Advancements in anomalous diffraction for cation order determination

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Isoelectric cations are hard to distinguish by routine laboratory X-ray diffraction, as their scattering power is very similar. Besides neutron radiation, anomalous X-ray diffraction is commonly used to overcome this problem, utilizing the strong energy dependency of scattering factors close to the element-specific X-ray absorption edges. A variant of this, Multiple Edge Anomalous Diffraction (MEAD) [1] was found by us to work particularly well for the purpose of determination of cation arrangement within a known parent structure. This method calls for measuring the energy dependency of the intensity of individual Bragg peaks around the X-ray absorption edge of chemical elements (Fig. 1).

Figure 1. Observed and simulated MEAD spectra of Cu₂ZnGeSe₄ for Bragg peak 011. The compound adopts the Kesterite structure type, with only a small degree of Cu/Zn cation disorder. The order parameter Q has been estimated from this experiment.

The energy range of 5 – 14 keV of beamline KMC-2 at BESSY II, HZB, Berlin [2] allows to do measurements at the absorption edges of technically relevant elements, in particular the transition metals of the 4th period. Mn, Fe, Cu, Zn, Ga, Ge form a wide range of chalcogenides semiconductors, many of which have drawn wide attention for their potential applications in different fields [3]. Depending on their band gaps these materials are interesting for thin film solar cells, high-temperature thermoelectric materials, and nonlinear optics. Solid solutions of both cations and anions allow fine tuning of physical properties. It is well established that the cation arrangement in the respective structure is crucial for the electronic properties.

The compounds listed above crystallize in structure types derived by cation ordering from the cubic sphalerite type or the hexagonal wurtzite type crystal structure. The particular cation arrangement results either in kesterite or wurzt-kesterite structures, stannite or wurzt-stannite structures, or defect chalcopyrite types. These can be distinguished by MEAD and / or Joint Rietveld refinement at multiple energies.