Among the materials used for thin film solar cells, Cu(In,Ga)Se₂ currently yields the highest efficiencies with a record value above 20% on laboratory scale [1]. Stoichiometric Cu(In,Ga)Se₂ crystallizes in the chalcopyrite crystal structure with the lattice constants a and c as shown schematically in Fig. 1. The group-III lattice site is occupied randomly by In and Ga atoms leading to different first nearest neighbour configurations of the Se anions. Due to the different properties of the neighbouring Cu, Ga and In cations, the Se is typically displaced from its ideal lattice site depending on the specific atomic environment. These subtle structural variations have been predicted to influence important material properties such as the energy band gap [2]. A detailed knowledge of the atomic-scale structure of Cu(In,Ga)Se₂ is therefore indispensable for a more comprehensive understanding of this highly relevant yet complex material system.

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. EXAFS measurements of Cu(In,Ga)Se₂ with different In/(In+Ga) = In/III and Cu/(In+Ga) = Cu/III ratios were performed at the Cu, Ga and In K-edges (8.979, 10.367, and 27.940 keV, respectively) at Beamline C. Powder samples synthesized by solid state reaction from the pure elements were measured in transmission mode while polycrystalline thin films prepared in a three-stage co-evaporation process were analysed in fluorescence mode using a 7 pixel Si(Li) detector. All spectra were recorded at a temperature of 17 K in order to minimize thermal vibrations. Figure 2 (a) shows the $k^2$-weighted EXAFS spectra measured at the In K-edge of CuInSe₂ and CuIn₀.₇Ga₀.₃Se₂ thin films 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 pair are plotted in Fig. 3. For the Cu(In,Ga)Se$_2$ powder samples, a clear dependence of the In-Se bond length on the In/III ratio is observed (see Fig. 3 (a)) while no correlation was found with Cu/III (not shown). In contrast, 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 with In/III (not shown). For the Cu(In,Ga)Se$_2$ thin films, the bond length values agree very well with those of the powder samples. In contrast, the standard deviation is significantly lower for the films than for the powders indicating differences in the atomic-scale structure depending on the nature of the sample and the preparation process.

Similar results were also obtained from the spectra taken at the Cu and Ga K-edges. While the bond lengths match surprisingly well, the standard deviation of the first nearest neighbour distance distribution is lower for the thin films than for the powder samples. Comparing the different cation species, the In-Se, Ga-Se and Cu-Se bond lengths are found to be very different from each other and remain close to the values of the ternary compounds over the whole compositional range. Based on these experimental results, the anion position of the different first nearest neighbour configurations of the mixed Cu(In,Ga)Se$_2$ system was modelled [6]. It was found to depend strongly on the nature of the surrounding cations. This structural relaxation represents one origin of the non-linear behaviour of the band gap energy with changing In/III composition.

References