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Local Structure of CuIn₃Se₅

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ABSTRACT

The results of a detailed EXAFS study of the Cu-K, In-K, and Se-K edges CuIn₃Se₅ are reported. The Cu and In first nearest neighbor local structures were found to be almost identical to those in CuInSe₂. The Se first nearest neighbor local structures, however, are quite different. The fitted results indicated CuIn₃Se₅ consists of Se-centered tetrahedron with an average of 0.8 Cu and 2.4 In nearest neighbors. This result is consistent with first-principle total energy calculations for this system.

1. Introduction

The observed junction between α -CuInSe₂ and CuIn₃Se₅ appears to play an important role in the photovoltaic process. Several investigations have explored the structure of this compound; however, the reported structural solutions disagree significantly. To shed some light on this issue, we have studied the local structure of CuIn₃Se₅ using EXAFS measurement performed on the Cu, In, and Se K-edges. The first-principle total energy calculations are also performed to compare with experimental data.

2. Experiment

The samples were synthesized from Cu₂Se and In₂Se₃ powders placed in boron nitride (BN) coated evacuated quartz ampoules. These powder mixtures were slowly heated to ~ 150 °C above the melting temperature of In₂Se₃, then gradually cooled to 700°C and isothermally annealed for a week to reach equilibrium. The XAFS specimens were prepared by grinding the polycrystalline materials. Particle size analysis was done using a Horiba Capa-700 particle analyzer, which confirmed particles were less than ten microns in diameter. The fine powder was uniformly spread over a scotch tape. The XAFS measurements were performed on the MR-CAT beamline of the Advanced Photon Source (APS) at Argonne National Laboratory, which uses an APS undulator-A. The beamline optics incorporates a Si (111) double monochromator and a Rhodium coated harmonics-rejection mirror, which was set to reject second and higher harmonics. The X-ray intensities were monitored using ionization chambers, with Nitrogen and Argon respectively in the transmission and fluorescence ion chambers. Linearity was checked by attenuating the

primary beam.

3. Results

The XAFS data were analyzed by standard methods using the WinXAFS package [1]. To obtain quantitative information, the standard EXAFS equation was used in the least square analysis:

$$\chi(k) = \sum_j \frac{N_j}{kR_j^2} S_0^2 F_j(k) \exp(-2k^2\sigma_j^2) \exp\left(\frac{-2R_j}{\lambda(k)}\right) \sin[2kR_j + \delta_j(k)]$$

In this equation N_j is the number of atoms in j th shell; R_j is the mean distance between the absorbing atom and the j th shell; $F_j(k)$ is the magnitude of the backscattering amplitude of the j th neighbor atom; $\delta_j(k)$ is the electronic phase shift due to the atomic potentials; σ^2 is the corresponding mean-square relative displacement; S_0 is the amplitude reduction factor representing central atom shake-up and shake-off effects, and $\lambda(k)$ is the photoelectron mean free path. The backscattering amplitude, $F_j(k)$, and phase shift, $\delta_j(k)$, for Cu and In K-edges were extracted from the CuInSe₂ spectra using the known structural data.

The isolated first shell Cu-K EXAFS spectra for CuInSe₂ and CuIn₃Se₅ are almost identical except the spectrum for CuIn₃Se₅ has a slightly larger damping coefficient. This indicates the first nearest neighbor local structures (i.e. the bond length, $d_{\text{Cu-Se}}$, and the number of nearest neighbors, N) around the Cu atoms in these two semiconductor alloys are nearly the same. The least-squares fit results are given in Table 1.

The isolated first shell In-K EXAFS spectra for CuInSe₂ and CuIn₃Se₅ are also found to be almost identical. The least square fitting results are given in Table 1. The fitting results confirmed the In-Se inter-atomic distance is conserved between CuInSe₂ and CuIn₃Se₅.

Table 1. Least square fitting results

	Coordination number	bond length (Å)
Cu-K edge	4±0.2	$R_{\text{Cu-Se}} 2.424 \pm 0.005$
In-K edge	4±0.1	$R_{\text{In-Se}} 2.595 \pm 0.005$

The isolated Se-K edge first shell spectra for CuInSe₂ and CuIn₃Se₅ are given in Figure 1. It is clear that the two spectra are very different. This indicates that the first nearest neighbor environment around Se atoms in these two semiconductor alloys is also very different. The ab initio multiple-scattering code FEFF7 [2] was used to calculate $F_j(k)$, $\delta_j(k)$, and $\lambda_j(k)$ to obtain quantitative

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estimates of the number of nearest neighbors and their distances. The least square fitting results are listed in Table 2. The fitted results show the Se-K edge data are consistent with the Cu and In K-edge data. The results confirm that CuIn_3Se_5 does belong to the defect-tetrahedral structure, which is characterized by vacant tetrahedral site in the Se-centered tetrahedron. The data are consistent with the models proposed by [3], which suggested that the structure of CuIn_3Se_5 consists of three types of local tetrahedral cationic clusters around each Se: $\text{V}_{\text{Cu}}+\text{Cu}+2\text{In}$ ($k=7$), $2\text{Cu}+2\text{In}$ ($k=8$), and $\text{V}_{\text{Cu}}+3\text{In}$ ($k=9$). How these different types of tetrahedron arrange themselves and form the long-range order structures (e.g., symmetry) needs further study by other techniques.

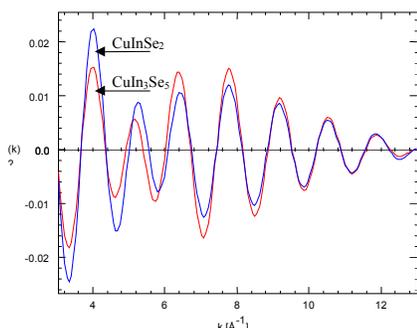


Figure 1. Fourier filtered EXAFS on the Se K edge for the first shell peaks in CuInSe_2 and CuIn_3Se_5 .

Table 2. EXAFS analysis results for CuIn_3Se_5 Se-K edge data

	S_0^2	0.737
Cu-Se	N:	0.8
	$R_{\text{Cu-Se}}(\text{Å})$:	2.424
	$\sigma^2(\text{Å}^2)$:	1.77×10^{-3}
In-Se	N:	2.4
	$R_{\text{In-Se}}(\text{Å})$:	2.598
	$\sigma^2(\text{Å}^2)$:	4.22×10^{-3}

We have also studied the local crystal structures of various CuInSe_2 , CuIn_3Se_5 and CuIn_5Se_8 compounds using the first-principles band structure method [4]. To choose the crystal structures, we have followed two guidelines: (a) The arrangement of atoms in the crystal has minimal deviations from the octet rule and (b) they have low Coulomb energy. Our total energy calculations show that the total energy differences between the six CuIn_5Se_8 structures being calculated are small, less than 8 meV/atom. Similar results are obtained for CuIn_3Se_5 and CuInSe_2 . These results indicate that although the local environment of ordered vacancy compounds (OVCs) are well defined, containing weighted $k=7$, $k=8$ and $k=9$ clusters, the long range order of the OVCs may depend sensitively on growth kinetics, history of annealing, and the configuration entropies. This could explain why different crystal structures of CuIn_3Se_5 have been observed. For example, the crystal structure proposed by Hanada et al. [5] for CuIn_3Se_5 has a space

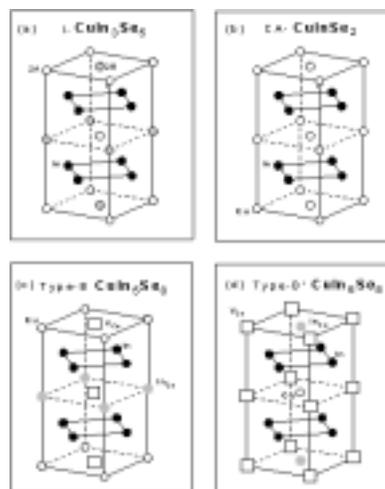


Figure 2. Structures for CuIn_3Se_5 , CuInSe_2 , and CuIn_5Se_8 .

The model structure of Hanada et al. can be well described as a superposition of three single phases: (i) 20% of the CA- CuInSe_2 (Figure 2b.), (ii) 40% of the type-B CuIn_5Se_8 (Fig. 2c), and (iii) 40% of type-B' CuIn_5Se_8 (Figure 2d.), where type-B' CuIn_5Se_8 is identical to type-B CuIn_5Se_8 except that its origin is shifted by $(1/2, 1/2, 1)a$. The equilibrium bond lengths in the various OVCs were calculated. It was found that, within a calculation uncertainty of about 0.005 Å, the Cu-Se bond lengths in these OVCs are independent of the stoichiometry and atomic configuration. For the In-Se bonds, the bond lengths were found to increase linearly with k with $R_{\text{In-Se}}(k=9) - R_{\text{In-Se}}(k=7) = 0.06$ Å. The average In-Se bond lengths in CuInSe_2 and CuIn_3Se_5 , however, are constant to within 0.01 Å, and decrease slightly as the Cu occupation decreases within the homogeneity range of the β -phases (OVCs). The theoretical results are consistent with the present EXAFS measurements. The calculated standard deviation from the average In-Se bond lengths is ~ 0.03 Å. Temperature-dependent EXAFS measurements are needed to further clarify this difference.

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