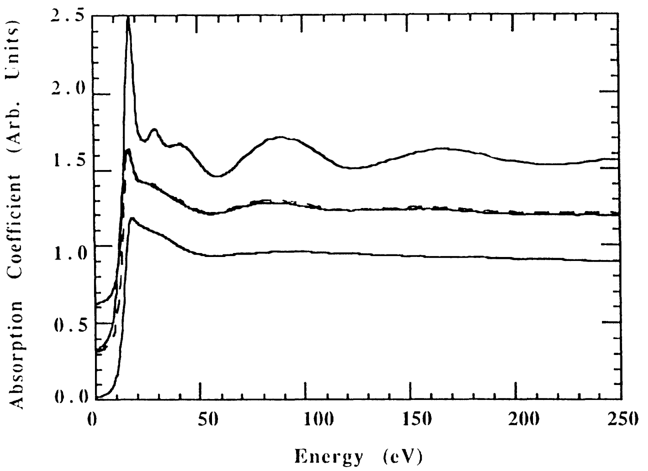

FIG. 1. Measured x-ray absorption spectra of, from top to bottom, $GeCl_4$, GeH_3Cl, and GeH_4. Data have been normalized and have had a linear pre-edge background removed. The dashed curve is an approximation of GeH_3Cl made by a linear superposition of $GeCl_4$ and GeH_4 as described in the text. Deviation between the solid and dashed lines for GeH_3Cl is due to multiple scattering.

EXPERIMENTAL RESULTS

The normalized spectra, with a linear pre-edge background subtracted, are shown in Fig. 1. The $GeCl_4$ and GeH_4 spectra are consistent with those previously published[13,15] provided the experimental energy resolution is taken into account. The oscillations well above the edge in the $GeCl_4$ and GeH_3Cl spectra are a consequence of SS (EXAFS) from the chlorine atoms; the amplitudes are in a 4:1 ratio as expected, and the small difference in frequency corresponds to the slightly different bond lengths (2.11 Å in $GeCl_4$ and 2.15 Å in GeH_3Cl). Furthermore, the size of the white line at the top of the edge increases with the number of chlorine atoms, suggesting that it is largely due to an EXAFS-like single scattering. $GeCl_4$ exhibits a series of rapid oscillations just past the white line which the other gases do not.

In GeH_4 and GeH_3Cl low-frequency oscillations that correspond to an effective distance of ≈ 1.5Å are observed at low k. We attribute this signal to EXAFS-like single scattering from hydrogen atoms, although it may be due to scattering from the central atom potential itself,[16] or a combination (e.g., a polarization effect). The amplitudes of the low-frequency oscillations scales with the number of hydrogens, so we believe that the effect is due to scattering from H atoms.

If MS were negligible, the spectrum of GeH_3Cl would simply be a linear superposition of the normalized spectra of GeH_4 and $GeCl_4$, as long as the slight differences in bond lengths r and disorder parameters σ^2 were accounted for. Figure 1 shows that superposition (and therefore the single-scattering approximation) works very well, but it is not perfect. The rapidly oscillating residual immediately above the white line is the MS contribution, which is given (per 4 Cl) by

$$[\mathrm{GeCl_4}]+3[\mathrm{GeH_4}]-4[\mathrm{GeH_3Cl}] \ .$$

The MS contribution is plotted in Fig. 2 along with the $GeCl_4$ spectrum.

Fourier transformation of the MS signal gives rise to a peak at ≈ 3.5 Å, which, when phase shifts are accounted for, corresponds well with that expected (3.8 Å) for the

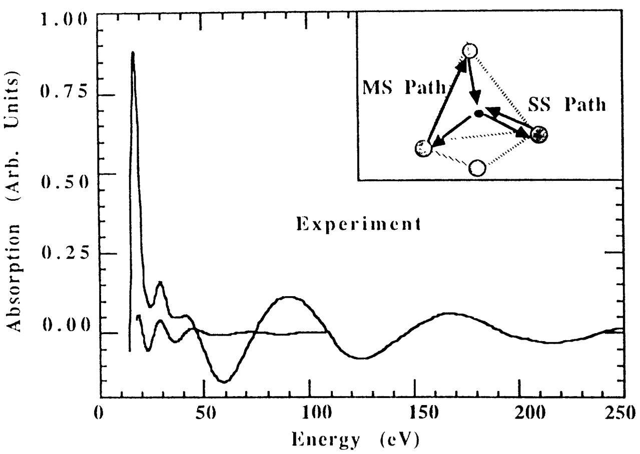

FIG. 2. The measured, normalized x-ray absorption of $GeCl_4$ and the multiple-scattering contribution to the x-ray absorption isolated by subtracting the single-scattering terms determined experimentally from GeH_3Cl and GeH_4. The MS contribution is given (per 4 Cl) by: $[GeCl_4]+3[GeH_4]-4[GeH_3Cl]$. Inset shows the single- and multiple-scattering paths in the $GeCl_4$ molecule.

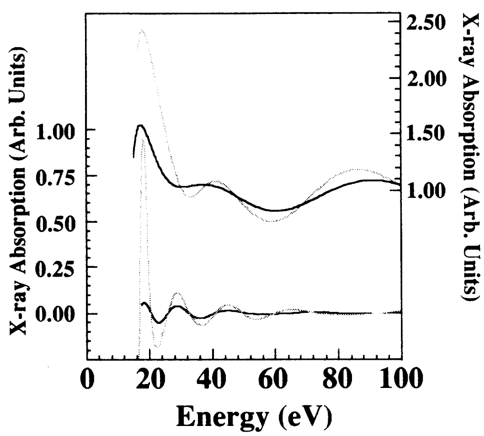

FIG. 3. Theoretical calculations of the x-ray absorption of $GeCl_4$ compared with experiment. The top plot is the calculated single scattering (dotted line) vs the experimental single scattering (solid line). The lower plot is the calculated (dotted line) and experimental (solid line) multiple scattering, determined by taking the difference between the full scattering and the single scattering.

shortest 7.6-Å "triangle" scattering path (Fig 2) among the Cl atoms. The close agreement with the frequency expected for the shortest MS path is good evidence that the residual term is due to MS and is not due to multielectron excitation or other effects. The MS to SS amplitude ratio decreases to less than 6% at 40 eV above the initial onset of the edge.

Our experimental energy resolution tends to decrease the MS to SS amplitude ratio near the white line. From simulations, comparison with data of better energy resolution, and our theoretical calculations, we estimate that the MS to SS ratio is reduced by $\approx 20-30\%$ near the white line in our data, but that data at 15 eV and above are essentially unaffected. In our theoretical calculations, which neglect the core hole broadening, the MS and SS are of approximately equal amplitude at the white line. Comparison with previously published high-resolution spectra[13,15] support our finding that the MS to SS ratio decays rapidly past the edge, and is less than 6% beyond 40 eV above the edge.

THEORETICAL SIMULATIONS

In this experimental system we can measure the total XAFS and separate the single- and multiple-scattering terms. We can compare these quantities with theoretical calculations of the full, single, and multiple scattering to obtain a good idea of the current state of theoretical calculations compared to experiment.

The muffin-tin scattering potential was constructed from truncated self-consistent atomic potentials. Atomic potentials were constructed for neutral Ge and Cl using charge densities generated for each atom by Herman-Skillman self-consistent field, Hartree-Fock-Slater calculations.[17] The atomic potentials were truncated for superposition at approximately half the bond distance of Ge—Cl for $GeCl_4$;[7] in this case, 2.5 bohr for Ge and 2.1 bohr for Cl. The XANES programs of Durham *et al.*[18] were used for the calculation of μ_0, partial wave scattering phase shifts up to angular momentum $l=4$, and the full multiple-scattering spectra. Single-scattering spectra were calculated using the formalism of Müller and Schaich.[19]

The potential construction outlined above was chosen, since it is the best in reproducing the edge features and the amplitude minimum of the oscillations, approximately 25 eV beyond the white line peak in the data. The calculation overstates the amplitude of the edge somewhat but does well in reproducing most of the other features observed in the data. The calculations indicate that multiple scattering in $GeCl_4$ damps out quickly beyond the edge and is negligible 50 eV beyond the edge maximum (lower plot in Fig. 3). The calculated MS amplitude is only comparable with the single-scattering amplitude within 40 eV of the edge maximum and is nowhere greater than 15% of the SS amplitude beyond 40 eV of the edge maximum. The calculation generally overestimates the amplitude and extent of the MS compared with experiment (Fig. 3, lower plot).

SUMMARY AND CONCLUSIONS

In a simple and direct way, we have *experimentally* isolated the multiple scattering from the single-scattering contributions to the Ge *K*-edge XANES spectra of gaseous $GeCl_4$. We find that the ratio of the experimental multiple-scattering amplitude to the single-scattering amplitude drops to less than 6% beyond 3 Ry ($\approx$40 eV) above the midpoint of the edge. Theoretical simulations tend to overestimate the importance of multiple scattering relative to the single scattering. Our results clearly show that, within ≈ 15 eV above the edge, XAFS is *not* a simple linear sum of contributions from the backscatterers. However, the MS is nowhere dominant over SS, and the MS terms die out very quickly above the edge. These conclusions are consistent with that observed[2] for MnO_4^-, and are in marked contrast with the claims of Benfatto *et al.*[3] that significant MS extends up to 160 eV above the edge.

We also find evidence for EXAFS-like single scattering from hydrogen at low energy, since the spectra of GeH_3Cl cannot be adaquately modeled without the inclusion of H scattering from GeH_4. This conclusion is also supported by our theoretical calculations.

Because of the path lengths involved, multiple scattering can always be neglected for EXAFS studies of the first shell.[20] MS must be considered in analysis of higher shells, but when $k > 3$ Å^{-1}, our results suggest it probably can be neglected in many systems. In the range $1 < k < 3$ Å^{-1}, if the MS is neglected, bounds on the amplitude and phase errors that are introduced can be estimated[21] from the MS to SS amplitude ratio.

Our conclusions are very similar to those of Pendry.[22] The limited MS information that is present in experimental spectra places severe restrictions on the ability to directly determine three-body correlation functions from x-ray absorption spectra. Practical analysis of the XANES spectra is limited by the size of the MS relative to the noise in the data, and, more importantly, by the small size of the MS (beyond $k \sim 3$ Å^{-1}) relative to that of the unknown single-scattering terms from more distant shells of atoms. Theorectical simulations are not yet quantitatively accurate and are no substitute for experiment, but if used with caution they are useful for gaining qualitative insight into the XANES, and for helping to distinguish between a small number of hypothetical structural models.

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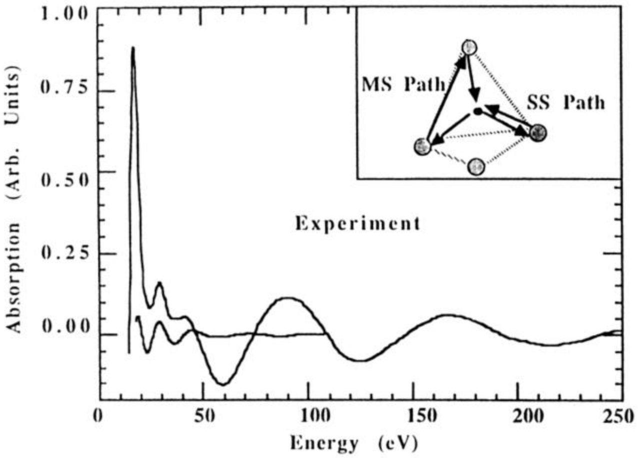

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