

CRYSTAL CHEMICAL BASES FOR A DATA BANK ON SULPHUR *K*-EDGE XANES SPECTRA IN SULPHIDE AND SULPHOSALT MINERALS

Figueiredo, M.O.¹ & Susini, J.²

¹ Cryst. Miner. Centre, ICT, Al. D. Afonso Henriques, 41-4°, 1000-123 Lisboa, Portugal

² European Synchrotron Radiation Facility (ESRF), BP 220, 38043 Grenoble, France
e-mail: crysmin@clix.pt

The general trend of the X-ray absorption spectrum close to an edge – either *K* for low atomic number elements or *L* for heavier ones – is known to respond to the electronic state of the absorber, allowing for deducing the formal valence of this element mainly through the energy shift observed for the discontinuity.

The atomic vicinity of the absorbing species within the host condensed-phase (that is, the chemical binding) also affects the energy region close to an edge. Beyond depending on the nature of coordinating species, the particular features of pre- and post-edge regions in XANES spectra also reflect the joint influence of geometry and symmetry of the coordination polyhedron – features that are well established in solids with known crystal structure.

Minerals are then suitable model compounds for interpreting XANES data, both through the direct comparison of collected spectra and via theoretical modeling using any of the available calculation codes – e.g. FEFF (ANKUNDINOV et al., 1998), WINXAS (RESSLER et al., 1999). A crystal chemical approach to the mineral crystal structures therefore becomes most useful for disclosing true cause-effect relations.

Sulphur-containing minerals are essentially sulphates with SO_4^{2-} tetrahedra as anionic groups linked to a diversity of cations and not seldom to water molecules, sulphides (isolated S^{2-} anions), disulphides (S_2^{2-} dimers) and sulphosalts where various situations may coexist, including a high coordination number for peculiar S-atoms – e.g. in tetrahedrites (FIGUEIREDO & FERREIRA, 2002). Coordination environments of S^{2-} by metal ions in sulphides range from tetrahedral in sphalerite-type to octahedral in galena-type sulphides, being less regular in sulphosalts (FIGUEIREDO et al., 1988). Both cubic crystal structure types, $\text{Zn}^{\text{I}}[\text{S}^{\text{I}}]$ and $\text{Pb}^{\text{0}}[\text{S}^{\text{0}}]$, as well as the cubic disulphides typified by pyrite $\text{Fe}^{\text{0}}[\text{S}_2^{\text{I}}]$, display wide morphotropic domains. Accordingly, it is possible to find suitable examples for modeling different bonding situations.

If the electronic state of the metal(s) is also studied, the success of theoretically modeling the S *K*-edge XANES spectra is highly enhanced. The building up of a data bank could then be envisaged, under the requisite of strictly quoting the provenance of mineral samples and their physical characteristics. The aim of this work is just to settle the crystal chemical bases for such a data bank, starting with a small illustrative group of sulphide and sulphosalt minerals.

References

- ANKUNDINOV, A.L., RAVEL, B., REHR, J.J. & CONRADSON, S.D (1998): Phys. Rev. B, **58**: 7565-7576.
FIGUEIREDO, M.O., BRIANSÓ, J.L., BASTO, M.J. & ALVAREZ, A. (1988): Acta Geol. Hisp., **23**: 33-38.
FIGUEIREDO, M.O. & FERREIRA, J.A. (2002): 9th Int. Symp. Exp. Miner. Petrol. & Geochem. EMPG-IX, Zürich. Poster MPC-25.
RESSLER, T., WONG, J. & ROOS, J. (1999): J. Synchr. Rad., **6**: 656-658.