

# Atomic-scale structure of Cu(In,Ga)Se<sub>2</sub> by EXAFS

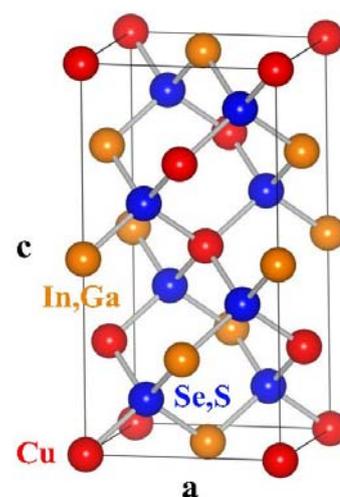
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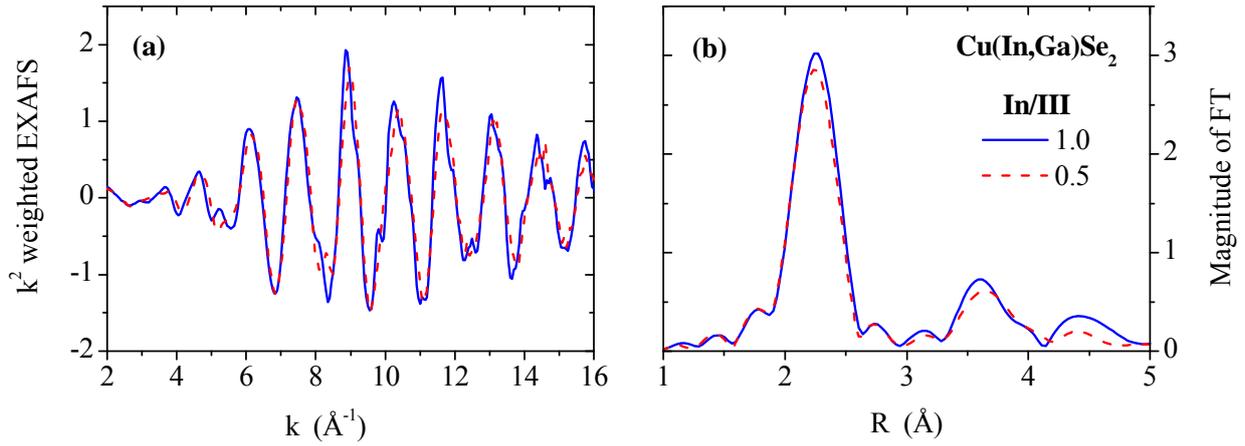
Among the materials used for thin film solar cells, the Cu(In,Ga)(Se,S)<sub>2</sub> system (CIGS) is a very promising candidate. It has already demonstrated record efficiencies close to 20 % on laboratory scale and offers much potential for optimization due to its tolerance for large deviations from stoichiometry and significant amounts of native defects [1]. However, many aspects of these complex multinary compounds are still not fully understood.

Stoichiometric CIGS crystallizes in the chalcopyrite type crystal structure which can be derived from the zincblende type crystal structure by introducing a mixed cation sublattice (Cu and In/Ga). This leads to a doubling of the unit cell in c-direction as shown schematically in Fig. 1. Other non-cubic features of the structure are a tetragonal distortion  $\eta=c/2a$  unequal to one, where  $a$  and  $c$  denote the lattice constants, and a displacement of the anions (Se,S) from their ideal lattice sites due to the different properties of the neighbouring cations. These subtle variations of the atomic-scale structure have been predicted to influence important material properties such as the energy band gap [2]. Furthermore, non-stoichiometry is typical for these compounds leading to intrinsic point defects that directly correlate with the electrical and optical properties of the material. Extended x-ray absorption fine structure spectroscopy (EXAFS) has proven to be a powerful technique for studying the local structural environment around the various atomic species in compound materials thus complementing the information obtained by other techniques such as diffraction.

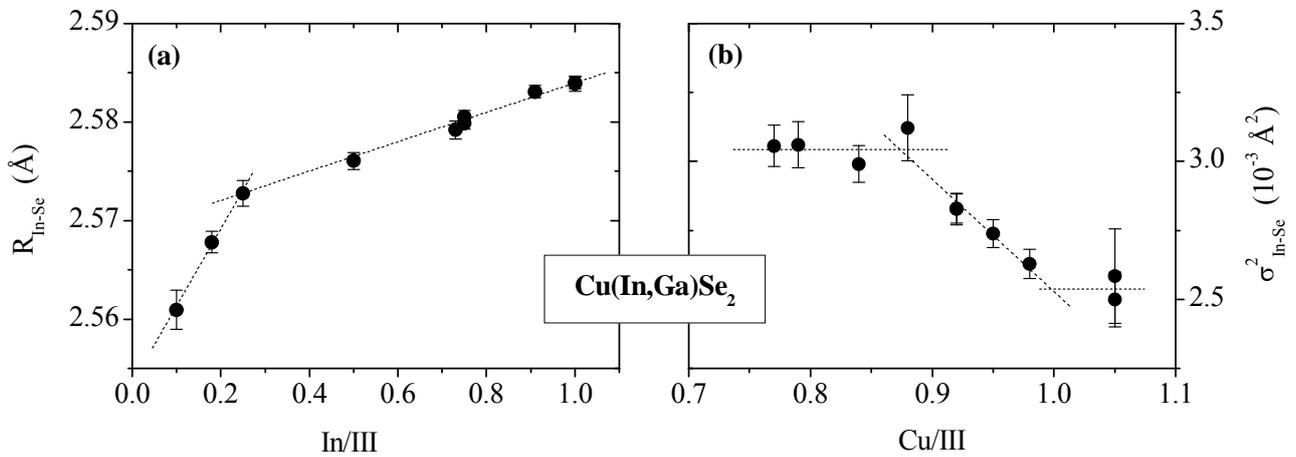


**Figure 1:** Schematic showing the chalcopyrite type crystal structure of Cu(In,Ga)(Se,S)<sub>2</sub>.

EXAFS measurements of Cu(In,Ga)Se<sub>2</sub> powder samples with different In/(In+Ga) = In/III ratios and varying Cu content were performed at the Cu, Ga and In K-edges (8.979, 10.367, and 27.940 keV, respectively) at Beamline C. The spectra were recorded in transmission mode at a temperature of 17 K in order to minimize thermal vibrations. Figure 2 (a) shows the  $k^2$ -weighted EXAFS spectrum measured at the In K-edge of CuInSe<sub>2</sub> and CuIn<sub>0.5</sub>Ga<sub>0.5</sub>Se<sub>2</sub> versus photoelectron wave number  $k$ . The corresponding Fourier transformations are plotted in Fig. 2 (b). The spectra were analysed using the IFEFFIT software package [3,4]. Scattering amplitudes and phase shifts were calculated with FEFF9 [5] while the mean value  $R$  and the standard deviation  $\sigma^2$  of the first nearest neighbour distance distribution were determined from least-square fits. The results for the In-Se bond are plotted in Fig. 3. A clear dependence of the In-Se bond length on the In/III ratio is observed (see Fig 3 (a)) in contrast to the results obtained by Antonioli *et al.* [6]. However, these authors determined the In-Se bond lengths from a measurement of the Se K-edge where the signals originating from Cu, Ga and In neighbours overlap. A determination of  $R_{\text{In-Se}}$  from spectra taken at the In K-edge is expected to be much more precise since in this case the signal constitutes only scattering from first nearest neighbour Se atoms. Interestingly, the slope with which  $R_{\text{In-Se}}$  changes with In/III ratio varies for Ga-rich and In-rich compounds although the lattice constants were shown to change linearly over the whole compositional range [7]. The standard deviation  $\sigma^2_{\text{In-Se}}$  depends on the Cu content of the material (see Fig. 3 (b)) while no correlation was observed for  $R_{\text{In-Se}}$  with Cu/III or for  $\sigma^2_{\text{In-Se}}$  with In/III (not shown). Analysis of the spectra taken at the Cu and Ga K-edges are currently under way.



**Figure 2:** (a)  $k^2$ -weighted EXAFS versus the photoelectron wave number  $k$  measured at the In K-edge of  $\text{CuInSe}_2$  (solid line) and  $\text{CuIn}_{0.5}\text{Ga}_{0.5}\text{Se}_2$  (dashed line) and (b) magnitude of the corresponding Fourier transformations versus radial distance  $R$ .



**Figure 3:** (a) In-Se bond length  $R_{\text{In-Se}}$  versus In/III ratio and (b) standard deviation  $\sigma_{\text{In-Se}}^2$  of the In-Se distance distribution versus Cu/III ratio for  $\text{Cu(In,Ga)Se}_2$  as determined from EXAFS measurements at the In K-edge. The lines are a guide to the eye.

## References

- [1] I. Repins, M.A. Contreras, B. Egaas, C. DeHart, J. Scharf, C.L. Perkins, B. To, and R. Noufi, *Prog. Photovolt: Res. Appl.* **16**, 235 (2008).
- [2] J.E. Jaffe and A. Zunger, *Phys. Rev. B* **29**, 1882 (1984).
- [3] M. Newville, *J. Synchrotron Rad.* **8**, 322 (2001).
- [4] B. Ravel, M. Newville, *J. Synchrotron Rad.* **12**, 537 (2005).
- [5] J.J. Rehr, J.J. Kas, F.D. Vila, M.P. Prange, and K. Jorissen, *Phys. Chem. Chem. Phys.* **12**, 5503 (2010).
- [6] G. Antonioli, S. Bini, P.P. Lottici, and C. Razzetti, *J. Physique* **47**, 431 (1986).
- [7] D. Abou-Ras, R. Caballero, C.A. Kaufmann, M. Nichterwitz, K. Sakurai, S. Schorr, T. Unold, and H.-W. Schock, *Phys. Stat. Sol. RRL* **2**, 135 (2008).