

X-ray Absorption for the Structure of ZnS Nanoparticles

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Introduction

Structure determination, particularly the presence of polytype structures, can be challenging for small nanoclusters, for which x-ray diffraction data are broadened, masking subtle structural modifications. X-ray absorption spectroscopy (XAS) is inherently a short-range structural probe and hence is likely to be valuable in detecting crystal structure modifications in nanoscale systems. XAS additionally describes unoccupied electronic states — important in excited state processes, such as optical absorption, luminescence, and photocatalysis. Hence, theoretical approaches are invaluable to understand the contributions to x-ray absorption fine structure. We have performed experimental and theoretical studies of XAS in bulk polytypes and nanoparticles of ZnS to evaluate XAS as a structural probe for nanoscale materials.

Methods and Materials

X-ray absorption near-edge structure (XANES) spectra were acquired at the major absorption edges of bulk ZnS in the zinc blende (cubic) and wurtzite (hexagonal) phases. The zinc and sulfur site symmetry is lowered in wurtzite versus zinc blende, but the nearest-neighbor geometry is virtually unchanged. Zn K-edge XANES spectra were acquired at XOR beamline station 4-ID-D at the APS. Lower-energy XANES spectra were acquired at the Synchrotron Radiation Center, Madison, WI.

Results

As shown in Fig. 1, the XANES spectra at all edges demonstrate that only sulfur L-edge spectroscopy can resolve the polytypes, which differ mainly in the energy positions of unoccupied *d*-band states [1]. Multiple scattering calculations are in good agreement to the experimental data at all edges. A comparison between theory and experiment indicates that XANES spectra are sensitive to crystal geometry within a radius of 10 Å (S L edge) to 14 Å in ZnS (Zn K edge) around the photoexcited atom. Thus, XAS is potentially suitable for use as a short-range structural probe in nanoscale ZnS.

We used XOR beamline station 4-ID-D to acquire *in situ* Zn K-edge XANES and extended x-ray absorption fine structure (EXAFS) from a suspension of 3-nm ZnS

nanoparticles [2]. We have shown that ZnS nanoparticles are sensitive to the surface environment [3] and that working at the Zn K edge on a high-flux beamline enabled the nanoparticles to be studied without drying. Figure 2 shows that the XANES lineshape of the nanoparticles is close to the bulk zinc blende lineshape, plus additional broadening. We calculated theoretical XANES spectra for two 3-nm model ZnS nanoparticles. For one calculation, the model nanoparticle had a perfect zinc blende structure. For a subsequent calculation, the nanoparticle structure was relaxed in a molecular dynamics (MD) simulation to a lower-energy configuration. The calculation parameters for the nanoparticle theoretical XANES were identical for the calculation of the bulk theoretical XANES, also shown in Fig. 2. As no atomic positions in nanoparticles are truly equivalent, the whole-nanoparticle XANES spectra were obtained by summing the contributions from each Zn atom in the structure.

Discussion

The model nanoparticle with the perfect zinc blende structure results in better agreement with the experimental nanoparticle XANES than the model with a relaxed structure. However, this result is contrary to conclusions from x-ray diffraction data, for which the experimental nanoparticle data are in better agreement with the relaxed than with the unrelaxed model structures [2]. From additional simulations, we concluded that XAS spectra are more sensitive than x-ray diffraction to the distribution of structural disorder within nanoparticles, and together these approaches provide a rigorous test of MD structure predictions.

Acknowledgments

Financial support for this work was provided by the U.S. Department of Energy (DOE), Lawrence Berkeley National Laboratory laboratory-directed research and development (LDRD), and the National Science Foundation. Use of the APS was supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. References 1 and 2 are the sources for this article.

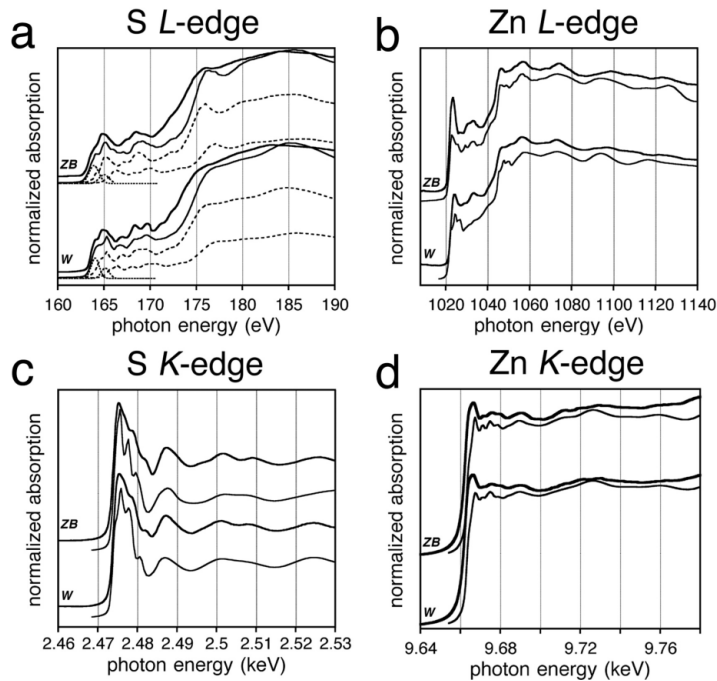


FIG. 1. Experimental and calculated XANES of ZnS zinc blende (ZB) and wurtzite (W) polytypes. For each polytype, the upper thick curve indicates the experiment, and the lower thin curve indicates the calculation. Clockwise from top: Panel a shows the S L edge. The sulfur 2p spin-orbit splitting is 1.1 eV, and the full $L_{2,3}$ spectrum is displayed, including L_2 , L_3 , and exciton prepeak components (dashed lines). Panel b shows the Zn L edge. The zinc 2p spin-orbit splitting is 23.1 eV, and the calculated full $L_{2,3}$ spectrum is displayed. Panel c shows the S K edge. Panel d shows the Zn K edge. Reprinted from Ref. 1 with permission, copyright (2002) by the American Physical Society.

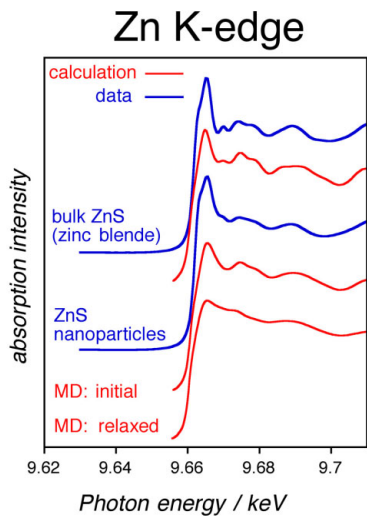


FIG. 2. Experimental and calculated Zn K-edge XANES of bulk ZnS (zinc blende) and 3-nm ZnS nanoparticles. The nanoparticle XANES are compared with two calculations based on a 3-nm model nanoparticle. The model initially had a perfect zinc blende structure, which was subsequently relaxed in an MD simulation. All spectra are offset for clarity.

References

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