ESRF	**Experiment title:** Atomic-scale structure of $Cu(In,Ga)_3Se_5$ and $Cu(In,Ga)_5Se_8$ as a function of composition	**Experiment number**: HC-1284
Beamline: BM08	**Date of experiment**: from: 26/02/2014 to: 04/03/2014	**Date of report**: 13/05/2014
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Report:

It was the aim of this project to study the atomic-scale structure of $Cu(In,Ga)_3Se_5$ (1-3-5 phase) and $Cu(In,Ga)_5Se_8$ (1-5-8 phase) as a function of composition using low-temperature EXAFS measurements. Together with our previous investigations of $Cu(In,Ga)Se_2$ (1-1-2 phase) [1,2], this yields a comprehensive understanding of local structural parameters, including the average bond lengths, the bond length variations and the asymmetry parameters, with relation to both the In/Ga ratio and the Cu content.

A total of 25 samples were investigated at the Cu, Ga and In K-edges (8.979, 10.367 and 27.940 keV, respectively). Eleven samples each were studied for the 1-3-5 and 1-5-8 phase with In/III = In/(In+Ga) ratios ranging from 0 to 1 in steps of 0.1 while three samples of the 1-1-2 phase with In/III = 0.0, 0.5 and 1.0 were also measured to allow a direct comparison to the previous study. The powders were mixed with cellulose, ball-milled and then pressed into pellets. For each sample, two pellets were prepared with the amount of material optimized for measurement at either the Cu and Ga or the In K-edge. All spectra were recorded in transmission mode up to a *k*-value of 18 $Å^{-1}$. The sample temperature was 80 K in order to minimize thermally induced disorder.

Compared to our previous study of the 1-1-2 phase [1,2], the current measurements were characterized by three major differences which could, in principle, affect the comparability of the data. The previous measurements were performed at Beamline C at HASYLAB in Hamburg with hand-filled sample holders at 20 K while the current measurements were performed at BM08 at ESRF with pellets at 80 K. The different sample preparation was

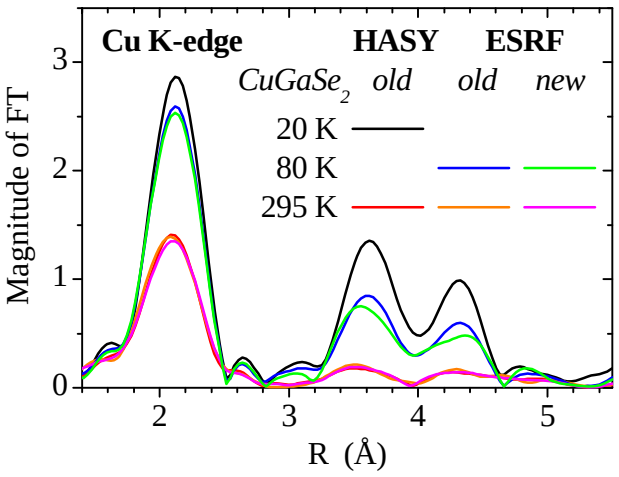

Figure 1: *Magnitude of the Fourier transformation (FT) versus radial distance R for k^2-weighted EXAFS spectra of $CuGaSe_2$ recorded at the Cu K-edge. A manually filled sample holder (old) and a pellet (new) were measured at either HASYLAB or ESRF using sample temperatures of 20, 80 or 295 K.*

necessary due to the sensitivity of BM08 to sample inhomogeneities. It was the first time that we prepared pellet samples and despite our best efforts the sample quality was mixed, especially for the very first pellets. However, the homogeneity did significantly improve with the number of pellets prepared and will be further optimized at our home institute for future experiments. In order to estimate the influence of the sample quality on the data recorded, we repeated the measurements for several samples in different spots or on different pellets. These variations mostly influence the determination of the bond length variation (σ^2) while the average bond lengths and the asymmetry parameter should be unaffected. σ^2 is also strongly influenced by the sample temperature as can be seen in Figure 1. As σ^2 increases going from 20 to 80 to 295 K due to increasing thermal vibrations of the atoms, the peak height decreases. Based on these and similar other measurements we can now estimate the effect of the different measurement temperatures on the bond length variation. Figure 1 also demonstrates that neither the sample preparation nor the choice of beamline affects the measured first nearest neighbour scattering contribution which is an excellent result. We are thus able to fully compare our new data of the 1-3-5 and 1-5-8 phases with the previous 1-1-2 results.

As an example, Figure 2 plots the spectra recorded at the In K-edge for pure In compounds of the 1-1-2, 1-3-5 and 1-5-8 phase. Obviously, the peak height decreases with decreasing Cu content corresponding to an increase of the bond length variation and thus an increase of structural disorder. In contrast, only a small change of the average bond length is expected for the samples shown in Figure 2. A detailed analysis of all spectra measured at the Cu, Ga and In K-edges is currently under way using the IFEFFIT software package [3] and the computer code FEFF9 [4]. This provides the element-specific Cu-Se, Ga-Se and In-Se atomic-scale structural parameters as a function of both In/III ratio and Cu content.

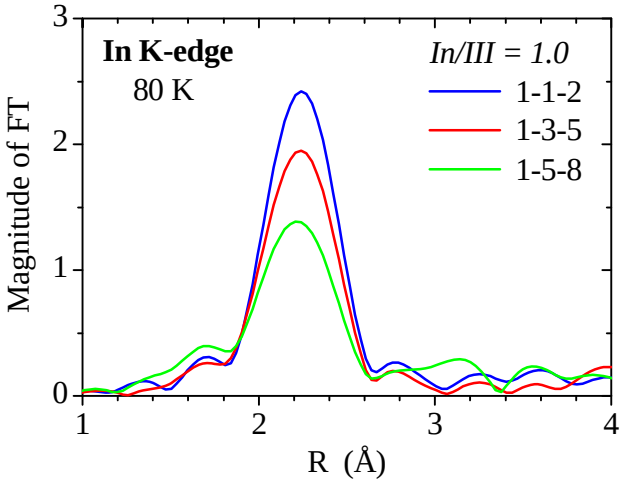

Figure 2: *Magnitude of the Fourier transformation (FT) versus radial distance R for k^2-weighted EXAFS spectra of $CuInSe_2$ (1-1-2), $CuIn_3Se_5$ (1-3-5) and $CuIn_5Se_8$ (1-5-8) taken at the In K-edge at 80 K.*

[1] C.S. Schnohr *et al.*, Phys. Rev. B 85, 245204 (2012).
[2] S. Eckner *et al.*, Appl. Phys. Lett. 103, 081905 (2013).
[3] B. Ravel and M. Newville, J. Synchrotron Radiat. 12, 537 (2005).
[4] J. J. Rehr *et al.*, Phys. Chem. Chem. Phys. 12, 5503 (2010).