

# ***PROGRAM AND PROCEEDINGS***



## **NCPV Program Review Meeting 2000**

**April 16-19, 2000**

**Adam's Mark Hotel**

**Denver, Colorado**



## NOTICE

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at <http://www.doe.gov/bridge>

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from:

U.S. Department of Energy  
Office of Scientific and Technical Information  
P.O. Box 62  
Oak Ridge, TN 37831-0062  
phone: 865.576.8401  
fax: 865.576.5728  
email: [reports@adonis.osti.gov](mailto:reports@adonis.osti.gov)

Available for sale to the public, in paper, from:

U.S. Department of Commerce  
National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
phone: 800.553.6847  
fax: 703.605.6900  
email: [orders@ntis.fedworld.gov](mailto:orders@ntis.fedworld.gov)  
online ordering: <http://www.ntis.gov/ordering.htm>



# Local Structure of CuIn<sub>3</sub>Se<sub>5</sub>

C.-H. Chang<sup>1\*</sup>, Su-Huai Wei<sup>2</sup>, N. Leyarovsky<sup>3</sup>, J.W. Johnson<sup>1</sup>, S.B. Zhang<sup>2</sup>, B.J. Stanbery<sup>1</sup>, T.J. Anderson<sup>1</sup>,  
R. Duran<sup>1</sup>, and Grant Bunker<sup>4</sup>  
University of Florida, Gainesville, FL 32611<sup>1</sup>  
National Renewable Energy Laboratory, Golden, CO 80401<sup>2</sup>  
Advanced Photon Source, Argonne National Laboratory, IL 60438<sup>3</sup>  
Illinois Institute of Technology, Chicago, Illinois 60616<sup>4</sup>

## ABSTRACT

The results of a detailed EXAFS study of the Cu-K, In-K, and Se-K edges CuIn<sub>3</sub>Se<sub>5</sub> are reported. The Cu and In first nearest neighbor local structures were found to be almost identical to those in CuInSe<sub>2</sub>. The Se first nearest neighbor local structures, however, are quite different. The fitted results indicated CuIn<sub>3</sub>Se<sub>5</sub> 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  $\alpha$ -CuInSe<sub>2</sub> and CuIn<sub>3</sub>Se<sub>5</sub> 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 CuIn<sub>3</sub>Se<sub>5</sub> 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 Cu<sub>2</sub>Se and In<sub>2</sub>Se<sub>3</sub> powders placed in boron nitride (BN) coated evacuated quartz ampoules. These powder mixtures were slowly heated to  $\sim 150$  °C above the melting temperature of In<sub>2</sub>Se<sub>3</sub>, 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;  $\sigma^2$  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 CuInSe<sub>2</sub> spectra using the known structural data.

The isolated first shell Cu-K EXAFS spectra for CuInSe<sub>2</sub> and CuIn<sub>3</sub>Se<sub>5</sub> are almost identical except the spectrum for CuIn<sub>3</sub>Se<sub>5</sub> 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 CuInSe<sub>2</sub> and CuIn<sub>3</sub>Se<sub>5</sub> 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 CuInSe<sub>2</sub> and CuIn<sub>3</sub>Se<sub>5</sub>.

Table 1. Least square fitting results

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

The isolated Se-K edge first shell spectra for CuInSe<sub>2</sub> and CuIn<sub>3</sub>Se<sub>5</sub> 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

\* Current address: Oregon State University, Chemical Engineering Department, Corvallis, OR 97330

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  $\text{CuIn}_3\text{Se}_5$  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  $\text{CuIn}_3\text{Se}_5$  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.

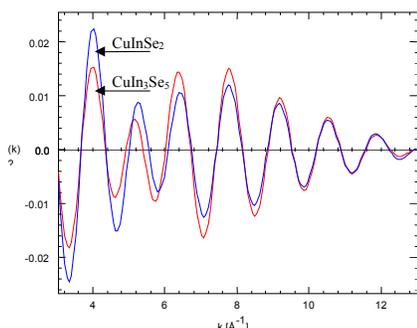


Figure 1. Fourier filtered EXAFS on the Se K edge for the first shell peaks in  $\text{CuInSe}_2$  and  $\text{CuIn}_3\text{Se}_5$ .

Table 2. EXAFS analysis results for  $\text{CuIn}_3\text{Se}_5$  Se-K edge data

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

We have also studied the local crystal structures of various  $\text{CuInSe}_2$ ,  $\text{CuIn}_3\text{Se}_5$  and  $\text{CuIn}_5\text{Se}_8$  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  $\text{CuIn}_5\text{Se}_8$  structures being calculated are small, less than 8 meV/atom. Similar results are obtained for  $\text{CuIn}_3\text{Se}_5$  and  $\text{CuInSe}_2$ . 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  $\text{CuIn}_3\text{Se}_5$  have been observed. For example, the crystal structure proposed by Hanada et al. [5] for  $\text{CuIn}_3\text{Se}_5$  has a space

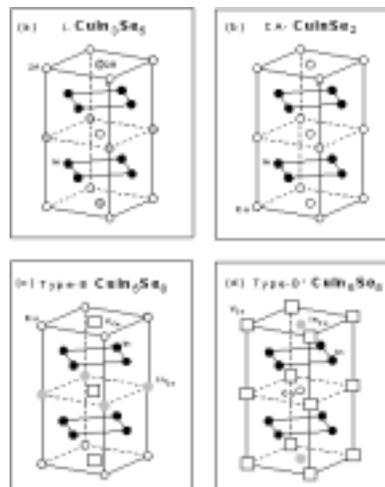


Figure 2. Structures for  $\text{CuIn}_3\text{Se}_5$ ,  $\text{CuInSe}_2$ , and  $\text{CuIn}_5\text{Se}_8$ .

The model structure of Hanada et al. can be well described as a superposition of three single phases: (i) 20% of the CA- $\text{CuInSe}_2$  (Figure 2b.), (ii) 40% of the type-B  $\text{CuIn}_5\text{Se}_8$  (Fig. 2c), and (iii) 40% of type-B'  $\text{CuIn}_5\text{Se}_8$  (Figure 2d.), where type-B'  $\text{CuIn}_5\text{Se}_8$  is identical to type-B  $\text{CuIn}_5\text{Se}_8$  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  $\text{CuInSe}_2$  and  $\text{CuIn}_3\text{Se}_5$ , however, are constant to within 0.01 Å, and decrease slightly as the Cu occupation decreases within the homogeneity range of the  $\beta$ -phases (OVCs). The theoretical results are consistent with the present EXAFS measurements. The calculated standard deviation from the average In-Se bond lengths is  $\sim 0.03$  Å. Temperature-dependent EXAFS measurements are needed to further clarify this difference.

The work at University of Florida was supported by the DOE/NREL Thin Film PV Partnership Program under subcontract XAF-5-14142-10.

## REFERENCES

- [1] T. Ressler, *J. Physique IV*, **7** (1997) C2-269.
- [2] A.L. Ankudinov and J.J. Rehr, *Phys. Rev. B.* **52**, 2995, 1995.
- [3] S. B. Zhang, Su-Huai Wei, and Alex Zunger, H. Katayama-Yoshida, *Phys. Rev. B.* **57**, 9642, 1998.
- [4] S.-H. Wei and H. Krakauer, *Phys. Rev. Lett.* **55** 1200 (1985)
- [5] T. Hanada, A. Yamana, Y. Nakamura, O. Nittono, and T. Wada, Technical Digest: 9<sup>th</sup> International Photovoltaic Science and Engineering Conference (International PVSEC-9, Tokyo, 1996), p.595.