



## How metallic is the binding state of indium hosted by excess-metal chalcogenides in ore deposits?

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Discovered in 1863, indium is nowadays a strategic scarce metal used both in classical technologic fields (like low melting-temperature alloys and solders) and in innovative nano-technologies to produce “high-tech devices” by means of new materials, namely liquid crystal displays (LCDs), organic light emitting diodes (OLEDs) and the recently introduced transparent flexible thin-films manufactured with ionic amorphous oxide semiconductors (IAOS).

Indium is a typical chalcophile element, seldom forming specific minerals and occurring mainly dispersed within polymetallic sulphides, particularly with excess metal ions [1]. The average content of indium in the Earth’s crust is very low but a further increase in its demand is still expected in the next years, thus focusing a special interest in uncovering new exploitation sites through promising polymetallic sulphide ores – e.g., the Iberian Pyrite Belt (IPB) [2] – and in improving recycling technologies. Indium recovery stands mostly on zinc extraction from sphalerite, the natural cubic sulphide which is the prototype of so-called “tetrahedral sulphides” where metal ions fill half of the available tetrahedral sites within the cubic closest packing of sulphur anions where the double of unfilled interstices are available for further in-filling. It is worth remarking that such packing array is particularly suitable for accommodating polymetallic cations by filling closely located interstitial sites [3] as happens in excess-metal tetrahedral sulphides – e.g. bornite, ideally  $\text{Cu}_5\text{FeS}_4$ , recognized as an In-carrying mineral [4].

Studying the tendency towards In-In interactions able of leading to the formation of polycations would efficiently contribute to understand indium crystal chemistry and the metal binding state in natural chalcogenides. Accordingly, an X-ray absorption near-edge spectroscopy (XANES) study at In L3-edge was undertaken using the instrumental set-up of ID21 beamline at the ESRF (European Synchrotron Radiation Facility, in Grenoble/France). Polymetallic chalcogenide minerals and various model compounds displaying distinct bonding situations of indium to other ligands (oxygen and halides) were studied. Encouraging results from a first experiment [5] showed the presence of a “white line” in the XANES spectra collected from  $\text{InF}_3$  and from In-hosting bornite; however, the impossibility of clearly identifying the nanoscale phase hosting indium in sulphide ore samples has hindered a full interpretation of X-ray absorption data.

The crystal chemistry of indium in natural chalcogenides is now reanalysed and XANES results obtained so far for polymetallic sulphides are accordingly re-evaluated, disclosing a challenging clue for indium binding state in these host minerals within sulphide ores.

[1] M.O. Figueiredo et al. (2007) *Proc. 9th Biennial SGA Mtg.*, Dublin/Ireland, ed. C. Andrew et al., 1355-1357. [2] O.C. Gaspar (2002) *Canad. Miner.* 40, 611-636. [3] M.O. Figueiredo & T.P. Silva (2009) *ICANS 23*, 23rd Int. Conf. Amorphous & Nano-crystalline Semiconductors, Netherlands, August 23-28. Poster ID 229 (abstract). [4] T. Seifert & D. Sandmann (2002) *Ore Geol. Reviews* 28, 1-31. [5] M.O. Figueiredo & T.P. Silva (2009) *XVIII Int. Mater. Res. Congr.*, Mexico, August 16-20. Symp. 20, Poster nr. 1 (abstract).

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