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Tin oxidation number and the electronic structure of $SnS-In_2S_3-SnS_2$ systems

I. Lefebvre
Universität des Saarlandes, Saarbrücken, Germany

M. Lannoo
Laboratoire d'Etude des Surfaces et Interfaces, 41 Boulevard Vauban, 59046 Lille CEDEX, France

J. Olivier-Fourcade and J. C. Jumas
Université du Languedoc, place Eugene Bataillon, 34060 Montpellier CEDEX, France

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We analyze the meaning of the chemical notion of tin oxidation number from the study of several phases isolated in the $SnS-In_2S_3-SnS_2$ diagram. From ^{119}Sn Mössbauer spectroscopy it has been concluded that two oxidation numbers II and IV exist for tin in these compounds. This has been used to make some hypotheses on the local atomic structure. Tight-binding calculations are performed to characterize Sn II and Sn IV and to check these hypotheses. We conclude that the difference between Sn II and Sn IV mainly corresponds to a variation of about 0.7 Sn 5*s* electrons, in agreement with Mössbauer results, and that the Sn II atoms are always in strongly distorted sites. The validity of the predicted densities of states is also checked by comparing them with available photoemission spectra.

INTRODUCTION

Tin atoms have an electronic configuration $4d^{10}5s^25p^2$. In compounds, their configuration can be different and is often characterized by its so-called oxidation number, which is assigned in a conventional way. However, this assignment corresponds to extreme hypothetical situations and, therefore, it does not take the real electronic structure into account. In the sulfur binary compounds SnS and SnS_2, tin atoms are found with the oxidation numbers II and IV, respectively. When Sn is in its lowest state (II), it is believed to be characterized by a lone pair $5s^2$, which does not take part in the bonding. On the contrary, for Sn IV atoms, some of the 5*s* electrons should participate in the bonding. In the pseudoternary system (Fig. 1) $SnS-In_2S_3-SnS_2$, several phases have been isolated.[1-3] Among them, some must contain both Sn II and Sn IV atoms and are named mixed-valence tin compounds. A solid-solution region has been pointed out in the ternary system where mixed-valence materials are based on the spinel form of In_2S_3. These spinel-type compounds seem to be good intercalation host materials for lithium and can offer the possibility of reversible electrodes.

Up to now, a structural study of these phases has been carried out using mainly x-ray-diffraction spectroscopy. But, as Sn and In atoms have nearly the same atomic number, it is not possible to differentiate between them in terms of x-ray diffraction. To solve this problem in the structural study, ^{119}Sn Mössbauer spectrometry (which gives information on the electronic distribution around tin atoms) is used to propose structural hypothesis on the environment of Sn II and Sn IV atoms.

The aim here is to characterize the tin oxidation numbers in sulfurs from a solid-state-physics point of view. This will allow us to determine the detailed electronic structure of Sn atoms in relation to the local environment and to check the structural hypotheses that have been proposed. We first choose three well-known sulfurs to describe the oxidation number: $Sn^{II}S$, $Sn^{IV}S_2$, both of which correspond to typical cases, and Sn_2S_3, which is a mixed-valence tin compound. Then we consider two compounds in the ternary diagram where S and In atomic positions have been deduced from ^{119}Sn Mössbauer spectroscopy: $In_2Sn_3S_7$ (mixed valence) and $In_{16}Sn_4^{IV}S_{32}$ (spinel-type compound) in order to check the hypothesis on the atomic positions.

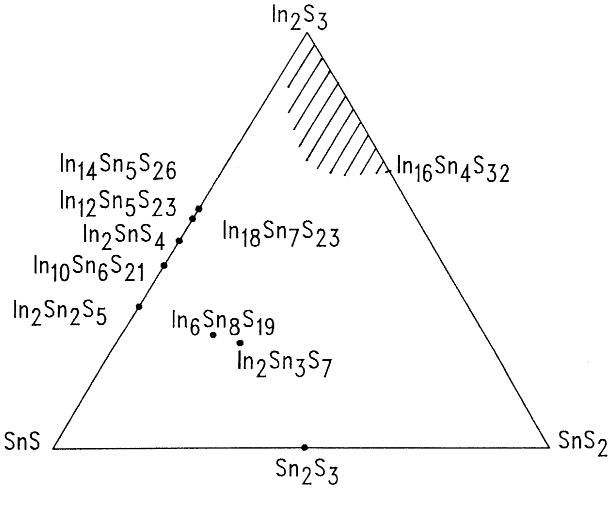

FIG. 1. Pseudoternary diagram for the $In_2S_3-SnS-SnS_2$ system. The solid solution for the spinel structure is shaded.

In the first part we recall the notation of oxidation state (or oxidation number) as used in chemistry. We also show how Mössbauer spectroscopy can be used to differentiate between oxidation numbers and helps to form hypotheses concerning the local atomic structure. We then use the tight-binding method, which allows us to perform band-structure calculations even for large numbers of atoms per unit cell (up to 52 for spinel forms), which characterize these systems. This method is introduced in Sec. II. We apply it in Sec. III to analyze the tin valence state in the sulfur compounds. Finally, we examine the case of the indium sulfurs (Sec. IV).

I. OXIDATION NUMBERS IN INORGANIC CHEMISTRY

Let us first recall the definition of the oxidation number of an atom in a molecular or crystalline environment. It is the *net charge* (in units of e) that the atom would have if the bonds were treated in the *purely ionic limit*, i.e., if all the electrons of a bond were assigned to the more electronegative atom. Of course such a definition depends on the use of an electronegativity scale, such as Pauling's. It suffers from some ambiguity, e.g., when two elements are of comparable electronegativity or when the atomic structure becomes too complex with several different types of atoms. However, in a fairly large number of situations, the oxidation number represents a very useful tool that characterizes the electronic structure of an atom in a given local environment, as confirmed by a great deal of experimental information.

Let us illustrate this notion in cases of increasing complexity. For heteropolar diatomic molecules involving oxygen, this one is the most electronegative element so that it takes its maximum negative oxidation number II^-. On the other hand, in a molecule like HCl, Cl is the most electronegative element and hydrogen has the oxidation number I^+. If we now consider ionic solids like NaCl, Pauling's electronegativities are 0.9 for Na and 3.0 for Cl, so that the oxidation numbers are Na I^+ and Cl I^-. More complex molecules like the permanganate anion $\text{MnO}_4{}^-$ follow the same rules: the oxygens are all in the state O II^-, so that the oxidation number of Mn is VII^+. The case of SbCl_5 is similar and one finds Sb V^+.

Here we shall be concerned with tin atoms. Neutral Sn has an electronic configuration $4d^{10}5s^25p^2$. With sulfur it can give rise to two binary compounds SnS and SnS_2. Pauling's electronegativities are 1.8 for Sn and 2.5 for S. According to our definition, the oxidation number of Sn will thus be II in SnS and IV in SnS_2 (from now on we drop the superscript + for Sn, which will always have a positive oxidation number for the systems considered here). The corresponding electronic configuration of Sn would thus be $4d^{10}5s^2$ (II) and $4d^{10}$ (IV). In this oversimplified picture, the bonding corresponding to the two oxidation numbers should thus be completely different. For Sn II, two $5p$ electrons should be engaged in bonds while the two $5s$ electrons should form a lone pair, inducing a distortion of the local environment.[4] This effect is called the lone-pair stereochemical activity. Of course, this would not occur for Sn IV. However, such simple reasoning, even if it can lead to the correct conclusion concerning the distortion of the local environment around the Sn atom, is obviously not strictly correct. This is due to the fact that the bonds are never perfectly ionic, which means that the amount of $5s$ electrons on Sn IV is certainly nonzero. Furthermore, the notion of atomic charge in a solid is ill-defined since it depends on what is chosen as the atomic volume. However, one can hope that whatever the definition of the atomic charge is, there will be some correlation between the calculated charge and the corresponding oxidation number.

An experimental tool that reflects the oxidation number of Sn is ^{119}Sn Mössbauer spectroscopy (Fig. 2 shows such a correlation for the isomer shift). This technique allows us to study the electronic structure of solids on an atomic scale. It is based on the charge in transition energy between two nuclear levels, caused by electrostatic interaction of the nuclear charge distribution with the electronic distribution around atoms (here, around Sn atoms). One of the Mössbauer parameters is the isomer shift δ, which can be written as (in units of the Système International)

$$\delta = \left[S(Z)\frac{1}{5\epsilon_0} Ze^2 R_{\text{eff}}^2 \left[\frac{\Delta R}{R} \right] \right] \times [|\Psi_a(0)|^2 - |\Psi_s(0)|^2] \ , \qquad (1)$$

where the first term is a nuclear factor: $S(Z)$ for the relativistic effect,[5] R_{eff} for the effective radius of the Sn nucleus,[6] and $\Delta R / R$ is a nuclear calibration constant.[6,7] $|\Psi(0)|^2$ reflects the electron density at the nucleus and can be considered as proportional to N_s, the number of Sn($5s$) electrons in the valence band of the compounds. From the variation of δ one can derive the change in N_s and thus correlate the number of $5s$ electrons to the oxidation number.

For the class of solids considered here, a very interesting example of the usefulness of the notion of oxidation number is $\text{In}_2\text{Sn}_3\text{S}_7$. The electronegativities of the constituting elements are 1.7 (In), 1.8 (Sn), and 2.5 (S). Although they are comparable for In and Sn, we apply strictly the simplified reasoning, leading us to conclude that S will be found as S^{2-} while In will take the ionic

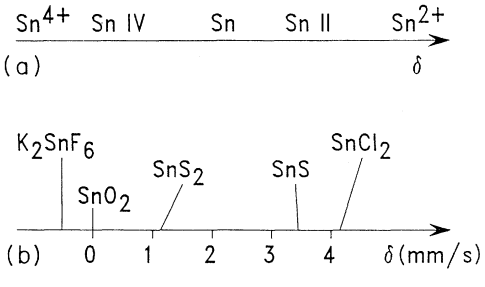

FIG. 2. Scales for the Mössbauer isomer shift: (a) the qualitative one showing the correlation between δ and the oxidation number of tin; (b) the quantitative one where extreme cases and tin sulfides are positioned.

form In^{3+}. This means that the average oxidation number of Sn must be $(14-6)/3$, i.e., $+\frac{8}{3}$. This could correspond to an average oxidation number for each Sn in the structure. However, from the evidence that SnS and SnS_2 are stable, one could also assume that Sn could be found either as Sn II or Sn IV. If this is true, the only way to get an average value of $\frac{8}{3}$ with three Sn atoms is to have one Sn IV for two Sn II. The striking fact is that it is exactly what is found by Mössbauer spectroscopy.

This example shows the power of the notion of oxidation number. However, it has been used with care. For instance, the molecule H_2O_2 (hydrogen peroxide) is such that there is an O—O bond and two O—H bonds. In that case the two H become H^+ and the oxidation numbers are I^+ for H and I^- for O. This differs from O II^-, which would not be possible anyway since H cannot give more than one electron. Another more complex case is CuS, where standard reasoning would give Cu II^+ and S II^-. However, there are short S—S bonds[8] so that one must consider $(S_2)^{2-}$ and S^{2-} as separate entities. One must then find Cu in an average oxidation state, corresponding to a mixed-valence compound. This means that the oxidation number (or valence) is intimately related to the local atomic structure.

II. TIGHT-BINDING METHOD

We now want to characterize the tin oxidation numbers from a solid-state point of view for compounds containing indium and sulfur atoms. For this we have to perform a band-structure calculation and we use the empirical tight-binding (TB) method. This choice is mainly due to the fact that some of the compounds we study have a large number of atoms per unit cell (up to 54). The tight-binding approach is a well-documented procedure[9] that allows one to obtain much valuable information on the electronic structure of zinc-blende semiconductors.[9] It has been extended recently to more complex systems, such as antimony chalcogenides[10] or InP oxides.[11] In this method, the wave function is expressed as a linear combination of atomic orbitals (LCAO theory):

$$\Psi(r)=\sum_{j,\alpha} c_{j,\alpha}\varphi_{j,\alpha}(r) \ , \tag{2}$$

where $\varphi_{j,\alpha}$ is the αth orbital belonging to atom j. We make use of a "minimal basis set" of atomic functions φ, consisting of one s and three p orbitals for each atom. In this basis, the energy levels are the solutions of the secular equation

$$\det|H-ES|=0 \ , \tag{3}$$

where H is the Hamiltonian matrix, the elements of which are

$$H_{i\alpha,i\alpha}=\langle\varphi_{i\alpha}|H|\varphi_{i\alpha}\rangle \ , \tag{4}$$

the atomic energy in the solid, and

$$H_{i\alpha,j\beta}=\langle\varphi_{i\alpha}|H|\varphi_{j\beta}\rangle \ , \tag{5}$$

the hopping integral, and S is the overlap matrix, the terms of which are

$$S_{i\alpha,j\beta}=\langle\varphi_{i\alpha}|\varphi_{j\beta}\rangle \ . \tag{6}$$

In the TB approximation one takes $S_{i\alpha,j\beta}=\delta_{ij}\delta_{\alpha\beta}$. We also use (as is commonly done in TB calculations) the two-center approximation: $H_{i\alpha,j\beta}$ only depends on $i\alpha$ and $j\beta$. Then, the $H_{i\alpha,j\beta}$ can be expressed in terms of four independent nonvanishing terms: $H_{ss}(i,j)$ $H_{s\sigma}(i,j)$, $H_{\sigma\sigma}(i,j)$, and $H_{\pi\pi}(i,j)$, where σ and π correspond to p orbitals, respectively, pointing towards the neighbor and perpendicularly to the i,j bond. In order to have a coherent description of all compounds, we use the same semiempirical law to parametrize the interatomic interactions:

$$H_{\alpha\beta}(i,j)=\eta_{\alpha\beta}\frac{\hbar^2}{m}\frac{1}{\Sigma_{ij}^2}\exp\left[-2.5\left[\frac{d}{\Sigma_{ij}}-1\right]\right] \ , \tag{7}$$

where Σ_{ij} is the sum of the i and j atomic radii (In, 1.56 Å; Sn, 1.45 Å; S, 0.88 Å) (Ref. 12) and $\eta_{\alpha\beta}$ are empirically determined coefficients. Their values are[13] $\eta_{ss}=-1.32$, $\eta_{sp}=1.42$, $\eta_{pp\sigma}=2.22$, and $\eta_{pp\pi}=-0.63$. This law [Eq. (7)] has been successfully used to calculate the electronic structure of other complex families of compounds.[10,11,14] We also use the same cutoff distance $R_c(i,j)=1.4\Sigma_{ij}$ to take into account the extension of the atomic orbitals compared with the interatomic distance. The hopping interactions $H_{\alpha\beta}(ij)$ are neglected for distances greater than R_c. The intra-atomic terms are the atomic energy levels tabulated by Herman and Skillman[9] (Table I).

As this method is semiempirical, the results have to be tested by comparing the results to experimental data. The tight-binding method generally gives a correct prediction of valence bands. If the TB parameters used are good, the calculated density of states should reflect what is experimentally obtained with x-ray photoemission spectroscopy. To do this, we have taken advantage of the transitional periodicity of the crystal by the use of Bloch's theorem. We have thus to diagonalize a $4N\times4N$ matrix for each $\mathbf{k}$ vector (where N is the number of atoms per unit cell). To determine the density of states, the energy $E(k)$ is calculated for "special k points" in the Brillouin zone.[15] It allows one to determine histograms that are broadened by convolution with a Gaussian to compare results with experiment. One has also to take into account the effect of the photoemission cross sections. This can be done simply by multiplying the partial densities of states by the corresponding cross sections that are tabulated[16] for the free atoms (Table II). However, this must be used with caution because atoms in solids do not necessarily have the same cross sections as the free atoms. So we only take them as a guide in order to have

TABLE I. Atomic energies (in eV) from Herman-Skillman values (Ref. 9).

	In	Sn	S
E_s	-10.12	-12.50	-20.80
E_p	-4.69	-5.94	-10.27

TABLE II. Photoemission cross sections for free atoms (Ref. 16) at 1487 eV (Al $K\alpha$ line) in units of 13 600 b.

Atom	Level	Cross section
S	$3s_{1/2}$	0.1465
	$3p_{1/2}$	0.0262
	$3p_{3/2}$	0.0512
In	$5s_{1/2}$	0.0755
	$5p_{1/2}$	0.0065
	$5p_{3/2}$	0.0126
Sn	$5s_{1/2}$	0.0922
	$5p_{1/2}$	0.0203
	$5p_{3/2}$	0.0377

TABLE III. For each compound, the number N and distance d (in Å) of X-S bonds.

	X	N	d
SnS_2	Sn	6	2.564
SnS	Sn	1	2.627
		2	2.665
		2	3.290
		1	3.388
Sn_2S_3	Sn_0	1	2.497
		2	2.543
		1	2.551
		2	2.611
	Sn_{tb}	2	2.644
		1	2.741
		1	3.152
$In_2Sn_3S_7$	Octahedron	1	2.514
		1	2.580
		2	2.605
		2	2.630
	Octahedron	2	2.585
		2	2.589
		1	2.656
		1	2.670
	Bicapped trigonal prism	1	2.707
		2	2.885
		2	3.046
		2	3.309
		1	4.433
In_2S_3			
	(In)	4	2.474
	[In]	6	2.614
$In_{16}Sn_4S_{32}$			
	(X)	4	2.452
	[X]	6	2.606

some insight concerning the experimental spectra. On the figures, we only present the partial and total densities without the cross-section effect, which is discussed in the text. To analyze the difference between the II and IV oxidation numbers of tin atoms, we also calculate the number of 5s and 5p electrons on Sn in the valence band. These numbers can be written as

$$N_\alpha = 2\sum_{n,k} f_{n,k} |\langle \Phi_\alpha | \Psi_{n,k} \rangle|^2 , \tag{8}$$

where $\Psi_{n,k}$ is the Bloch state of wave vector k belonging to band n, $f_{n,k}$ is the occupancy factor equal to unity for filled bands and zero for empty bands, and the Φ_α are the s and p states of one of the Sn atoms.

III. TIN IN SULFIDES

We first study the case of binary tin sulfide compounds, where the tin atom positions are not ambiguous. In the pseudobinary system SnS-SnS_2, only the Sn_2S_3 compound has been synthesized and studied. The oxidation number of tin in these materials is IV in SnS_2, II in SnS, and intermediate in Sn_2S_3 (as we shall see, there will be an equal number of Sn II and Sn IV in this case). Our ^{119}Sn Mössbauer data used here[3,17,18] are in good agreement with the literature.[19–25]

The semiconducting tin dichalcogenide crystallizes in the hexagonal CdI_2 type of structure.[26] Tin atoms have a perfect octahedral environment of sulfur atoms (Table III) and the Mössbauer isomer shift [$\delta = 1.13$ mm/s (Ref. 3)] is, by definition, characteristic of Sn IV. Williams *et al.*[27] have already studied its band structure by photoemission spectroscopy and a tight-binding calculation[28] (where parameters were fitted) but the detailed electronic population on tin has not been calculated. In order to compare the tin electronic state with other compounds, we have calculated the SnS_2 band structure with the method explained above. The theoretical density of states (DOS) (Fig. 3) is characterized by two features. There is one peak corresponding to S(3s) states at the bottom of the valence band, which begins to appear on the experimental spectrum. The structure near the top of the valence band is composed of three peaks, as it is for the photoemission spectrum. Peak I mainly corresponds to S(3p) states and peaks II and III to the interaction of S(3p) with Sn(5s) and Sn(5p), respectively. There is also good agreement between the experimental forbidden band gap [2.3 eV (Ref. 29)] and the theoretical value (2.57 eV). To define Sn IV in sulfurs, we calculate (Table IV) the number of Sn(5s) and Sn(5p) electrons in the valence band (as explained in Sec. II). We find that there is 1.22 Sn(5s) valence electrons.

The tin monosulfide $Sn^{II}S$ crystallizes in the orthorhombic GeS type of structure.[26] The local environment of tin atoms is a sulfur distorted octahedron (Table III): three Sn—S bonding distances are short (around 2.6 Å) while the other Sn—S bond lengths are greater than the cutoff distance. This distorted environment corresponds to the notion of stereochemical activity of the Sn($5s^2$) lone pair discussed in Sec. I and to the oxidation number II [$\delta = 3.31$ mm/s (Ref. 17)]. The theoretical DOS (Fig.

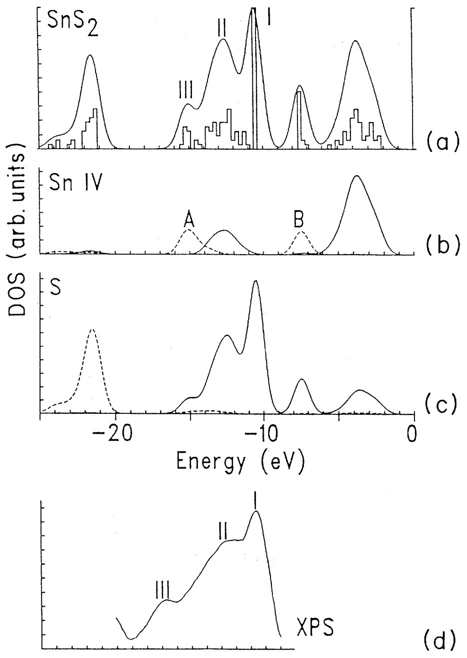

FIG. 3. SnS$_2$ theoretical densities of states: (a) the total one; (b) and (c) the partial *s* states (dashed lines) and *p* states (solid line), compared to (d) the x-ray photoemission spectrum.

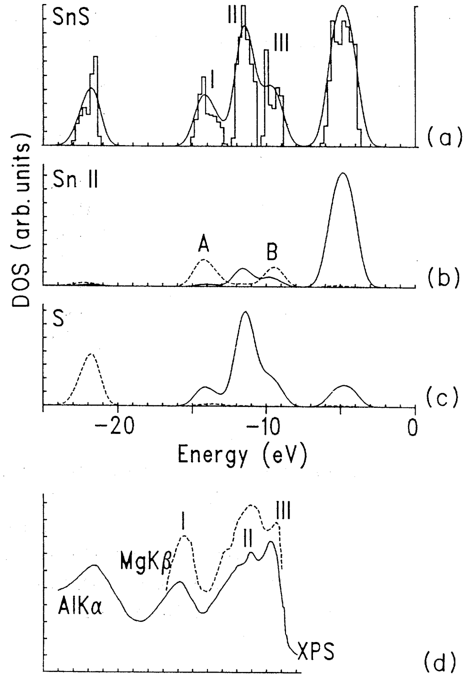

FIG. 4. SnS theoretical densities of states: (a) the total one; (b) and (c) the partial *s* states (dashed lines) and *p* states (solid line), compared to (d) the x-ray photoemission spectrum for the Al *Kα* line (solid line) and the Mg *Kα* line (dashed line).

4) is characterized by one peak S(3*s*) at the bottom of the valence band and three others at its top (I, II, and III) On the photoemission spectra,[30,31] peak II is as high as peak III. This is due to the cross-section effect, which increases peaks with Sn(5*s*) character (see Table II) as peaks I and III. So we obtain good agreement between the experimental and theoretical DOS. We calculate the number of Sn(5*s*) and Sn(5*p*) electrons in the SnS valence band (Table IV) and find that this oxidation state is characterized by 1.94 Sn(5*s*) valence electron. It is striking that this number corresponds almost exactly to the notion of the lone pair with two 5*s* electrons.

On the Mössbauer spectrum of Sn$_2$S$_3$,[18] two peaks are observed. Their positions correspond to the isomer shift $\delta = 1.16$ mm/s, attributed to Sn IV, and to $\delta = 3.53$ mm/s due to Sn II. Thus Sn$_2$S$_3$ is a mixed valence tin compound. It crystallizes in an orthorhombic form.[26] Tin atoms are located on two types of environment (Table III): one is in a weakly distorted octahedron (denoted Sn$_o$); the other has four S atoms as neighbors arranged on a trigonal bipyramid (denoted Sn$_{\rm tb}$). This last environment can be characteristic of a lone-pair activity and is then attributed to Sn II. We calculate the electronic structure and numbers of electrons. The partial and total DOS are shown in Fig. 5. There are 1.18 Sn$_o$(5*s*) electrons and 1.92 Sn$_{\rm tb}$(5*s*) electrons. From this result, one can conclude that Sn IV is in the octahedral site and Sn II corresponds to the trigonal bipyramid, in agreement with the previous reasoning. Note that again, as in Sec. I, Sn has an average oxidation number (here equal to 3), which is realized by an equal number of Sn II and Sn IV sites, confirming the usefulness of the notion of oxidation number.

It is interesting to relate the theoretical number N_s of Sn(5*s*) valence electrons to the experimental isomer shift.

TABLE IV. Experimental values of the Mössbauer isomer shift (δ in mm/s) and related theoretical numbers of Sn(5*s*) and Sn(5*p*) valence electrons for the IV and II oxidation states of tin atoms. *T* is the temperature of measurements (in K). The last column indicates the reference.

			Sn IV				Sn II			
	δ	$n(5s)$	$n(5p)$	Total	δ	$n(5s)$	$n(5p)$	Total	T (K)	Reference
SnS$_2$	1.13	1.22	1.47	2.69					80	3
SnS					3.31	1.94	1.06	3.00	80	17
Sn$_2$S$_3$	1.16	1.18	1.30	2.48	3.53	1.92	1.08	3.00	80	18
In$_2$Sn$_3$S$_7$	1.19	1.25	1.29	2.54	3.82	1.92	0.96	2.88	77	18
In$_{16}$Sn$_4$S$_{32}$	1.16	1.20	1.30	2.50					80	34

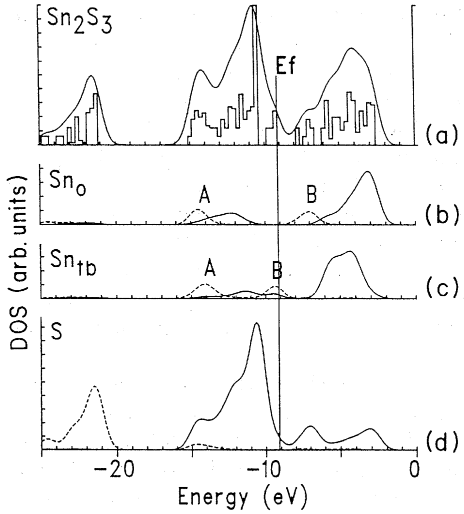

FIG. 5. Sn_3S_3 theoretical density of states: (a) the total one; (b)–(d) the partial s states (dashed lines) and p states (solid line).

From Eq. (1), we can write that the difference $\Delta\delta$ in the isomer shift for two absorbers is related to the difference ΔN_s by

$$\Delta\delta(\mathrm{mm/s}) = 21.65\times10^3 \frac{\Delta R}{R}\Delta N_s , \quad (9)$$

where numerical values are given in the references cited in Sec. I. The value of $\Delta R/R$ has been determined by many authors and here we take the ones most commonly used: 1.35×10^{-4} for Svane[6] and 1.61×10^{-4} for Grodzicki.[7] With these numbers, from SnS to SnS_2, the experimental variation $\Delta\delta_{\mathrm{expt}} = 2.18$ mm/s is close to the calculated ones $\Delta\delta_{\mathrm{theor}} = 2.10$ and 2.51 mm/s. The same comparison also occurs between Sn II and Sn IV for Sn_2S_3, where $\Delta\delta_{\mathrm{expt}} = 2.37$ mm/s and $\Delta\delta_{\mathrm{theor}} = 2.16$ and 2.58 mm/s. The theoretical variation ΔN_s around 0.7 electrons between the two oxidation states is in good agreement with the experimental isomer shifts. This difference in the Sn(5s) electronic density is also easily observed on the two main peaks A and B of the partial DOS. For Sn II they are both in the valence band, but for Sn IV peak B is in the conduction band.

IV. TIN IN THE TERNARY SYSTEM SnS-SnS_2-In_2S_3

We now deal with compounds in the SnS-SnS_2-In_2S_3 system. These compounds have been studied by x-ray-diffraction spectroscopy but, as explained in the Introduction, this experiment does not allow us to differentiate between In and Sn atoms. Mössbauer spectroscopy has thus been used to eventually detect the existence of Sn II and Sn IV, taking into account the following points: (i) Sn II, which is the only atom with a lone pair, corresponds to the most distorted environment; (ii) when different symmetrical environments are possible for Sn IV, the other Mössbauer parameters (the quadrupolar splitting Δ, related to the electric-field gradient around Sn atoms, and the linewidth Γ, related to the site distribution, i.e., number and order) are used with reference models to define the coordination. To check the first point, we study the case of $In_2Sn_3S_7$, which is a mixed valence compound. The second point is then examined from the study of the spinel form of $In_{16}Sn_4^{IV}S_{32}$.

A. $In_2Sn_3S_7$

The x-ray-diffraction study of $In_2Sn_3S_7$ (Ref. 18) provides the possible sites for In or Sn and the sites occupied by S atoms. The Mössbauer spectrum shows the existence of only two oxidation states II and IV for tin. As we have discussed in Sec. I, this can only happen if there is one Sn IV for two Sn II atoms, which agrees with the ratio of Sn II to Sn IV around 2 determined from Mössbauer spectra. In this structure (Table III), In and Sn atoms can be put in three octahedral environments and two bicapped trigonal prisms "btp." The lone pair of Sn II would imply that it is positioned in the btp site, the most distorted environment. The In and Sn IV atoms must then be placed in the octahedral sites by comparison with $PbIn_2S_4$, which has a similar structure but where the x-ray problem does not occur.

Figure 6 shows the DOS found with the atomic structure defined with this hypothesis. The Sn(5s) partial DOS confirms that Sn IV atoms are located at octahedral sites (peak B is in the conduction band) and Sn II atoms are in the btp sites. The theoretical numbers of Sn(5s) valence electrons (Table IV) are also in good agreement with the previous results. In a second case, we have calculated the electronic structure for another distribution of In and Sn on the octahedral sites. We obtain nearly

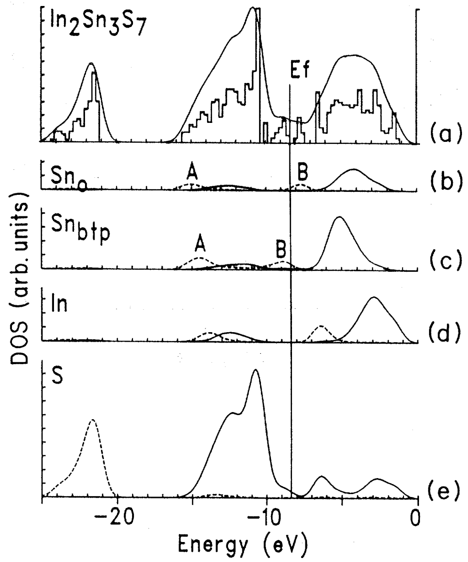

FIG. 6. $In_2Sn_3S_7$ theoretical densities of states: (a) the total one; (b)–(e) the partial s states (dashed lines) and p states (solid line).

the same results. But in a third case, we put In on the btp site, and all the Sn and the rest of the In on the octahedral sites. The results are no more coherent with the Mössbauer isomer shift values because we obtain different numbers of Sn(5*s*) valence electrons (1.61, 1.43, and 1.39). Thus, in conclusion, it is not possible to put In atoms in the most distorted environments, confirming the fact that Sn II characterizes this type of site.

B. Spinel-type compounds

On the ternary diagram, there exists a zone where all the compounds are constructed on the spinel form of In_2S_3. In these structures, 32 sites (named 32*e*) are occupied by sulfur atoms. There exist sixteen sites (named 16*d*) that are at the centers of sulfur octahedra and eight sites (named 8*a*) at the centers of sulfur tetrahedra. These 16*d* or 8*a* sites can be occupied or vacant and the vacant sites are randomly distributed.

In order to check our method for spinel compounds, we first calculate the electronic structure of In_2S_3 whose atomic structure is well defined and for which photoemission spectra have already been recorded.[32] Its detailed formula is $(In_{5.33})[In_{16}]S_{32}$, where ( ) stands for a tetrahedral site and [ ] for an octahedral site relative to S atoms. We notice that the number of vacancies is very small compared with total number of electrons and their influence is of minor importance on the band structure. Thus, their random distribution on tetrahedral sites has no influence for this study where interactions are considered between the nearest neighbors. On the density of states (Fig. 7), one observes three peaks (I, II, and III) at the top of the valence band and one at the bottom corresponding to S(3*s*) states. As explained in Sec. II, the relative intensities of peaks I, II, and III have to be modulated by photoemission cross sections. Then, the intensity of peak III will be higher due to the In(5*s*) partial density. The agreement is good between theory and experiments. As Ihara *et al.*,[32] we find that the In(5*s*) and In(5*p*) states are mainly attributable to peaks II and III, respectively. The theoretical value of the forbidden band gap (2.5 eV) again compares well with the experimental one around 2 eV.[33]

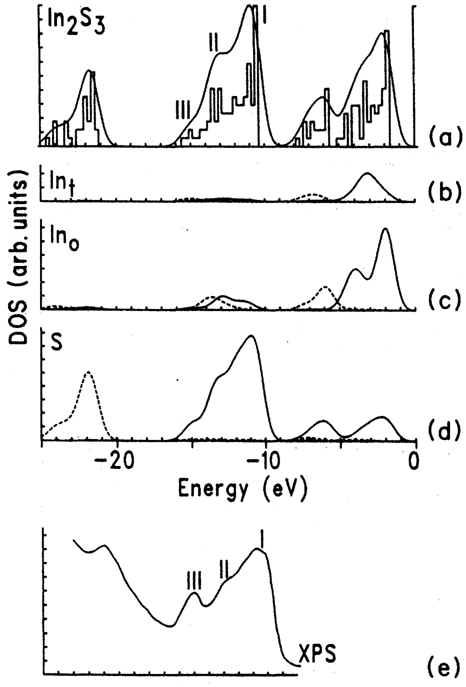

FIG. 7. In_2S_3 theoretical densities of states: (a) the total one; (b)–(d) the partial *s* states (dashed lines) and *p* states (solid line), compared to (e) the x-ray photoemission spectrum.

We now deal with another spinel form: $In_{16}Sn_4S_{32}$.[3,34] From x-ray diffraction, it is shown that the 32*e* site is fully occupied by S atoms. The 16*d* site is also fully occupied but not the 8*a* site (Table III). The Mössbauer spectrum only shows one peak that corresponds to the oxidation number IV of Sn ($\delta = 1.23$ mm/s).[3,34] The linewidth of the Mössbauer peak ($\Gamma = 1.10$ mm/s) proves that the tin atoms would be situated only on the one type of site (8*a* or 16*d*). The quadrupolar splitting ($\Delta = 0.67$ mm/s) is in agreement with a distorted site like the 16*d* site rather than the 8*a* one. From data about other spinel tin sulfides,[35] one can observe that Sn IV in octahedral sites are characterized by $1.13 < \delta < 1.44$ mm/s and by $0.39 < \Delta < 0.51$ mm/s. Then it seems reasonable to assume that the tin atoms are located at octahedral sites.

Let us then calculate the electronic structure for all the Sn atoms at octahedral sites. Figure 8 represents the corresponding DOS. As peak *B* of the partial Sn(5*s*) density is in the conduction band, the oxidation state of Sn is IV. The number of Sn(5*s*) electrons is calculated to be 1.20. However, if we calculate the situation where all Sn atoms are at tetrahedral sites, the number of Sn(5*s*) valence electrons is 1.15, corresponding to a theoretical difference in

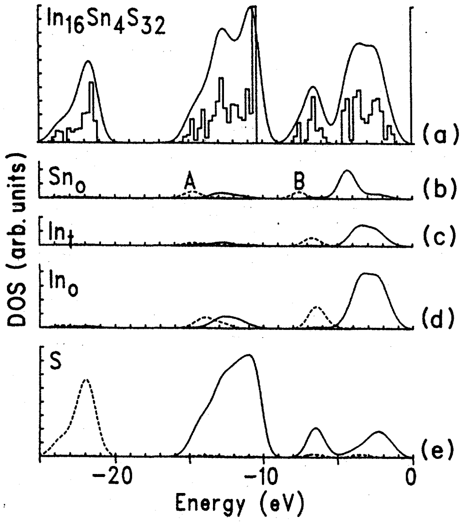

FIG. 8. $In_{16}Sn_4S_{32}$ theoretical densities of states: (a) the total one; (b)–(e) the partial *s* states (dashed lines) and *p* states (solid line).

δ of about 0.11–0.15 mm/s, i.e., an oxidation degree for Sn again equal to IV. This result shows that it is not possible from δ to decide if Sn atoms are in tetrahedral or octahedral sites.

CONCLUSION

In this work we have analyzed the relation that exists between the tin oxidation number (II and IV), the Mössbauer isomer shift, and the local atomic structure in the SnS-In_2S_3-SnS_2 system. For this, we have calculated the electronic structure by a tight-binding technique whose parameters were taken from empirical rules derived for other systems. As a positive test we have obtained fairly good agreement between our predicted densities of states and photoemission spectra, when available. We have then used the same theoretical procedure to calculate the electronic population on the Sn atoms. Our main conclusions are the following.

(i) The calculated number N_s of 5*s* electrons on Sn takes essentially two values, $N_s = 1.2$ and 1.9, respectively, characteristic of the binary systems SnS_2 and SnS, in perfect agreement with Mössbauer data for the isomer shift.

(ii) The formal oxidation number (Sn II or Sn IV), which characterizes these two binary systems, respectively, is thus a good indicator of the local situation occurring for Sn in this class of compounds. Sn II corresponds to a distorted environment, while Sn IV reflects a more isotropic situation.

(iii) However if one calculates the tight-binding oxidation number (i.e., the net positive charge on the atom), one finds (Table IV) a much larger spread of values (from 1.31 to 1.52 for Sn IV situations and from 1.00 to 1.12 for Sn II situations) than for N_s (from 1.18 to 1.25 for Sn IV and from 1.92 to 1.94 for Sn II). Thus N_s reflects the local properties around Sn in a much better way.

The main lesson to be learned from this study is that, in this class of systems, the atomic configuration that locally minimizes the energy around each Sn atom essentially corresponds to two values of its 5*s* population, 1.21 or 1.93, confirming the Mössbauer results. These two possible local situations are usually labeled by the formal oxidation numbers, Sn II and Sn IV corresponding to the binary compounds SnS and SnS_2, but this is somewhat misleading since the calculated oxidation numbers show a much larger spread than the 5*s* population values. It remains to understand why the 5*s* population is a driving parameter for the local arrangements. Simple arguments would attribute this to the lone-pair stereochemical activity but this should be shown explicitly by total-energy calculations.

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