



	Experiment title: Tetrahedrite Cu ₁₀ (Fe,Zn) ₂ Sb ₄ S ₁₃ and tennantite Cu ₁₀ (Fe,Zn) ₂ As ₄ S ₁₃ : the influence of cation substitution to the mixed-valence state of Cu	Experiment number: HS-2643
Beamline:	Date of experiment: from: 29/04/2005 to: 03/05/2005	Date of report: 24/01/2007
Shifts: 12	Local contact(s): Denis Testemala	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Andrzej Grzechnik ^{1*} , Karen Friese ^{1*} , Tonči Balić-Žunić ^{2*} , Emil Makovicky ² ¹ Departamento de Física de la Materia Condensada, Universidad del País Vasco, Bilbao, E-48080 Spain ² Geological Institute, University of Copenhagen, DK-1350 Copenhagen, Denmark.		

Report:

Phases of the tetrahedrite-tennantite solid solution series with the general composition (Cu,Ag)₁₀(Fe,Zn,Hg,Cu,...)₂(Sb,As)₄S₁₃ are among the most frequent complex sulfides in ore deposits. The crystal structures of the tetrahedrite-tennantite family can be derived from the sphalerite structure type, where a part of the tetrahedra is replaced by other coordination polyhedra. Cu(1) is still coordinated tetrahedrally by S(1), but the coordination around Sb in tetrahedrite (or As in tennantite) is in the form of a trigonal pyramid SbS(1)₃. The Cu(2) atom has a trigonal planar coordination.

The four phases investigated here do not deviate from the ideal stoichiometry M₁₂(Sb,As)₄S₁₃, yet some of the Cu atoms are substituted by Fe. The nominal compositions of the samples are Cu_{11.5}Fe_{0.5}Sb₄S₁₃, Cu₁₀Fe₂Sb₄S₁₃, Cu_{11.5}Fe_{0.5}As₄S₁₃, and Cu₁₀Fe₂As₄S₁₃. If the amount of substitution is low, iron is incorporated as Fe³⁺. With increasing substitution, Fe³⁺ is converted into Fe²⁺, the conversion being complete at a composition of Cu₁₀Fe₂(Sb,As)₄S₁₃. The lattice parameters of tetrahedrite and tennantite can be directly related to the Cu/Fe substitution.

Previous structural studies showed highly anisotropic displacement parameters of the triangular-coordinated Cu(2). In a more recent single crystal investigation of unsubstituted Cu-poor synthetic tetrahedrite, the Cu(2) atom in trigonal planar coordination was modelled using a non-harmonic development of the atomic displacement factor.

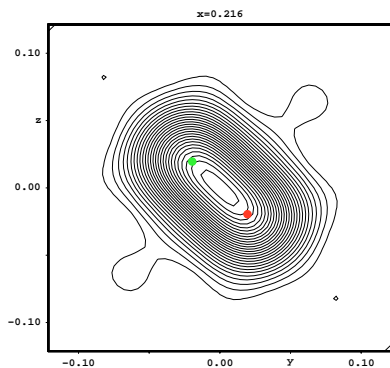
In the present study, based on synchrotron powder diffraction experiments, the Cu2 sites have been modelled (JANA2000) as a pair of flat-pyramidal Cu sites slightly above and below an S1-S2-triangle. This approach is supported by complementary neutron diffraction studies where the Cu(2) position appears clearly split into these two sites with partial occupancy.

Our temperature dependent studies show that with the exception of the y coordinate of Cu(2), the changes in the fractional coordinates of all atoms are very small ($\approx 0.01\text{\AA}$). In the compounds with low substitution the angular distortion of the Cu1S₄ tetrahedra slightly decreases. General decrease of the S-Cu-S angles expresses the increased departure of C2 from the plane of the S1-S1-S2 triangle.

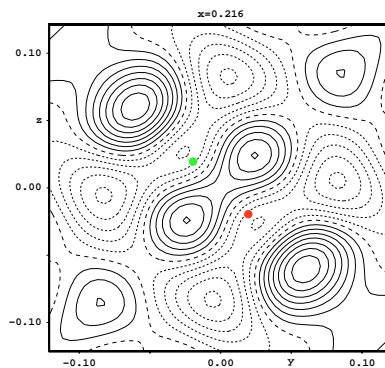
With increasing temperature, the centres of occupancy of the Cu2 site drift further apart. Split/deviation from the triangle plane is about 20% larger in tennantite than in the corresponding tetrahedrite. With rising temperature, Cu2-Cu2 distances approach 2.70-2.75Å, typical for Cu-Cu interactions, which in other sulphides are known to contribute to the stability of the structures.

*Fobs-Fourier Central point $x(\text{Cu}_2), 0, 0$; distances in the three directions $2.5 \times 2.5 \times 2.5 \text{ \AA}$; Contour lines 2.
Difference Fourier Central point $x(\text{Cu}_2), 0, 0$; distances in the three directions $2.5 \times 2.5 \times 2.5 \text{ \AA}$; Contour lines 0.1.*

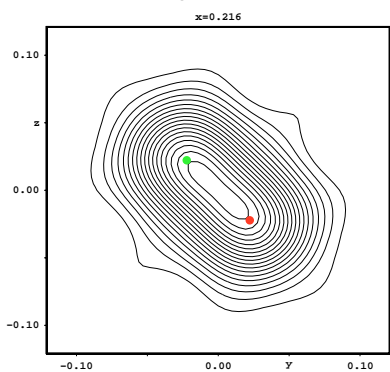
Tetraedrite 1:



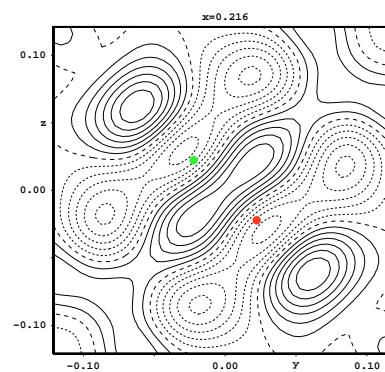
Room Temperature: 55.2



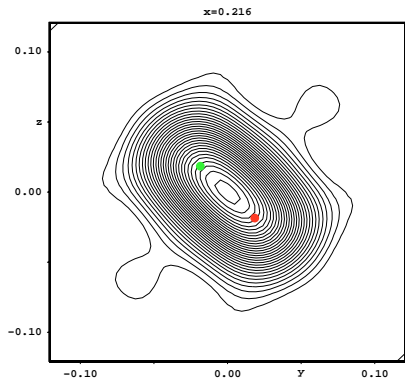
0.83 / -0.55



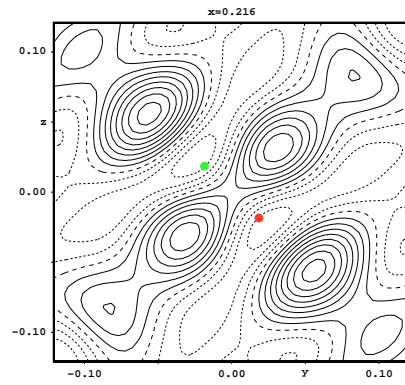
250°C: 37.0



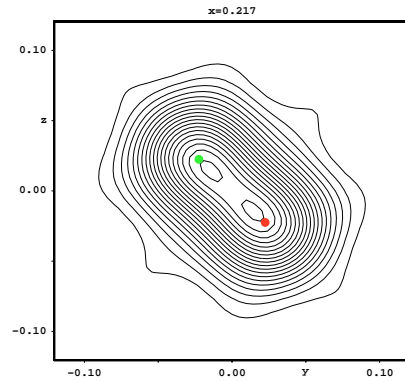
0.87 / -0.58



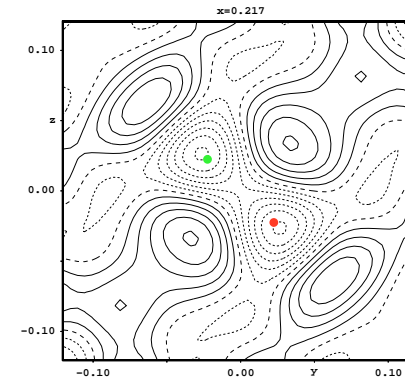
Room Temperature: 61.1



0.95 / -0.71

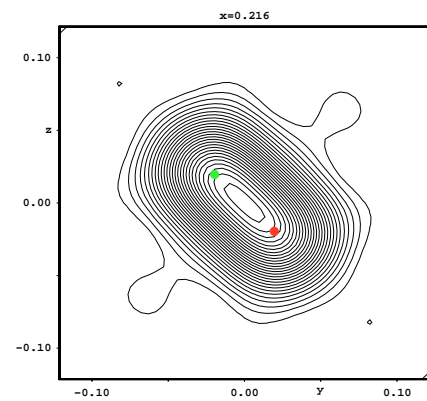


250°C: 38.6

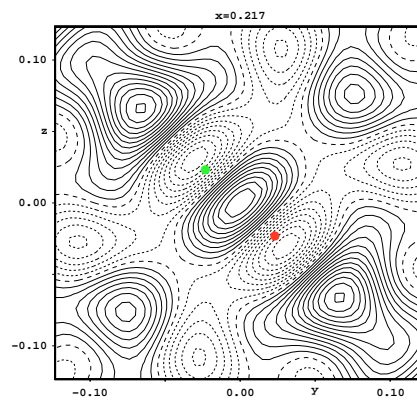


0.64 / -0.66

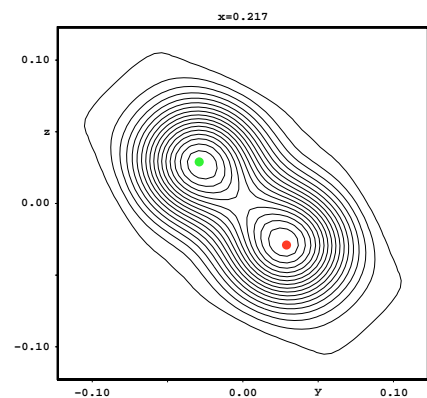
Tetraedrite 4



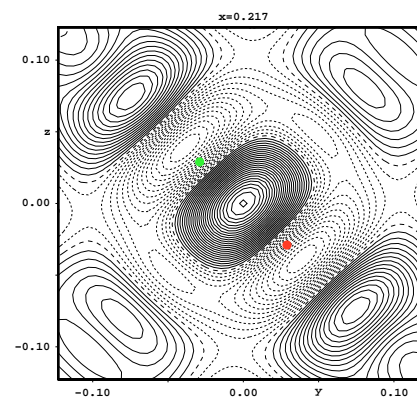
Room Temperature: 58.0



1.40 / -1.10



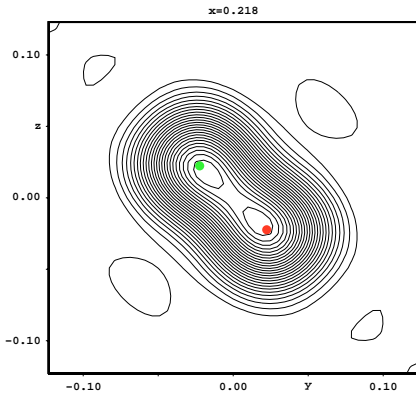
250°C: 45.7



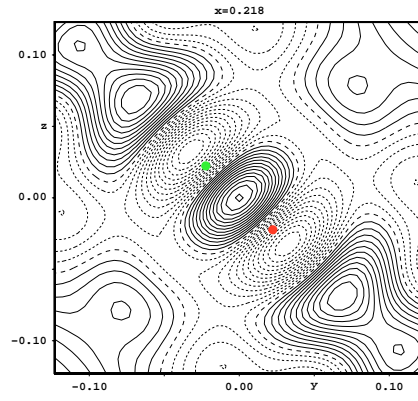
2.60 / -1.97

Tennantite 5

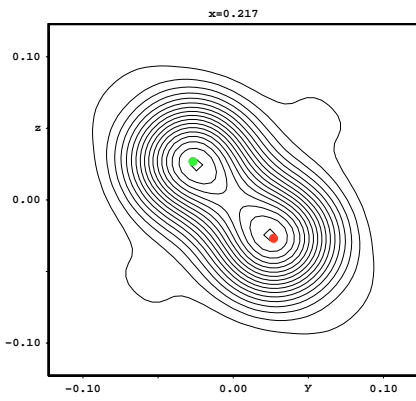
Tennantite 8



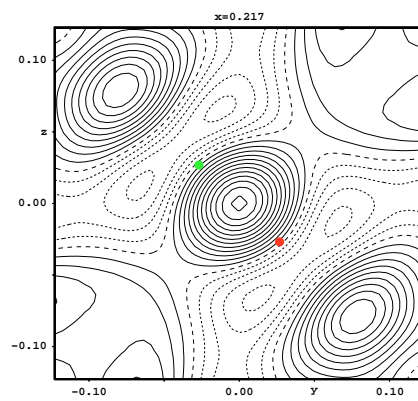
Room Temperature: 55.04



1.54 / -1.37

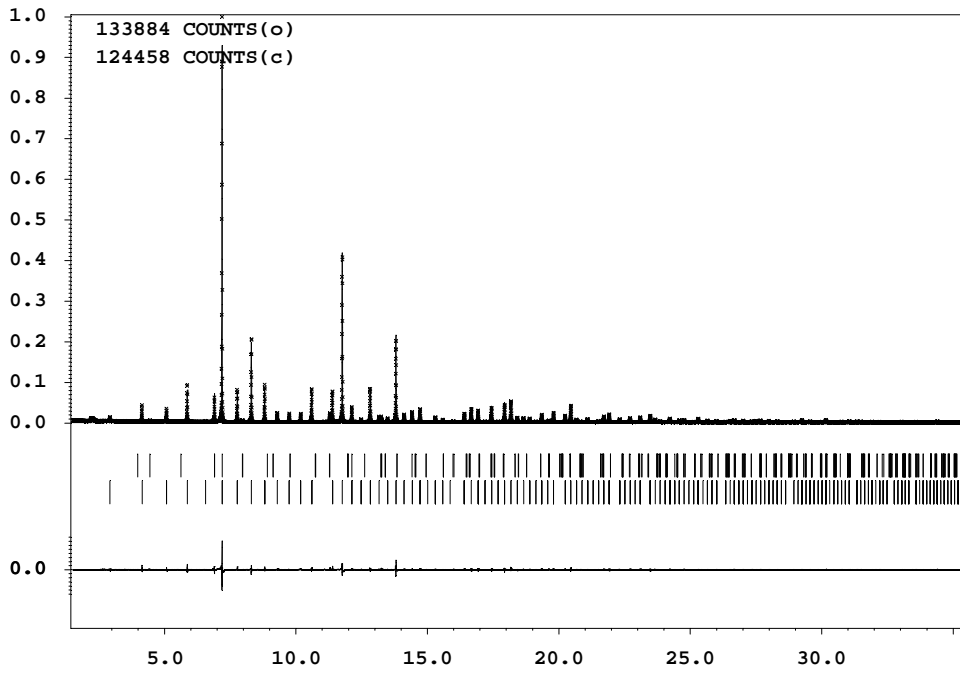


250°C: 43.93



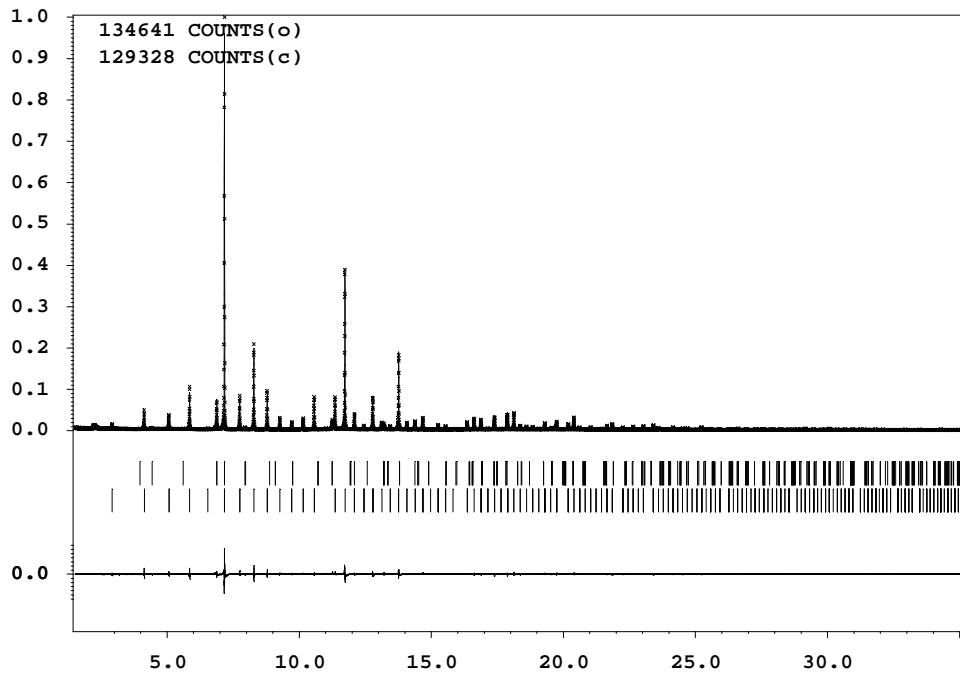
1.24 / -0.87

Powder profile based on prf file



Tetraedrite 1: $Cu_{11.5}Fe_{0.5}Sb_4S_{13}$, Room Temperature: Tetraedrite + Famatinite

Powder profile based on prf file



Tetraedrite 1: $Cu_{11.5}Fe_{0.5}Sb_4S_{13}$, 250C: Tetraedrite + Famatinite