THE BINDING STATE OF In AND Sn IN NATURAL SULPHIDES: FIRST RESULTS OF A COMPARATIVE STUDY BY X-RAY ABSORPTION SPECTROSCOPY AT THE L-EDGE *

M.O. FIGUEIREDO[1,2] **& T.P. SILVA** [2,1]
[1] CENIMAT/I3N, Materials Sci. Dpt., Fac. Sci. Technol., New Univ. Lisbon, 2829-516 Caparica & [2] LNEG, Geol. Data Centre, Apt. 7586, 2721-866 Alfragide, Portugal

LNEG
Laboratório Nacional de Energia e Geologia

Problematic

One electron in the outer shell makes the difference between In and Sn, two scarce metals with *very distinct crystal chemical behaviour* in the Earth's crust: *indium is clearly chalcophile*, seldom forming specific minerals and occurring mostly dispersed in excess-metal polymetallic sulphides, while *tin is markedly lithophile*.

Indium is nowadays widely used in many technologic fields ranging from solders to high-tech devices and its consumption is expected to increase in the near future, focusing a special interest on the improvement of recycling technologies and on the exploitation of promising *poly-metallic sulphide ores* - e.g., the Iberian Pyrite Belt (fig.1). Despite being extracted mainly from the natural oxide (cassiterite, SnO_2), tin occurrence in sulphide ores is also economically valuable and deserves attention.

The recovery of indium stands mostly on zinc extraction from natural cubic ZnS – sphalerite, the prototype of so-called «*tetrahedral structures*» (fig.2) where the metal ions fill half of the available tetrahedral sites within a cubic closest packing of sulphur anions. This anionic array (fig.3) is particularly suitable to accommodate poly-cations within close edge-sharing tetrahedral sites [1,2], as occurs in excess-metal copper sulphides (e.g., bornite, Cu_5FeS_4), recognized to be relevant In-carrier minerals in polymetallic sulphide ore deposits. Various natural Sn sulphides (e.g., stannite, Cu_2FeSnS_4) display a similar structural situation.

The relevance of assessing the *binding state of In & Sn in natural sulphides* then becomes clear, and the present work describes a contribution to that problematic by using *synchrotron radiation X-ray absorption spectroscopy*.

Fig. 1 — Iberian Pyrite Belt; Lagoa Salgada.

ESRF Grenoble/France

Fig. 5

ID 21 beamline

MAIN CRYSTAL STRUCTURE-TYPES (STP) adopted by NATURAL SULPHIDES

Disulphides |S=S| dimers
$Fe^o[|S_2^t|]^{<c>}$
PYRITE

Octahedral Sulphides
SULPHO-SALTS: Polysomatic series made-up from slabs extracted from galena structure
$S^=$ anions
GALENA $Pb^o[S^o]^c$

Tetrahedral Sulphides
WURTZITE (hexagonal closest-packing of anions) $Zn^1[S^1]^h$
Superstructures:
1) lacunar closest-packings
2) insertion of extra cations

BLENDE / SPHALERITE (cubic closest packing of anions) $Zn^1[S^1]^c$

Fig. 2
Crystal chemical formulae according to J. Lima-de-Faria & M.O. Figueiredo (1976) *J. Solid State Chem.* 16, 7-12.
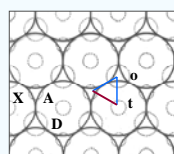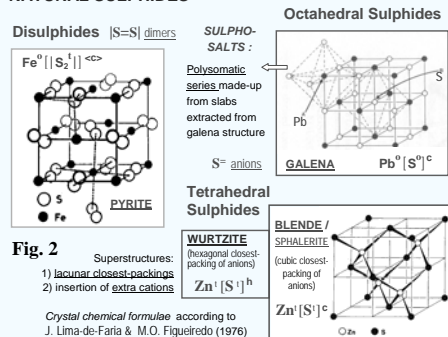

Fig. 3 - Condensed-model [3] standard sheet for $A_1^t D^o[X]^{c/h}$
Large circles, closest-packing atoms (X); A, tetrahedral (t), D, octahedral (o) interstices
Ideal radii: $r_A = 0.225\ r_X$
$r_D = 0.414\ r_X$
[t-o] & [t-t] distances are shown

Experimental

X-ray absorption experiments at In & Sn L_3-edge were carried out at the **ESRF** (European Synchrotron Radiation Facility), using the instrumental set-up of **beamline ID-21** [10,11] (fig. 5).

Polymetallic chalcogenide ores (In ~90 ppm) from Lagoa Salgada [12] (fig.6) were irradiated, along with In & Sn (*metals*) and *model compounds* displaying distinct bonding situations towards various ligands (oxygen, 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, and irradiating directly sample fragments with a beam-size of $1 \times 0.3\ \mu m^2$. A fixed-exit Si (111) monochromator was used for the energy scans, assuring an *energy resolution* of 0.4 eV at the studied L_3-edges.

Fig. 7 - Topochemical mapping of irradiated area in sample LS5-180.6. Red, maximum, and blue, minimum, concentration of the selected element (In or S)

In & Sn Crystal Chemistry: similarities & differences

Assigned in Transbaikalia as a *native metal* associated to lead [4], *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. With one more electron, *tin* (Z=50) has an electronic structure [Kr] $4d^{10}\ 5s^2\ 5p^2$, and *stable formal valences* (2+) and (4+). Contrary to tin that is largely widespread as an oxide (*cassiterite*), indium seldom forms specific minerals; *roquesite* ($CuInS_2$) was the first In-mineral to be described [5], followed by *indite* ($FeIn_2S_4$) - both with In in tetrahedral coordination by $[S^=]$ anions - and *dzhalindite*, $In(OH)_3$, with octahedral cations In^{3+} [6].

Excess-metal copper-rich "*tetrahedral sulphides*" may incorporate both In and Sn in diadochic replacement, as exemplified by the rare mineral *sakuraite*, $(Cu,Ag)_2(Zn,Fe)(In,Sn)\ S_4$ [7]. The synthesis of *excess-metal In-Se chalcogenides* [8] disclosed the occurrence of *polymetallic indium ions* − $[In_2]^{4+}$ *dimmers* and $[In_3]^{5+}$ *trimers* (fig.4). Conversely, metal-metal binding seems unfavorable for tin, as illustrated by the regular double tetrahedra $[Sn_2S_6]$ occurring in meso-structured semiconductor phases [9].

In_6Se_7 — Dimers — Trimers — In_4Se_3

Fig. 4 — Reproduced from [8]

Fig. 6 - Photomicrograph from a polished section of ore sample LS 5-180.6
In black, a fissure; dark grey, pyrite (FeS_2): light grey, sphalerite (ZnS); white, galena (PbS). 100 μm

Results

X-ray absorption spectra reflect the **local symmetry** and the **chemical bonding** of the absorbing element and the **band character** of the compound through the position of the *edge jump* and the *details* that follow.

L_3-edge XANES spectra collected by irradiating selected points (fig.7) in the ore sample (figs.8a & 9b) display *two shoulders* (s_1 & s_2, see fig.10 [13]) separated by ~10eV (fig.11). once In & Sn are both $4d^{10}$ elements, such details may indicate electronic transitions to unoccupied *d* states above the Fermi level, possibly 5d orbitals fivefold degenerated by the ligands [14]. Beyond these shoulders, a "*white-line*" [15] was observed at 3726.5 eV (fig.8a) and it constitutes the unique detail registered before the edge (3730 eV) in the In L_3-edge XANES spectrum collected at another point of the studied chalcogenide ore sample.
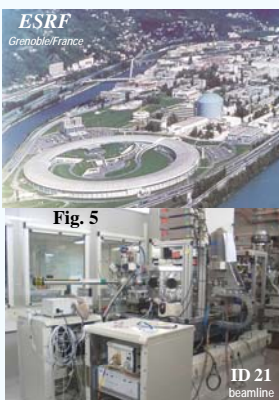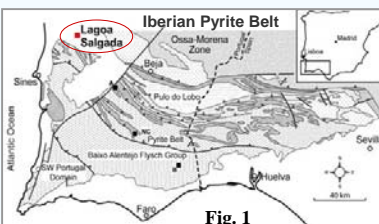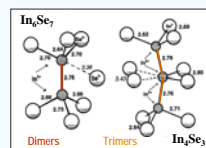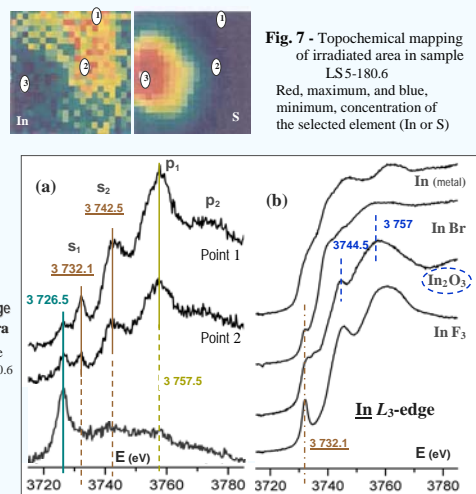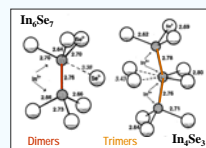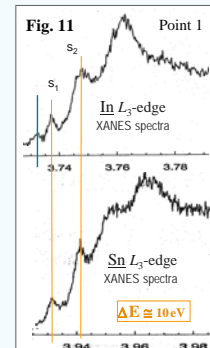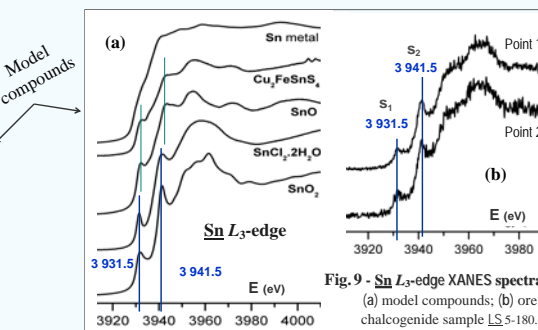

Fig. 8 - In L_3-edge XANES spectra
(a) points in ore sample LS 5-180.6
(b) model compounds.

Point 1, Point 2; s1 3 732.1, s2 3 742.5, 3 726.5, 3 757.5, p1, p2, 3 732.1
In (metal), In Br, In2O3 3744.5 / 3 757, In F3
In L_3-edge

Fig. 9 - Sn L_3-edge XANES spectra: (a) model compounds; (b) ore chalcogenide sample LS 5-180.6

(a) Sn metal, Cu_2FeSnS_4, SnO, $SnCl_2.2H_2O$, SnO_2; Sn L_3-edge; 3 931.5, 3 941.5
(b) Point 1, Point 2; s2 3 941.5, s1 3 931.5

Fig. 10 - In L_3-edge XANES spectra of indium nitride and oxynitrides with wurtzite crystal structure-type [13]

In L_3-edge; N0/O30, N30/O20, N30/O10, N30/O00; In_2O_3; $In_2^6[O_3\square]^{Qs}$ Bixbyite structure; wz-InN; $In^1[N]^h$ Wurtzite STP; F=0.38, F=0.49; Calculated spectra fig.2(b); From [13] fig.2(a)

Fig. 11 Point 1
In L_3-edge XANES spectra
Sn L_3-edge XANES spectra
$\Delta E \cong 10\ eV$

Final Comments

The *closest packing array* built up by $S^=$ anions in *tetrahedral sulphides* is particularly *suitable to house polymetallic ions by filling closely located interstitial sites* (fig.3). Once synthetic In-selenides display metal-metal bonding, it is not to exclude that *interactions may also occur between In-cations in natural chalcogenides*. This fact could account for the mentioned singularity of an extra *white line* present in the L_3-edge XANES spectra of In but not observed for Sn compounds [16].

The exact nature of this absorption detail is yet to be interpreted and further study of natural-plus-synthetic phases is in progress.

References

[1] M.O. FIGUEIREDO *et al.* (2007) *Procd. 9th Biennial SGA Mtg.*, Dublin/Ireland, edt. C. Andrew *et al.*, 1355-1357..
[2] M.O. FIGUEIREDO & T.P. SILVA (2009) *ICANS 23, 23rd Int. Conf. Amorphous & Nano-crystalline Semiconduct.*, Netherlands, August 22-23. Poster, Book of Abstracts, p. 173.
[3] J. LIMA-de-FARIA (1965) *Zeit. für Kristallogr.* 122, 346-358.
[4] V.V.IVANOV (1964) Cf. *Handbook of Geochem.* (1974) Springer-Verlag, vol. II-4, p. 49-A.
[5] P. PICOT & R. PIERROT (1963) *Bull. Soc. Fr. Min. Crist.* 86, 7-14.
[6] A. GENKIN & I.V. MURAVEVA (1963) Cf. *Amer. Min.* 49, 493.
[7] M. SHIMIZU *et al.* (1986) *Can. Min.* 24, 405-9.
[8] M. EPPLE *et al.* (2000) *Zeit. für Kristallogr.* 215, 445-453.
[9] K.K. RANGAN *et al.* (2002) *Nano-Letters* 2, 513-517.
[10] J. SUSINI *et al.* (2000) *Amer. Inst. Phys.* 507, 19-28.
[11] J. SUSINI *et al.* (2002) *Surf. Rev. Lett.*, 9, 203-211.
[12] D. OLIVEIRA *et al.* (2009) *10th Biennial SGA Mtg.*, Townsville/ Australia, edt. P.J. Williams *et al.*, vol. I, 424-426.
[13] J. T-THIERPRASERT *et al.* (2008) *Appl. Phys. Lett.* 93, 051903.
[14] T.K. SHAM (1985) *Phys. Rev. B* 31, 1888-1902.
[15] Y. CAUCHOIS & N.F. MOTT (1949) *Phil. Mag.* 40, 1260.
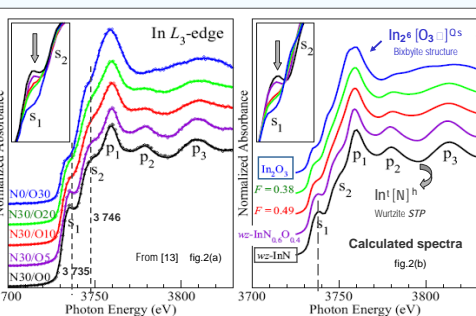[16] Z. LIU *et al.* (2004) *J. Electr. Spectr. Related Phen.* 135, 155-158.