

Background subtraction for fluorescence EXAFS data of a very dilute dopant Z in $Z + 1$ host

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When conducting EXAFS at the Cu K -edge for ZnS:Cu with very low Cu concentration ($<0.04\%$ Cu), a large background was present that increased with energy. This background arises from a Zn X-ray Raman peak, which moves through the Cu fluorescence window, plus the tail of the Zn fluorescence peak. This large background distorts the EXAFS and must be removed separately before reducing the data. A simple means to remove this background is described.

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1. Introduction

A common technique for investigating the local structure about dilute atomic species is to use fluorescence extended X-ray absorption fine structure (EXAFS). Typically, the fluorescence mode becomes better than the transmission mode for concentrations of a few percent (depending on the host material) and, in some cases, data for concentrations below 0.01% are possible. However, when studying impurity atoms with atomic number Z in a host of atoms with atomic number $Z + 1$, a large background in the fluorescence signal may be observed if the impurity concentration is very low.

For such systems the normally weak X-ray Raman emission line from the $Z + 1$ host atoms, which occurs at a fixed energy below the incident X-ray energy, can add a significant background signal near the fluorescence energy of the Z dopant. The Raman emission peak shifts to higher energy and becomes larger in intensity as the X-ray energy is scanned. Consequently, for solid-state fluorescent detectors with a resolution of 200–400 eV, the $Z + 1$ Raman peak will partially overlap the window set up for collecting the fluorescence for the dilute Z atom; the resulting background in the fluorescence signal is not oscillatory, but produces a large upward slope of the data as the energy is scanned.

2. Discussion

As an example, we consider a recent study of 0.02% Cu ($Z = 29$) in a ZnS host ($Z = 30$ for Zn). For this very low Cu concentration the fluorescence detector system as set up for Cu K -edge EXAFS produces a large background that increases rapidly with energy as the scanned energy approaches the Zn K -edge, as can be seen in Fig. 1 (dashed line). This background is not obvious in the EXAFS data for samples of higher concentration Cu in ZnS (0.5%), for which the average amplitude above the edge is roughly constant (solid line in Fig. 1). In looking at the output of the fluorescence detector at various energies using a multi-channel analyzer, it became apparent that there were two factors contributing to this steep background: a small peak passing through the Cu K -edge fluorescence window as the incident X-ray energy increased [identified as the Zn Raman line (Sánchez *et al.*, 2006)], and a small part of the tail from the Zn

fluorescence peak, just below the Zn K -edge, that is within the Cu K -edge fluorescence window. A similar background would be present in fluorescence EXAFS spectra for any system with a dilute atomic number Z in a host with $Z + 1$.

This background produces difficulties for EXAFS analysis since the EXAFS oscillations, χ , are most rigorously extracted using $\chi(E) = \mu(E)/\mu_o(E) - 1$, where $\mu(E)$ is the total absorption at energy E and $\mu_o(E)$ is the average function through the oscillations, obtained from a fit of the data to a series of splines (Teo, 1986; Koningsberger & Prins, 1988). This is quite straightforward for transmission data; for fluorescence data, however, the experimental $\chi_{\text{exp}}(E)$ is obtained from $\chi_{\text{exp}}(E) = [I_f(E) - \bar{I}_f(E)]/\bar{I}_f(E)$, where $I_f(E)$ is the measured fluorescence signal and $\bar{I}_f(E)$ is the average spline through the data. The corrected χ must be extracted from $\chi_{\text{exp}}(E)$ using some self-absorption code (see, for example, Booth & Bridges, 2005). If $\bar{I}_f(E)$ increases with E , the amplitude of χ (corrected) decreases at high E and distorts the EXAFS signal.

Because fluorescence EXAFS typically uses a fairly narrow detector window (~ 200 – 300 eV wide for Cu) around the dopant

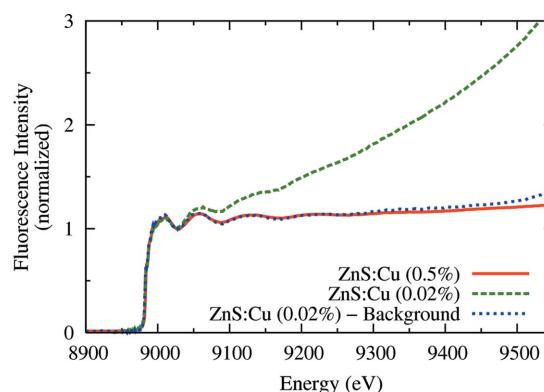


Figure 1

A comparison of the fluorescence E -space data at the Cu K -edge for two ZnS:Cu samples: an extremely dilute 0.02% Cu sample (dashed green line) and a higher concentration 0.5% Cu sample (solid red line); and the background-subtracted data for the 0.02% sample (dotted blue line). For comparison, the data were normalized at 9000 eV.

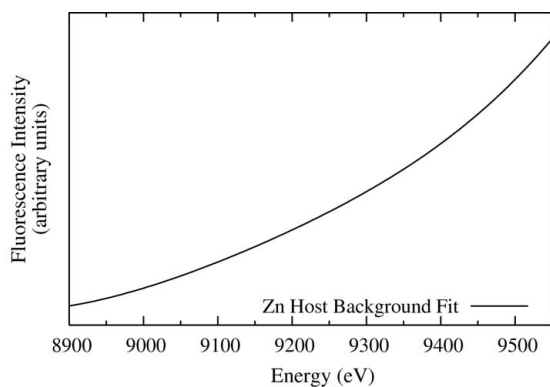


Figure 2
Fluorescence detector output for a Cu *K*-edge scan for a Zn foil sample, using the same parameters as for collecting Cu *K*-edge EXAFS data in ZnS:Cu.

fluorescence peak to eliminate other fluorescences and the scatter peak, the effect of the Zn Raman line here is more complex; the extra background arises from a convolution of the Raman line with the window used for data collection. As the energy is scanned for the Cu edge, the Zn Raman line grows in magnitude and its peak energy increases. The line passes through the window set up for Cu fluorescence and eventually would merge with the Zn fluorescence peak if the scan energy reached the Zn *K*-edge. To measure this effect, it is necessary to collect the background data in the same way (with the same window) as the Cu fluorescence data are collected.

To quantify the effect, we replaced our ZnS:Cu sample with a Zn foil and scanned over the same Cu *K*-edge energy range (8740–9550 eV) with all other experimental parameters unaltered. This scan produced an increasing fluorescence signal as the energy increased towards the Zn *K*-edge, as shown in Fig. 2. We then parameterized these data using a sixth-order polynomial and subtracted a constant background such that the resulting background function $B(E)$ starts at zero at the beginning of the scan.

To correct the Cu fluorescence data (after a preliminary pre-edge subtraction), we multiply $B(E)$ by a constant a such that the scaled background function has the same post-edge slope as the Cu EXAFS data (to account for different sample thicknesses) and then subtract it from the fluorescence EXAFS data, obtaining corrected data with a post-edge slope that is roughly zero. The background-subtracted data for 0.02% Cu are shown in Fig. 1 as a dotted line. The corrected data can then be reduced using standard procedures such as *RSXAP* (Booth, 2010) to obtain *k*-space and *r*-space data.

3. Conclusion

Although, for low concentrations, the Raman peak of the host atoms can be comparable with the fluorescence peak of the dopant, resulting in artificially low *k*-space data at high *k* and, therefore, an erroneously large value for σ , it can easily be removed to minimize these distortions in the EXAFS data and obtain the proper magnitude at high *k* and a correct value for σ .

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