ESRF	**Experiment title:** Structural and electronic transitions in $Cu_{12+\delta}Sb_4S_{13}$ tetrahedrites	**Experiment number**: HC2046
Beamline: ID22	**Date of experiment**: from: 13.11.2015 to: 17.11.2015	**Date of report**: 10.07.2016
Shifts: 12	**Local contact(s)**: Carlotta Giacobbe	*Received at ESRF:*

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Report:

The experiment was devoted to the temperature-dependent structural investigation of synthetic tetrahedrites. We planned to study two compounds, $Cu_{12}Sb_4S_{13}$ and $Cu_{14}Sb_4S_{13}$. The key question concerning the former compound was the investigation of its structural change across the metal-semiconductor transition (MST) at T ~ 85 K. Additionally, the high-temperature studies of the compound were planned. In regard to the $Cu_{14}Sb_4S_{13}$ compound, we planned to focus on the detection of an extra-copper site in the tetrahedrite structure and, besides, on the study of the compound in the wide temperature range.

$Cu_{12}Sb_4S_{13}$ (space group I-43m), the copper-poor tetrahedrite (see structure view in Fig. 1), is a compound with promising thermoelectric properties, undergoing a phase transition at T ~ 85 K, according to the heat-capacity, electrical resistivity, and magnetic susceptibility measurements. However, no information on structural changes across this transition was reported. Thus, during the experiment at ID 22, we examined the low-temperature crystal structure of the compound.

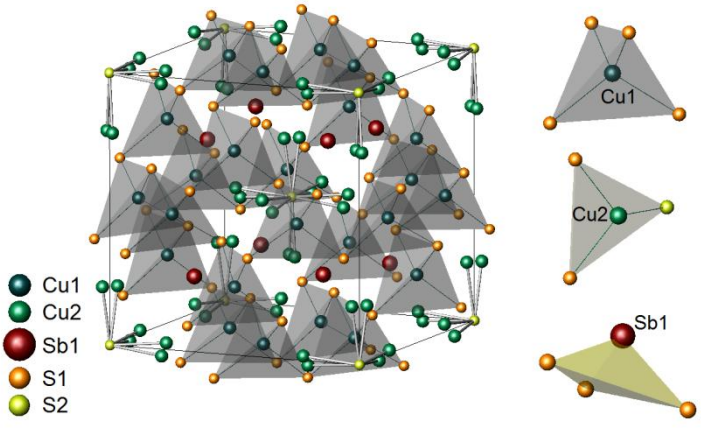

Fig. 1 The overall view of the $Cu_{12}Sb_4S_{13}$ tetrahedrite structure and the polyhedra of individual atoms.

Neither a structural transformation was found upon passing the MST transition, nor any sign of superstructure peaks or reflection splitting was observed. However, the change in the unit cell parameter (see Fig. 2) clearly pointed to structural changes upon passing the MST temperature. The analysis of the interatomic distances showed that these changes are associated with the shift of the Cu(2) atom out of the S_3 triangle plane. Moreover, high values of the atomic displacement parameters (ADPs) for the Cu(2) and S(2) atoms, increasing sharply below the MST temperature, were found. Thus, the positions of Cu(2) and S(2) were examined in more detail for temperatures below the MST. The best refinement results were obtained for the model with S(2) shifting to the 25% occupied 8-fold *x,x,–x* position. Therefore, below the MST temperature the S(2) atoms are displaced from their high-symmetry 2*a* site towards the triangle plane of the $Cu(2)_6$ octahedra, with the displacement increasing upon cooling. At the same time, the Cu(2) atoms move closer to their ideal 12*e* position in the center of the triangular S_3 plane, which is composed of two S(1) and one S(2) atoms (see Fig. 3). These results are published in Chem. Mater., DOI: 10.1021/acs.chemmater.6b02720 (2016).

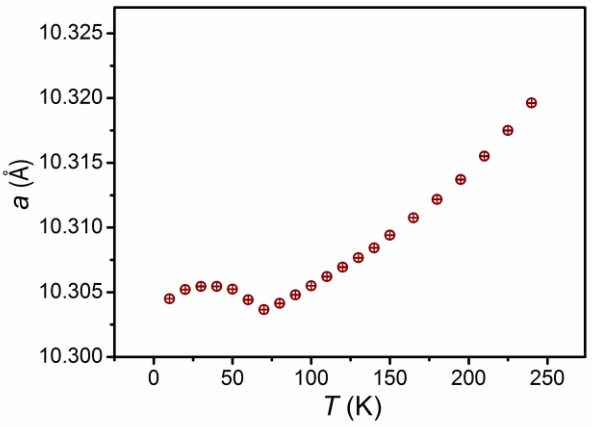

Fig. 2 Temperature dependence of the unit cell parameter for $Cu_{12}Sb_4S_{13}$.

The investigation of the $Cu_{12}Sb_4S_{13}$ structure at high temperatures showed that the compound melts with decomposition in the temperature range between 540 and 570 K.

$Cu_{14}Sb_4S_{13}$, copper-rich tetrahedrite, is the purely Cu^{1+} compound that likely has diamagnetic insulating properties. Similar to $Cu_{12}Sb_4S_{13}$, $Cu_{14}Sb_4S_{13}$ crystallizes in the cubic unit cell with the same I–43m space group, albeit with the slightly larger lattice parameter, around 10.42 Å vs. 10.32 Å. The most important question concerning the $Cu_{14}Sb_4S_{13}$ structure is the position of 2 extra Cu atoms, compared with the parent $Cu_{12}Sb_4S_{13}$ structure.

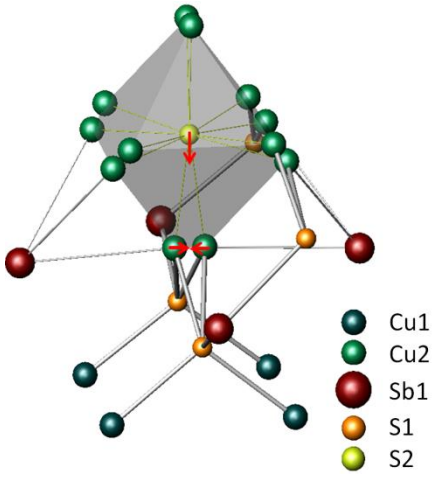

Fig. 3 Structural changes of the tetrahedrite structure, accompanying the MST.

Surprisingly, we were unable to detect any additional position of Cu in $Cu_{14}Sb_4S_{13}$. The two extra Cu atoms per formula unit were simply missing in the refinement. This may be related to the presence of foreign phases in the sample under investigation. Additionally, the extra Cu atoms can be randomly distributed within the tetrahedrite structure. Therefore, further experiments focusing on the local structure may be interesting.

High-temperature investigations of $Cu_{14}Sb_4S_{13}$ showed that the compound melts with decomposition above 500 K.