

**ELECTRONIC STATE OF SULFUR IN TETRAHEDRITE-TENNANTITE SERIES:
A MICRO-XANES STUDY**

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Tetrahedrites (*s.l.*) are an important group of economically valuable sulphosalt minerals with ideal simplified formula (WU & PETERSEN, 1977), $(M^{1+})_{10} (M^{2+})_2 (M^{3+})_4 [S_{13}]$, where M^{1+} ions are mainly Cu with some Ag, divalent ions being Cu, Zn, Fe, Hg, Cd, Pb, and trivalent ions Sb, As, Bi. The cubic crystal structure of tetrahedrite (*s.l.*) contains two formula units per unit cell. The atomic array derives from the arrangement in sphalerite - the prototype of so-called "tetrahedral structures" where each one of the constituting ions (Zn^{2+} and S^{2-}) is surrounded by a tetrahedron of species with opposite sign, by leaving unoccupied (vacant) four out of sixteen cubic closest-packing anion positions, and further replacing this tetrahedral cluster of vacancies by one sole S-atom. This replacement process provides pyramidal and triangular coordinations to some of the metal ions, and gives rise to a peculiar coordination and binding situation for one out of thirteen sulphur atoms in the formula unit. The S-atom replacing a tetrahedral cluster of packing vacancies becomes octahedrally coordinated by six close Cu/Ag and additionally by four Sb/As (themselves in pyramidal coordination by S^{2-}) with the lone electron pair probably oriented towards that peculiar central S-atom.

X-ray absorption experiments at the sulphur *K*-edge were performed using the instrumental set-up of beam line ID-21 (SUSINI et al., 2000) at the ESRF* with the purpose of disclosing the influence of the environment (geometry and nature of metal ions coordinating sulphur) and of eventual bonding effects upon details of S 1s XANES spectra.

Samples of minerals belonging to the tetrahedrites-tennantite series with varied chemical composition and geologic provenance (Neves-Corvo mine in Portugal and Atacocha mine in Perú), plus synthetics with established composition within the systems Cu-As-Sb-S were studied.

The general trend of S *K*-edge XANES spectra from tetrahedrites, compared to prototype minerals (e.g. chalcopyrite), is similar but the white line does not occur with similar intensity and some post-edge features display different relative intensity, being sometimes split.

Theoretical calculations and XANES spectra modelling with FEFF8.10 code (ANKUNDINOV et al., 2000) were performed with the purpose of interpreting the observed details, either for the model minerals or the tetrahedrite-tennantite series, both minerals and synthetics.

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References

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