Modeling X-Ray Absorption Processes in Sub-Stoichiometric Copper Sulfide ($Cu_{2-x}S$) Nanoparticles and Nanoheterostructures

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Abstract

This report summarizes x-ray absorption spectroscopy (XAS) computer modeling research conducted at the Cornell High Energy Synchrotron Source (CHESS). The primary goal of this research was to use computer-modeling software to successfully reproduce x-ray absorption spectra for several different phases of copper sulfide ($Cu_{2-x}S$) observed in the chemical transformation from roxbyite ($Cu_{1.81}S$) to zinc sulfide (ZnS) nanoparticles. These modeled XAS spectra will then be used to help interpret experimental XAS data collected during this chemical transformation.

Introduction

Zinc sulfide (ZnS) is an important semiconductor that has found uses in optoelectronics and photovoltaic cells. [1] Although ZnS is naturally occurring in mineral form as sphalerite and wurtzite, its synthesis from other compounds is important in materials science and engineering.

A method for producing nanostructured ZnS and ZnS-heterostructures from another starting material, such as copper sulfide, is nano-scale cation exchange. Typical bulk solid-phase ion exchanges are very slow and require high temperatures and pressures to supply the activation energy necessary for the diffusion of ions through the extended solid. However crystals on the nano-scale, such as the ones discussed in this paper, experience different kinetics. Nano-scale crystals can undergo cation exchange at remarkably fast rates, and at room temperature conditions, making nanoparticles reactions favorable. [2] Understanding the subtleties of reactions like these is vital for optimizing future synthetic routes to produce semiconducting nanomaterials.

Copper sulfide ($Cu_{2-x}S$) has a rather complex crystal lattice, allowing it to form sub-stoichiometric compounds. "Sub-stoichiometric" means that in the empirical formula of copper sulfide, $Cu_{2-x}S$, x can vary such that $0 < x < 1$. [3] Throughout the transformation of copper sulfide to ZnS, evidence of different stoichiometric phases of copper sulfide are observed at various stages of the reaction; this suggests that changes within the copper sulfide lattice are occurring. This paper addresses changes observed in experimental K-edge x-ray absorption spectra of copper sulfide ($Cu_{2-x}S$) phases in ZnS–$Cu_{2-x}S$–ZnS heterostructured nanoparticles.

X-Ray Absorption

When studying reactions on the molecular level, x-ray absorption is

very useful. Every crystal lattice produces a unique x-ray absorption spectrum, allowing materials to be identified accordingly. This is a result of the photoelectric effect and the multitude of pathways that photoelectrons would encounter as they scattered around a lattice before escaping the vacuum level. Thus, no two different compounds or lattices would produce the same x-ray absorption spectrum.

Nanoparticle samples taken from different points in time during the cation exchange synthesis of ZnS produce different copper K-edge XAS. If every lattice produces a unique absorption spectrum, as stated before, this implies that the crystal lattice changes throughout the reaction. All the forms of copper sulfide observed are structurally similar, but with a varying amount of vacancies in the lattice. The goal of this research was to computationally model the K-edge XAS of known phases of $Cu_{2-x}S$, which would then be used to help interpret the experimental XAS data.

XANES

The complete x-ray absorption spectrum is usually divided, somewhat arbitrarily, into two main parts; the part we are concerned with in this study is called the x-ray absorption near edge structure (XANES), shown in Figure 1, and is typically considered to span from ~20 eV below to ~30 eV above the specified absorption edge.

The copper K-edge refers to dipole allowed ($\Delta l \pm 1$) transitions from copper $1s \rightarrow np$ (n ≥4), which occurs at 8979 eV for metallic copper (Cu^0). From experimental data, the copper K-edge
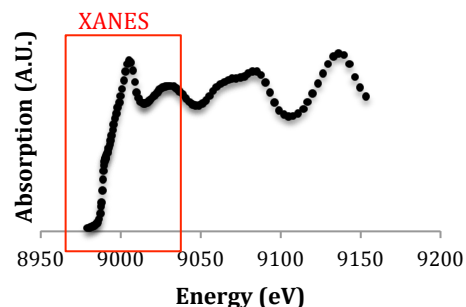
Figure 1 Copper K-edge x-ray absorption spectrum of a copper crystal modeled using FEFF9. The boxed region shows the XANES.

for all nanoparticle samples was determined to be ~8980 eV, which is consistent with copper in the 1+ oxidation state.

The XANES is easier to measure than the extended x-ray absorption fines structure (EXAFS), and is also easier to crudely interpret. It is dominated by multiple scattering of photoelectrons that are ejected at low kinetic energies. [4] The many intense multiple scattering (MS) features of XANES found within a small region, along with the ability to work with low concentrations, make it excellent for identifying compounds.

X-Ray Modeling with FEFF9.6

Computer programs like FEFF, created by John Rehr at the University of Washington, can be used to calculate theoretical x-ray absorption spectra of materials based on the coordinates of specified atoms within the lattice. FEFF performs calculations using an *ab initio* approach, which means "from the beginning". [5] The details of *ab initio* calculations are beyond the scope of this paper and lack any simple explanation, but are based on the

calculation of quantum-chemical force fields at the microscopic level.

Although these theoretical spectra may not match perfectly with the experimental XAS spectra, the ability to crudely interpret XANES MS peaks is sufficient to extract valuable information from these theoretical models.
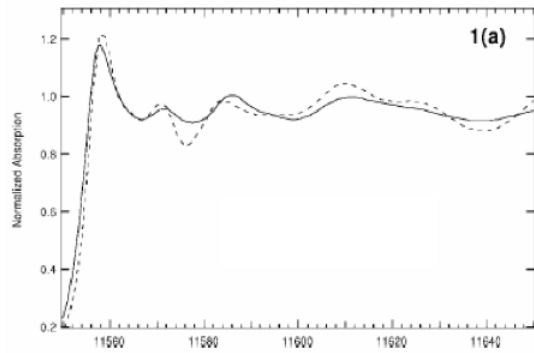

Figure 2 XANES spectra for platinum. The solid line is the actual absorption spectrum, the dotted line is the theoretical spectrum produced by FEFF. Modified from S.R. Bare's figure from the University of Chicago (http://cars9.uchicago.edu/xafs_school/APS_2005/Bare_XANES.pdf). [4]

Figure 2 demonstrates that the XANES calculated by FEFF can differ from the real experimental data, but is still useful for interpreting experimental data. Although the positions and heights of the MS peaks are different, the FEFF data still shows the important characteristic signatures of a platinum crystal.

FEFF9.6 Results for $Cu_{2-x}S$

Figure 3 shows the theoretical XANES for low chalcocite (Cu_2S), djurleite ($Cu_{1.94}S$), and roxbyite ($Cu_{1.81}S$); the three phases of copper sulfide that we are concerned with throughout the transformation to ZnS.
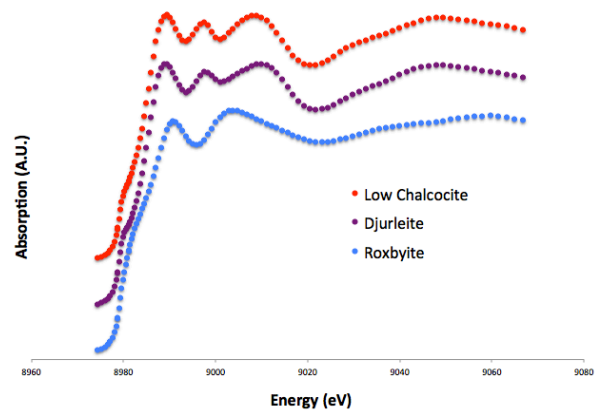
Figure 3 XANES spectra for low chalcocite, djurleite, and roxbyite produced using FEFF9 [5]

These XANES spectra were calculated from feff.inp files that were created using the data from crystallographic information files (CIF's) found in the American Mineralogist Crystal Structure Database.
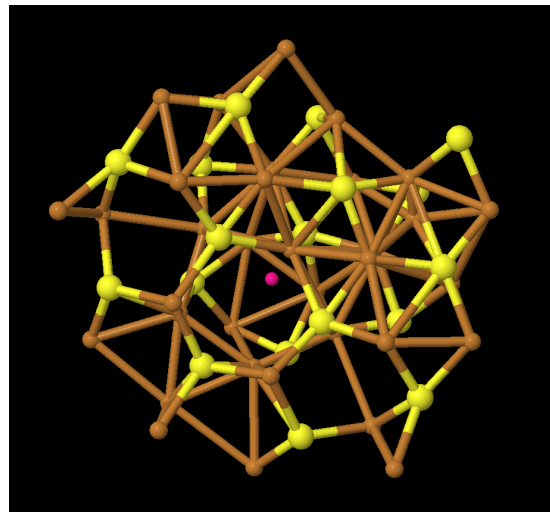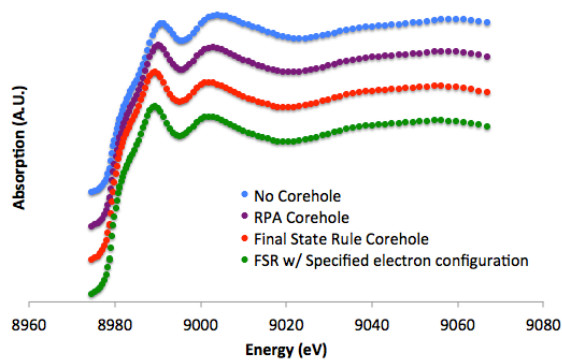

Figure 4 A model of a roxbyite crystal ($Cu_{1.81}S$), constructed using FEFF9 [5]

Crystallographic information files (CIF's) contain all the relevant information about the crystalline structure of known substances:

chemical formula, fractional coordinates of atoms, lengths of the sides of the parallelepiped crystal, and the angles between edges. Figure 4 is a cartoon image of a roxbyite crystal, which was based off the same feff.inp file that was used to create the XANES. [5]

Looking at Figure 3, there is a noticeable shift in the MS peaks from roxbyite to low chalcocite/djurleite. One of the primary differences between the three phases, roxbyite, djurleite, and low chalcocite are vacancies in the lattice, as briefly mentioned before. This is evident when comparing the XANES of low chalcocite and djurleite, which are the most structurally similar, and subsequently the XANES are almost identical.

The FEFF program includes several input options regarding the electron core hole of the absorbing atom, as well as an option to specify the electron orbital configuration of the absorbing atom. The white-line intensity of the "no core hole" option for all three copper sulfide phases modeled agrees best with the experimental data.
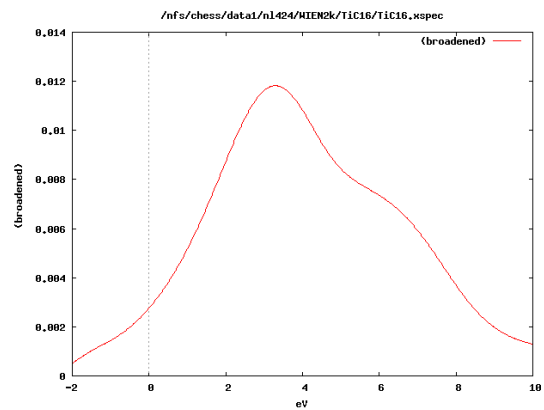
Roxbyite was used to test the effect of changing these options, as shown in Figure 5. Upon close inspection, it can be seen that changing the "core hole" option does indeed change the XANES output, but not by much. In addition, specifying the electron configuration produces no observable change in output at all. These variations were done to improve confidence in the theoretically calculated XANES produced by this modeling software, and indeed we see little effect from changing these options.

X-Ray Modeling with WIEN2k

WIEN2k is a computer program developed by Peter Blaha, at the University of Vienna, which can also be used for replicating x-ray absorption spectra of crystalline structures. [6] WIEN2k performs calculations using density functional theory (DFT), which is complex approach to computing the electronic structures of matter. Walter Kohn, who received the Nobel Prize in Chemistry in 1998 for its development, introduced DFT, which is currently the most successful approach to predicting molecular properties. [7]

Figure 5 XANES spectra of several core electron hole options for Roxbyite ($Cu_{1.81}S$), produced using FEFF9 [5]

Figure 6 Ti L_{III}-edge XAS spectrum for titanium carbide (TiC) produced using WIEN2k [6]

Depending on the complexity of the structure, DFT calculations can be very computationally expensive, often taking days, or even weeks to run. Figure 6 shows an XAS for TiC, which is a simple molecule with a basic structure of only 2 independent atoms. The initial information needed to produce the TiC spectrum can be found in the CIF file for TiC, the rest of the electronic calculations are done in WIEN.

Because of the extensive time required to perform DFT calculations, XAS spectra for the three phases of copper sulfide that we wanted to model were unable to be produced before the end of this research program. Low chalcocite, the simplest of the copper sulfides, contains 36 independent atoms. Djurleite and roxbyite contain 94 and 90 independent atoms, respectively. Although the x-ray absorption results produced in WIEN2k for copper sulfide could not be included in this summary, calculations are currently in progress.

Conclusion

As a result of this x-ray absorption modeling research, theoretical x-ray absorption spectra were successfully reproduced for different crystalline structures of copper sulfide observed during the cation exchange synthesis of ZnS nanostructures. The theoretical XAS for low chalcocite and djurleite are very similar, which corresponds their similarities in local (i.e. around the copper absorber) structure. Comparing roxbyite to low chalcocite/djurleite however, a noticeable shift in the MS peaks is observed. The direction of this MS peak shift is consistent with the MS peak shifts observed in the experimental data. This result helps to corroborate experimental XAS results and continues to improve the understanding of the copper sulfide phase change observed in the synthesis of ZnS from roxbyite nanoparticles.

References

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