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

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Introduction

Discovered in 1863, ***indium is a strategic scarce metal*** used both in classical technologic fields (e.g. low melting-temperature alloys & solders) 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).

Indium is a typical chalcophile element, seldom forming specific minerals and occurring mainly dispersed within poly-metallic 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 In demand is still expected in next years, thus focusing a special interest in uncovering new exploitation sites through promising polymetallic sulphide ores – like the Iberian Pyrite Belt (fig.1) [3] – and in improving the recycling technologies.

Indium recovery stands mostly on zinc extraction from sphalerite – the prototype of “tetrahedral sulphides”, where zinc cations fill half of the available tetrahedral sites in a cubic closest packing of sulphide anions (fig.2). It is worth remarking that this anionic packing (fig.3) is particularly suitable to accommodate polymetallic cations in close interstitial sites [4], as happens in excess-metal sulphides like bornite, known to be an In-carrier mineral [5].

The ***crystal chemistry of In in natural chalcogenides*** is reanalysed and X-ray absorption near-edge spectroscopy data so far obtained for polymetallic sulphides are discussed, disclosing a clue for ***In binding state*** in host minerals.

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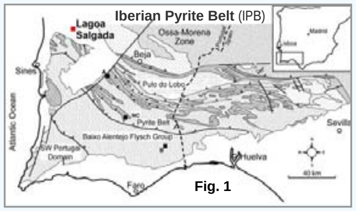


Fig. 1

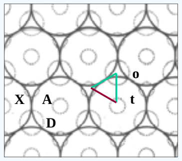
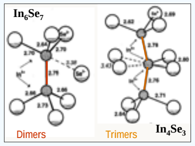


Fig. 3 - Condensed-model standard sheet [6] for $A^t_2 D^o [X]^{c/h}$
Large circles, closest packed atoms (X);
A, tetrahedral (t), and D, octahedral (o) sites.
Ideal radii: $r_t = 0.225\, r_X$; $r_o = 0.414\, r_X$
[**t-o**] and [**t-t**] distances are illustrated.

Fig. 4 – [In_2]$^{4+}$ & [In_3]$^{5+}$ Polycations [11]



MAIN CRYSTAL STRUCTURE-TYPES (*STP*) of NATURAL CHALCOGENIDES (Minerals)

Disulfides

|S=S|= dimers

$Fe^o[|S_2^t|]^{<c>}$

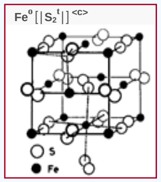


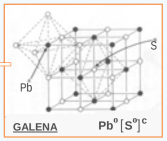
Fig. 2

Superstructures:
1) lacunar closest-packings
2) insertion of extra cations

Octahedral Sulfides

SULPHO-SALTS :

Polysomatic series made-up from slabs extracted from galena structure



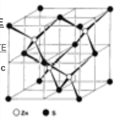
GALENA $Pb^o[S^o]^c$

$S^=$ anions

Tetrahedral Sulfides

WURTZITE
(hexagonal closest-packing of anions)
$Zn^t[S^t]^h$

BLENDE
or
SPHALERITE
$Zn^t[S^t]^c$



Crystal chemical formulae according to J. Lima-de-Faria & M.O. Figueiredo (1976) *J. Solid State Chem.* 16 7-12.

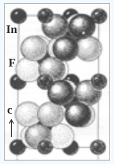
A Brief Survey of In Crystal Chemistry

Assigned in Transbaikalia as a *native metal* associated with lead [7], *indium* (Z=49) has the *electronic structure* [Kr] $4d^{10}\,5s^2\,5p^1$, and frequently assumes the *trivalent state*, thus suggesting the inertness of $5s^2$ electron-pair.

Similarly to gallium but unlike tin – two other important “high-tech” metals - indium seldom forms specific minerals. *Roquesite* ($CuInS_2$) was the first indium mineral to be described [8], followed by *indite* ($FeIn_2S_4$) and *dzhalindite*, $In(OH)_3$, the latter with octahedral In^{3+} [9].

Indium is mainly carried by sphalerite in Nature, either in *solid solution* or *diadochic replacement* and by *excess-metal copper-rich “tetrahedral sulphides”* like *bornite*, $Cu_5^tFe^t[S_4^t]^c$. Only very seldom does indium form specific minerals, an example being *sakuraite*, $(Cu,Ag)_2^t(Zn,Fe)^t(In,Sn)^t[S_4^t]^c$. However, the structural study of *synthetic chalcogenides* [10,11] – In_6Se_7, In_4Se_3, In_4Te_3, InTe, In_7Te_{10} – has revealed the presence of *polymetallic indium ions* – [In_2]$^{4+}$ *dimmers* and [In_3]$^{5+}$ *trimers* (fig.4).

Fig. 5 - Crystal structure of trigonal InF_3 [14], with ideal crystal chemical formula $In^o[F_3]^h$
In^{3+} ions fill only 1/3 of the available octahedral sites.



Problematic

Ascertaining the tendency to establish In-In interactions capable of leading to the formation of metallic polycations would efficiently contribute to the under-standing of In 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 [12] has disclosed the presence of a ”white line” [13] in the XANES spectra collected from InF_3 (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.

Acknowledgements

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Experimental

X-ray absorption experiments at **In *L*$_3$-edge** were carried out using the instrumental set-up of **ID-21 *beamline*** (fig.7).

Polymetallic chalcogenide ores (In ~90ppm) from Lagoa Salgada [15] were irradiated, along with *metallic indium* and various *model compounds* displaying distinct bonding situations of In to other ligands (oxygen and halides).

XANES spectra were collected in fluorescence yield (FY) mode using a photodiode detector mounted in the horizontal plane perpendicular to the X-ray beam. Small sample fragments were irradiated with a beam-size of 1x0.3 μm². A fixed-exit Si (111) monochromator was used, assuring a good *energy resolution* at the In L_3-edge (0.4 eV).

Fig. 7

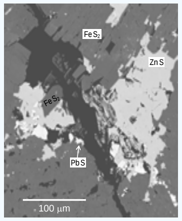
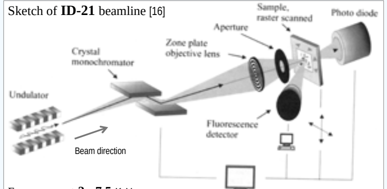


Fig. 6 – Photomicrograph of a polished section from ore sample LS 5-180.6 from Lagoa Salgada [15].
A fissure is shown in black.
Dark grey, pyrite (FeS_2);
light grey, sphalerite (ZnS);
white, galena (PbS).

Sketch of **ID-21** beamline [16]



Energy range: **2 - 7.5** KeV

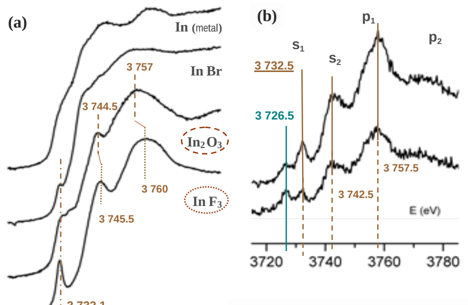


Fig. 8 – **In *L*$_3$-edge** XANES spectra (a) model compounds; (b) points in chalcogenide sample LS 5-180.6

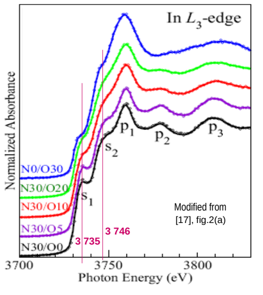
Results

A similar general trend is displayed by In L_3-edge XANES spectra from model compounds InF_3 & In_2O_3, both containing In^{3+} (fig.8a), and from two irradiated points in ore sample LS 5-180.6.

Indium fluoride XANES spectrum shows an intense “white line” at 3732.1eV, also visible - despite weak - in the oxide spectrum. A second shoulder with similar feature occurs in both spectra respectively at 3745.5 eV and 3744.5 eV.

Comparatively to the details observed for the model compounds, chalcogenide ore spectra show an additional *weak white-line* at 3726.5eV (fig.8b).

Fig. 9 – In *L*$_3$-edge XANES spectra of indium oxynitride, considered as an “alloy” phase [17]. Nitrogen-to-oxygen proportions in wurtzite-type InN samples are indicated.



Modified from [17], fig.2(a)

Comments and conclusions

The presence of a *“white line”* [12] in **In *L*$_3$-edge** XANES spectrum denotes non-occupied electronic states in In atoms as pointed out in a recent study [17] on indium oxynitride (wurtzite-type structure) (fig.9). By analogy with silver [18], such edge-shoulder can be formally assigned to the transition from 2*p* to 5*s* state enhanced by an *s*-*d* hybridization.

Although the In L_3-edge spectra from indium oxide was already studied in the context of ITO thin-films [19] and the spectra of the metal was discussed a few years ago [20], further study is clearly required to fully interpret the spectra collected from natural chalcogenides - also distinct from the XANES spectra of synthetic single-type In_2S_3 [21].

The *closest packing array* built up by $S^=$ *anions* in the minerals present in ore sample LS 5-180.6 (fig.6) – chalcopyrite, sphalerite, galena – is very *suitable to lodge polymetallic cations 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 InF_3 is also a hexagonal closest-packed compound (fig.5), it is liable that *interactions may occur* between neighbor In cations, thus accounting for singularities of the *observed white lines*. Further study is in progress to explore this hypothesis.