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**HOW METALLIC IS THE BINDING STATE OF INDIUM HOSTED BY EXCESS-METAL CHALCOGENIDES IN ORE DEPOSITS?**

M.O. FIGUEIREDO1,2, T.P. SILVA1,2, D.P.S. de OLIVEIRA1,3, D.R.N. ROSA1,3

1 INETI/INEG, Geological Data Centre, Apartado 7586, 2721-866 Alfragide, Portugal

**Introduction**

Discovered in 1863, indium is a strategic scarce metal used both in classical technological fields (e.g. low melting-temperature alloys & getters) and innovative nanotechnologies to produce "high-tech devices" using new materials, namely liquid crystal displays (LCDs), organic light emitting diodes (OLEDs), transparent flexible thin-films [1] with ionic amorphous oxide semiconductors (IAOS).

**Main text**

Indium is a typical chalcophile element, seldom forming specific minerals and occurring mainly dispersed within poly-metal sulphides, particularly with excess metal ions [2]. The average content of indium in the Earth’s crust is very low but a further increase in demand is still expected in next years, thus focusing a special interest in uncovering new exploration sites through promising poly-metallic sulphide deposits – like the Iberian Pyrite Belt (fig.1) [3] – and in improving the recycling technologies.

Indium recovery stands mostly on zinc extraction from sphalerite – the prototypical of "tetrahedral sulfides", where zinc cations fill half of the available tetrahedral sites in a cubic closest packing of sulphide anions (fig.1a). It is worth remarking that this anionic packing (fig.3) is particularly suitable to accommodate polyvalent cations in close interstitial sites, as happens in excess-metal sulphides like bornite, known to be an In-carrier mineral [4].

The crystal chemistry of indium in natural chalcogenides is still under study and X-ray near-edge spectroscopy data so far obtained for polyvalent sulphides are discussed, disclosing a clue for In-binding state in host minerals.

**Problematic**

Ascertaining the tendency to establish In-In interactions capable of leading to the formation of polyvalent polyhedrons would efficiently contribute to the under-standing of crystal chemistry and binding state in natural chalcogenides. Accordingly, an X-ray absorption near-edge spectroscopy (XANES) study was undertaken at the ESRF (European Synchrotron Radiation Facility, Grenoble/France). A first experiment [5] disclosed the presence of a "white line" [6] in the XANES spectra collected from In2S3 (fig.5) and from one sample of sulphide ore (fig.6) but the impossibility of clearly identifying the nanoscale phase hosting indium has hindered a full interpretation of X-ray absorption data.

**Results**

A similar general trend is displayed by In-L3-edge XANES spectra from model compounds In2F5, In2O3, both containing In5+ and In3+, and from two irradiated points in one sample LS 1803 of the Iberian Pyrite Belt (fig.6).

**Comments and conclusions**

The presence of a "white line" (fig.3) in In-L3-edge XANES spectrum denotes non-occupied electronic states in In atoms as pointed out in a recent study [7] on indium oxychloride (natrium azoixitrate) (fig.3) by analogy with silver [8], such edge-shape can be formally assigned to the transition from 2p to 5s state enhanced by an e/2 hybridization. Although the In-L3-edge spectra from indium oxide was already studied in the context of ITO thin-films [9] and the spectra of the metal was discussed a few years ago [10], further study is clearly required to fully interpret the spectra collected from natural chalcogenides – also distinct from the XANES spectra of synthetic spinel-type In2S3 [2].

The closest packing array built up by 5+ anions in the minerals present in ore sample LS 1803 (fig.6) – chalcopryte, sphalerite, galena – is very suitable to lodge polyvalent polyhedrons by filling in closely located interstitial sites. The condensed-model sheet of a single anionic layer figuring out the interstices available between successive packing layers clearly illustrated this (fig.3). Considering that WF6 is also a hexagonal closed-packed compound (fig.5), it is liable that interchanges may occur between locations, thus accounting for singularities of the observed white lines. Further study is in progress to explore this hypothesis.

**References**
