Chem. Mater. **1995,** *7,* 1193−1197

^{119}Sn Mössbauer Spectroscopy of Some Misfit Layer Sulfides

J. C. Jumas,* J. Olivier-Fourcade, and P. Lavela†

Laboratoire de Physicochimie des Matériaux Solides, Université Montpellier II, Sciences et Techniques du Languedoc, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

J. Morales and J. L. Tirado

Departamento de Química Inorgánica e Ingeniería Química, Facultad de Ciencias, Universidad de Córdoba, Adva. San Alberto Magno s/n, 14004 Córdoba, Spain

Received November 29, 1994. Revised Manuscript Received March 27, 1995⊗

^{119}Sn Mössbauer spectra of ternary sulfides with $(SnS)_{1.17}NbS_2$, $(SnS)_{1.20}TiS_2$, and $(SnS)_{1.16}TaS_2$ stoichiometries and misfit layer structures consist of an asymmetric profile in the Sn(II) region of chemical shifts, evidencing that little interaction occurs from the SnS sublattice to the TS_2 layers in these compounds. The origin of this profile is not due to texture or Goldanskii−Karyagin effects as evidenced by recording spectra either by rotating the sample at different angles defined between the γ incident flux and the electric gradient axis or near liquid helium temperature. The different Sn sites in the structure of these compounds, as a consequence of the misfit between SnS and TS_2 sublattices, account for two different coordination numbers of Sn(II) ions, which lead to two quadrupole doublets in the Mössbauer spectra located at different chemical shifts.

Introduction

Ternary sulfides with $(MS)_{1+y}TS_2$ stoichiometry (M = Sn, Pb, Bi, lanthanides and T = V, Cr, Ti, Nb, Ta) belong to a wide family of composite layered compounds built of alternate double layers of MS and sandwiches of TS_2.[1] The atomic arrangement of the MS unit is the same as that of the double layer in TlI and is based on a distorted NaCl structure. The TS_2 unit is geometrically identical with the TS_2 slab of the binary transition metal disulfide (Figure 1). Since the building units MS and TS_2 have different geometry, the two sublattice are mutually incommensurate in one direction, which means that the lengths of the two *a* axes have a nonrational ratio.

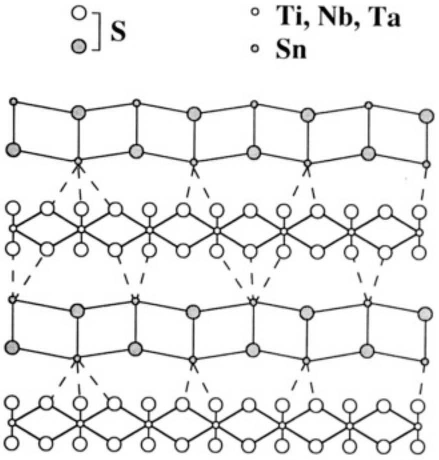

Figure 1. Idealized projection along [010] of the structure of misfit layer sulfides.

One of the first questions which arises from the study of these compounds is the reason for the stability of this misfit layer structure and the alternated stacking observed. In fact, these compounds are rather stable even at high temperature. The stability of the structure and the preference for the alternate stacking can be explained according to the occurrence of interactions between MS and TS_2 layers. These interactions are weak and the slabs are rather distant (≃3 Å) and bound basically by van der Waals forces. Thus, these compounds can intercalate lithium, resulting in a slight increase of the interlayer space.[2] The nature of these interactions is a point of controversy. Thus, from X-ray photoemission spectroscopy (XPS), X-ray absorption spectroscopy (XAS), and reflection electron energy loss spectroscopy (REELS), Ohno[3] has concluded that a charge transfer occurs clearly from MS (M = Sn, Pb) to the TS_2 layers. Electrical transport properties of "$SnNbS_3$"[4] and "$SnTiS_3$"[5] have also been interpreted by assuming that SnS acts as the donor part of the structure, leaving some Sn in the +4 valence state. In contrast, recent data reported by Ettema et al.,[6] obtained by using energy-dependent photoelectron spectra and ultraviolet photoemission spectroscopy conclude

---

* To whom correspondence should be addressed.

† On leave from Universidad de Córdoba.

⊗ Abstract published in *Advance ACS Abstracts,* May 15, 1995.

(1) Wiegers, G. A.; Meerschaut, A. *Incommensurate Sandwiched Layered Compounds*; Meerschaut, A., Ed.; *Trans. Tech. Publ.* **1992**, 101−172, and references therein.

(2) Hernán, L.; Lavela, P.; Morales, J.; Pattanayak, J.; Tirado, J. L. *Mater. Res. Bull.* **1991**, *26*, 1211. Barriga, C.; Lavela, P.; Pattanayak, J.; Morales, J.; Tirado, J. L. *Chem. Mater.* **1992**, *4*, 1021. Barriga, C.; Lavela, P.; Morales, J.; Tirado, J. L. *Solid State Ionics* **1993**, *183*, 129.

(3) Ohno, Y. *Solid State Commun.* **1991**, *72*(12), 1081; *Phys. Rev. B* **1991**, *44*, 1281.

(4) Wiegers, G. A.; Meetsma, A.; Haange, R. J.; de Boer, J. L. *Mater. Res. Bull.* **1988**, *23*, 1551.

(5) Wiegers, G. A.; Haange, R. J. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 1071.

(6) Ettema, A. R. H. F.; Wiegers, G. A.; Haas, C.; Turner, T. S. *Surf. Sci.* **1992**, *269/270*, 1161; *Phys. Scr.* **1992**, *T41*, 265. Ettema, A. R. H. F.; Haas, C.; Turner T. S. *Phys. Rev. B* **1993**, *47*, 12794.

0897-4756/95/2807-1193$09.00/0

that no significant charge transfer takes place from the MS (M = Sn, Pb) part to the TS_2 part. The cohesion of the layers is assigned to covalent interlayer interactions. Recent results obtained by Raman spectroscopy also conclude that the charge transfer between the two types of layers is small or absent.[7]

Mössbauer spectroscopy is now established as a technique which can provide valuable information on the distribution of electron density about a particular atom. In this work, ^{119}Sn Mössbauer spectroscopy studies have been carried out on some misfit layer sulfides with $(SnS)_{1+y}TS_2$ (T = Ti, Ta and Nb) stoichiometry in order to clarify the electronic local surrounding of tin. The comparison of the Mössbauer spectra with those of the binary tin sulfides, in which the electronic and structural environment of Sn atoms are well-known, will supply a more detailed description of the tin atom coordination in misfit layer sulfides, as well as additional information on the nature of the interlayer interactions.

Experimental Section

Three samples with tin in their composition were selected: $(SnS)_{1.17}NbS_2$, $(SnS)_{1.20}TiS_2$, and $(SnS)_{1.16}TaS_2$. These compounds were synthesized from direct combination of the elements (Strem Chemical and Aldrich) in a ratio Sn/T/S = 1/1/3. The mixtures were heated in evacuated quartz tubes under the same conditions described elsewhere.[4,5,8] The products were characterized by X-ray and electron diffraction. X-ray powder diffraction patterns showed a group of high-intensity peaks which are multiple-order reflections of the basal planes due to the preferential orientation of lamellar samples. However, the periodic values of d_{001} were close to those initially reported.[4,5,8] In addition, electron diffraction patterns showed the typical superposition of hexagonal and tetragonal sublattices which are characteristic of this type of compounds. However, the small differences between the exact stoichiometry and the mixture of elements used in the synthesis gave place to the occurrence of small quantities of TS_2 particles. These domains are easily detected by electron diffraction due to the presence of hexagonal patterns. Nevertheless, these impurities do not affect the study of the environment of tin atoms in the misfit compounds.

Mössbauer spectra were measured using an ELSCINT AME 40 constant acceleration spectrometer. The γ-ray source was ^{119m}Sn in a $BaSnO_3$ matrix used at room temperature. Cooled samples at 80 and 4 K were studied by using a liquid nitrogen and a liquid helium cryostat. The scale velocity was calibrated by using a ^{57}Co source and a metallic iron foil as absorber. The spectra were fitted to Lorentzian profiles by a least-squares method.[9] The goodness of fit was controled by χ^2 tests.[10] All isomer shifts reported here are given with respect to the center of a $BaSnO_3$ spectrum obtained with the same source at 293 K.

Results and Discussion

The room-temperature (RT) ^{119}Sn Mössbauer spectra and computer fits are shown in Figure 2. For all samples the presence of an asymmetric absorption profile in the region of isomer shifts corresponding to Sn(II) is observed. The origin of this effect can be deduced from the study of three hypothesis: the occurrence of a Goldanskii–Karyagin or/and texture effect and a characteristic arrangements of tin atoms as a consequence of the incommensurable structure of these compounds.

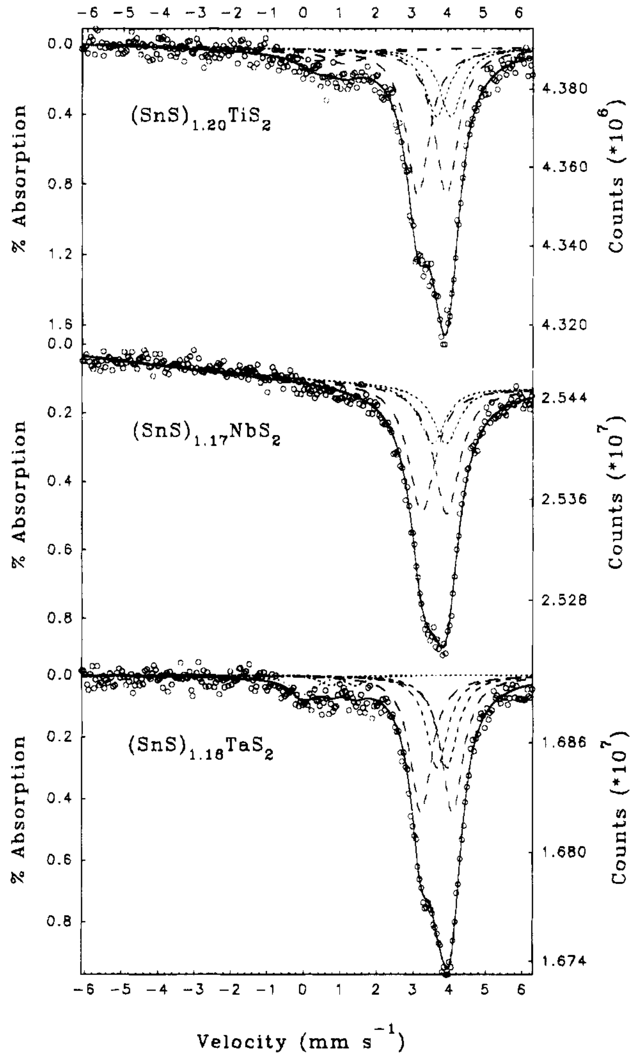

Figure 2. Experimental and calculated room-temperature ^{119}Sn Mössbauer spectra of misfit layer sulfides.

To elucidate the origin of these profiles, the occurrence of a possible Goldanskii–Karyagin effect[11] was first considered. The anisotropy in the Mössbauer coefficient, due to the nature of material, gives place to modifications of the signal intensities. This variation is large in isotropic powder spectra with symmetric quadrupolar double lines of $^1/_2 \rightarrow {}^3/_2$ transition, as in the case of ^{119}Sn. The anisotropy of the Mössbauer coefficient varies with temperature. In this way, a decrease in temperature would provide the homogeneity in the population of the excited states and, therefore, a sharp decrease in the profile asymmetry. Some examples can be found in the literature[12] in which the sharp modification of the intensity ratio is observed when the temperature is reduced at 77 K, making evident the occurrence of a Goldanskii–Karyagin effect. Thus, two experiments at 80 and 4 K (Figure 3) were carried out in order to verify the possible presence of this effect. From the fitting of the spectra, not pro-

---

(7) Sourisseau, C.; Cavagnat, R.; Tirado, J. L. *J. Raman Spectrosc.* **1992**, *23*, 647. Sourisseau, C.; Cavagnat, R.; Foussier, M.; Tirado, J. L.; Morales, J. *Chem. Phys.*, in press.

(8) Meetsma, A.; Wiegers, G. A.; Haange, R. J.; de Boer, J. L. *Acta Crystallogr.* **1989**, *A45*, 285.

(9) Rubenbauer, K.; Birchall, T. *Hyperfine Interact.* **1979**, *7*, 125.

(10) Gruverman, I. J.; Seidel C. W. *Mössbauer effect methodology*; Plenum Press: New York, 1970.

(11) Goldanskii, V. I.; Makarov, E. F.; Khrapov, V. V. *Phys. Lett.* **1963**, *3*, 344. Karyagin, S. V. *Dokl Akad. Nauk SSSR* **1963**, *148*, 1102.

(12) Calage, Y.; Duroy, M.; Ferey, G.; Varret, F. *Eur. J. Solid State Inorg. Chem.* **1990**, *27*, 633.

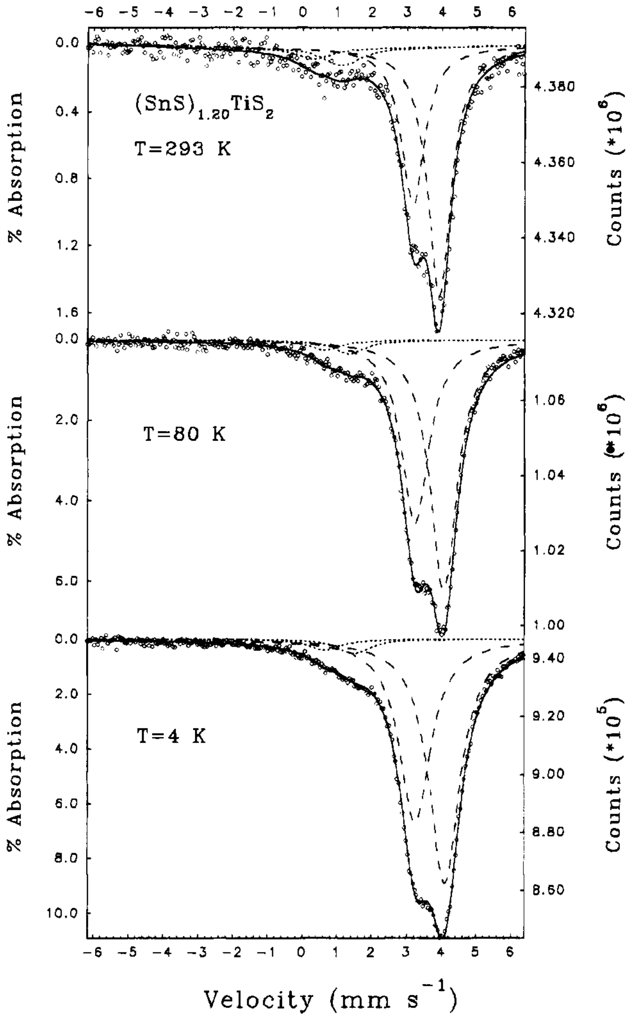

Figure 3. ^{119}Sn Mössbauer spectra of tin titanium misfit layer sulfide recorded at different temperatures.

nounced differences were found in the Goldanskii–Karyagin coefficients (about 13% between 4 and 293 K). This behavior was also common to the other two compounds. Hence, we can conclude that this effect is not the main cause of the asymmetric double line.

On the other hand, the presence of a texture effect was also tested as a cause of the asymmetry on the absorption lines. The presence of a texture component can be eliminated by taking into account the proportionality between the intensities of the spectra of thin absorbers and their thickness, the average of spectra measured at different γ-directions is equivalent to the average of absorber matrices. Grenêche and Varret[13] applied this phenomenon to obtain a random powder spectrum. The random distribution of the electric gradient fields with respect to the γ-flux gives place to $\langle \sin^2 \theta \rangle = {}^2/_3$ and $\langle \cos^2 \theta \rangle = {}^1/_3$. By reversing these functions, an angle of $\theta = 54.7°$ is obtained. Thus, the Mössbauer spectrum recorded under this angle, named magic angle, as defined between the γ incident flux and the electric gradient axis, would be equivalent to that of the sample without texture effect. In this way, the sample was oriented at 57.4° with respect to the incident γ-ray beam, and four measurements were carried out at $\alpha = k(\pi/2)$ (k = 1, 2, 3, and 4) by rotating a sample of (SnS)$_{1.20}$TiS$_2$ (Figure 4). Again, the spectra recorded at $\theta = 0°$ and $\theta = 54.7°$ were almost identical. Hence, it seems to be that no texture effect originates the asymmetric profiles in ^{119}Sn Mössbauer measurements of misfit layer sulfides.

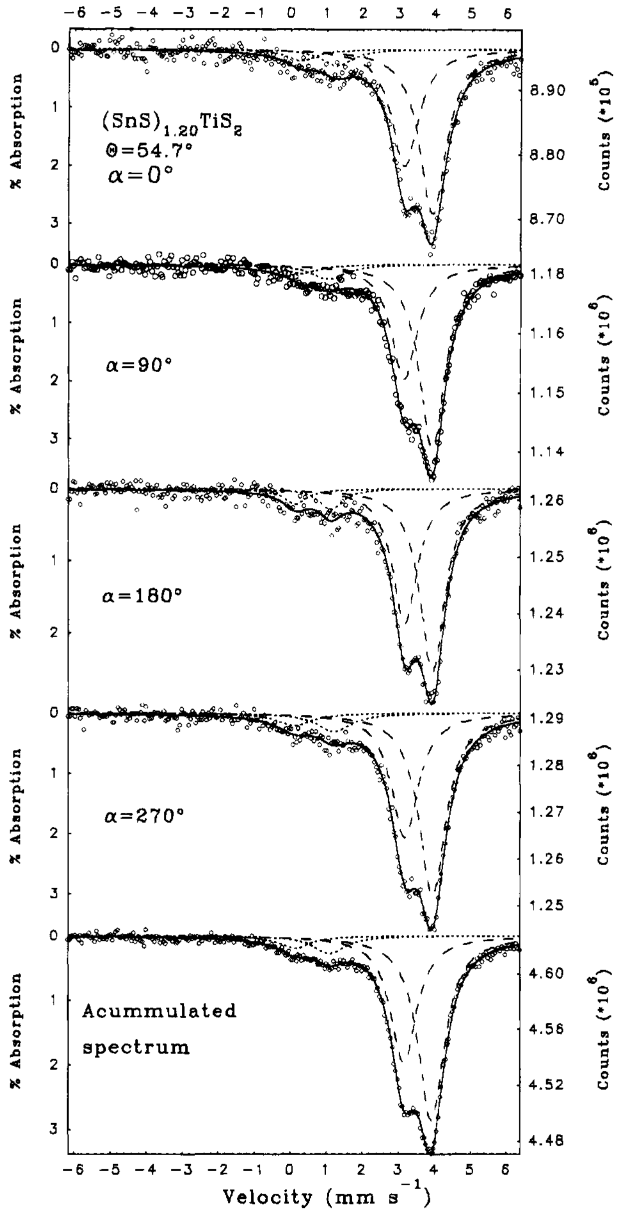

Figure 4. ^{119}Sn Mössbauer spectra of tin titanium misfit layer sulfide recorded at variable angle.

The examination of the structural data of these compounds accounts for an alternative explanation of the Mössbauer spectra. For the three compounds, tin atoms have a similar local structure.[8,14] Each Sn atom is coordinated by five sulfur atoms of the SnS layers. Four S atoms are located in the (a, b) plane, and their average distances to the central tin atom are about 2.9 Å. The fifth sulfur atom is nearly perpendicular to this plane, and the Sn–S bond distance is 2.6–2.7 Å. In fact, the SnS slices in (SnS)$_{1+y}$TS$_2$ are intermediate between those of α- and β-SnS.

The SnS double layer is corrugated with Sn atoms on the outside (see Figure 1). These atoms fall between rows of S atoms of the TS$_2$ adjacent layers running parallel to the a axis. This structural feature and the incommensurate character of the structures produce a

---

(13) Grenêche, J. M.; Varret, F. *J. Phys. (Paris)* **1982**, *L233*, 43.

(14) Wiegers, G. A.; Meetsma, A.; de Boer, J. L.; van Smaalen, S.; Haange, R. J. *J. Phys. Condens. Matter.* **1991**, *3*, 2603.

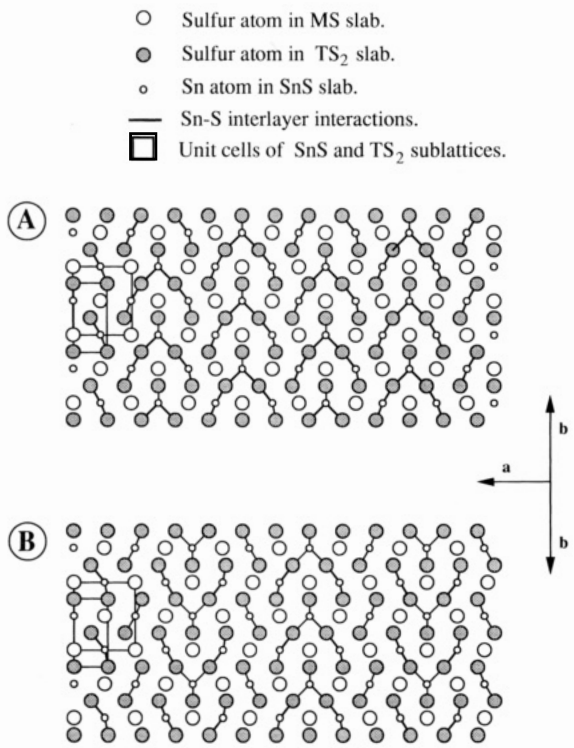

Figure 5. Idealized projection along [001] of the metal atoms exposed to an MS–TS_2 interlayer.

Table 1. Mössbauer Parameters of $(SnS)_{1+x}TS_2$ Recorded at 293 K[a]

		SnS	$(SnS)_{1.20}TiS_2$	$(SnS)_{1.17}NbS_2$	$(SnS)_{1.16}TaS_2$
first	δ (mm/s)	3.31	3.49	3.53	3.56
site	Δ (mm/s)	0.87	0.77	0.69	0.87
	Γ (mm/s)	1.26	0.81	1.12	0.70
	C (%)		66	68	60
second	δ (mm/s)		3.68	3.66	3.71
site	Δ (mm/s)		0.37	0.33	0.27
	Γ (mm/s)		0.81	1.12	0.70
	C (%)		33	31	39
	X^2	1.41	0.984	1.043	1.026

[a] Accuracy: δ, Δ, and Γ ±0.02 nm/s, and C ±2%.

change in the coordination of Sn by sulfur of the TS_2 slab which varies between 2 and 3. Figure 5 shows an idealized projection of the SnS–TS_2 interlayer space, for two different a_{SnS}/a_{TS2} ratios ($^5/_3$ and $^7/_4$) along (001). Two possible coordination numbers for tin atoms can be observed in this figure (5 + 2 and 5 + 3). For the holes formed by two and three sulfur atoms of TS_2 slab an approximate proportions of 2:1 and 3:1 were estimated for the ratios $^5/_3$ and $^7/_4$, respectively. Nevertheless, the incommensurability of the real structures makes it difficult to calculate the exact proportion of each site.

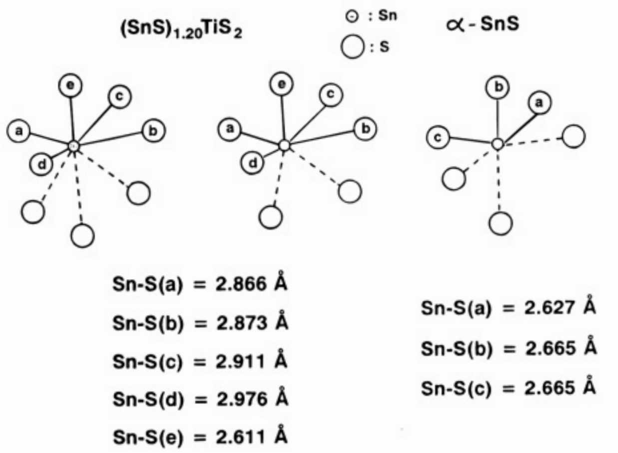

Figure 6. Coordination of tin atoms by sulfur atoms in α-SnS and $(SnS)_{1.20}TiS_2$.

To verify this assumption, the Mössbauer spectra were fitted by considering the presence of two different local electronic environments of tin atoms. The Mössbauer parameters obtained from the fits are listed in Table 1. Two symmetric quadrupolar double lines were found to be present with similar δ values. The parameter of fitting control (X^2) is in agreement with this model and, in addition, the percentage contributions (%C) of each site calculated from the Mössbauer spectra are close to those evaluated from Figure 5. The lower isomer shift signals, were assigned to Sn atoms with 5 + 2 coordination and the higher ones to 5 + 3 coordination. This conclusion is consistent with the decrease of quadrupole splitting value (Δ) when the coordination number is increased due to a more homogeneous distribution of the charge around the Sn atom.[15] It is well-known that the isomer shift is a consequence of the finite electronic density at the nucleus. Only the s electrons present a finite wave function in this atom region. Hence, the isomer shift is affected either by the direct influence of the population of these electrons or, indirectly, by the modification of the screening factor due to the variation of the population of p or/and d electrons. The latter effect gives place to changes in the effective charge and, therefore, in the interactions between the s electrons and the nucleus. The characterization of the 5s electron behavior is essential in order to describe the evolution of the structures and properties of the "lone-pair" species such as Sn(II) and Sb(III).[16]

Mössbauer spectral parameters of α-SnS have also been included in Table 1.[17] As compared with those of the misfit layer sulfides, the isomer shift is somewhat lower while the quadrupole splitting is greater. Although the interpretation of the isomer shift for Sn(II) compounds is complicated by the presence of the lone pair and by the wide variety of the structure adopted, a qualitative explanation for these differences can be attempted on the basis of the electronic environment of tin nucleus.

It should be noted that Sn atoms in α-SnS are surrounded by six S atoms forming a heavily distorted octahedron. Each Sn atom has three pyramidal S neighbors, one at 2.627 Å and two at 2.665 Å, the three remaining sulfur atoms are located at larger distances (two at 3.290 Å and one at 3.388 Å).[18] Thus, in addition to the lower coordination number, the average of the Sn–S short length bonds (2.62 Å) is shorter than those observed for misfit sulfides (2.85 Å; see Figure 6). The increase of the coordination number which is accompanied by higher Sn–S bonding distances provides an increase of the total charge density in the tin atoms what gives place to an increase of the isomer shift (Table 1).

---

(15) Parish, R. V. In *Mössbauer Spectroscopy*; Dickson, D. P. E., Berry, F. J., Eds.; Cambridge University Press: Cambridge, 1986; p 26.

(16) Olivier-Fourcade, J.; Ibanez, A.; Jumas, J. C.; Maurin, M.; Lefebvre, I.; Lippens, P.; Lannoo, M.; Allan, G. *J. Solid State Chem.* **1990**, *87*, 366.

(17) Jumas, J. C.; del Bucchia, S.; Philippot, E.; Maurin, M. *J. Solid State Chem.* **1982**, *41*, 50. Fano, V.; Ortalli, I. *J. Chem. Phys.* **1974**, *61*, 5017.

(18) Weidemeier, H.; von Schnering H. G. *Z. Kristallogr.* **1978**, *148*, 295.

Concerning the quadrupole splitting, for Sn(II) the valence shell contains a single lone pair, which normally contributes significantly to the electric gradient field (EGF). Moreover, the lone pair is more stereochemically active as the symmetry lowers.[16] In fact, when the tin atom occupies a site with rigorous cubic symmetry, $(V_{zz})_{\mathrm{nb}}$, the principal component of the contribution of the nonbonding electrons to the EGF, is zero. It seems that the higher coordination and homogeneity of Sn–S bond distances in misfit sulfides give rise to an increase in the symmetry of the electron density distribution and therefore to a more homogeneous charge distribution around Sn atoms. This reduces the concentration of negative charge along the major symmetry axis of the system which results in a decrease of the quadrupole splitting values. In fact, the sites of higher coordination number, second site in Table 1, have the lowest quadrupole splitting.

As described in the Introduction, several studies have been reported about the electronic structure of misfit layer sulfides.[3-6] The major interest has been concentrated in the study of the nature of the interlayer interactions as an important factor in the stability of the incommensurate structure and the alternated stacking of two sublattices with different geometry. The TS_2 type layer compounds are very well-known to act as electron acceptors in intercalation compounds in which metal atoms, organic polar molecules or organometallic compounds act as guest species. The partly occupied d band of the transition metal T has a high density of states at the Fermi level and can therefore easily accept a considerable number of electrons without changing too much the energy of the other states (rigid band model of intercalation). For misfit layer compounds, the MS sublattice may be considered the electron-donating guest species. Alternatively, bonding interaction between Sn atoms of the MS subsystems and S of TS_2 may be essential for the stability of the structure.

It has been suggested[3] that charge transfer occurs in $(SnS)_{1.17}NbS_2$ from SnS layers to TS_2 slabs by different chemical potentials. The effects on the XPS, XAS, and REELS spectra are quite similar to those of the intercalation compound of layered transition-metal disulfides. However, from the core level spectra of the 3d Sn electrons have the same binding energy in the misfit layer compound as that in the pure α-SnS compound. Thus, interlayer interaction should be so small that it can be considered that each layer has quasi-two-dimensional electronic structure. The compound may be then regarded as a non-redox intercalation product derived of the layered transition-metal disulfide. In this case, the inserted SnS molecules, forming a double layer, should have a similar electronic band structures to the bulk compound.

Resonant and core level photoemission spectroscopy studies of the $(SnS)_{1.20}TiS_2$ and $(SnS)_{1.16}TaS_2$ have not shown positive evidence about charge transfer from one layer to the other.[6] These authors conclude that charge transfer, whether it is present, is so small that it is insufficient to explain the high stability of the misfit layer compound. Direct evidence that the cohesion of the layers is due to covalent interlayer S–M, where S belongs to the TS_2 slab and M is the metal atom in the MS layer, has been obtained from the dispersion of the S $3p_z$ states at the bottom of the valence band measured by angle-resolved ultraviolet photoelectron spectroscopy.[19]

Table 2. Mössbauer Parameters of $(SnS)_{1.20}TiS_2$ Recorded at 80 and 4 K[a]

		first site	second site	third site	fourth site	X^2
4 K	δ (mm/s)	3.86	3.55	1.34	0.88	0.959
	Δ (mm/s)	0.61	0.90	0.60	0.96	
	Γ (mm/s)	0.99	0.99	0.99	0.99	
	C (%)	26	66	3	4	
80 K	δ (mm/s)	3.81	3.52	1.16	0.7	1.188
	Δ (mm/s)	0.59	0.89	0.65	1.00	
	Γ (mm/s)	0.84	0.84	0.84	0.84	
	C (%)	31	63	4	3	

[a] Accuracy: δ, Δ, and Γ ±0.02 mm/s, and C ±2%.

The occurrence of signals of less intensity than that corresponding to that of Sn^{2+} ions, in the range of ca. 0–1.5 mm/s, was observed in $(SnS)_{1.20}TiS_2$ and $(SnS)_{1.16}TaS_2$. For the compounds with Ta in their composition a small signal with an isomer shift of 0 mm/s can be ascribed at the presence of low concentrations of SnO_2 due to stockage or synthesis problems. On the other hand, a double line of very low intensity is observed with an isomer shift of 1.08 mm/s. The small percentage contribution of these peaks makes it difficult to elucidate its nature. However, a similar behavior is observed for $(SnS)_{1.20}TiS_2$. In this last case, the treatment at low temperatures has allowed us to obtain more precise data about this signal (Table 2). In these conditions, the spectra obtained are of better quality and statistic because, for Sn, the Mössbauer factor increases strongly. This results in reliable parameters for the small components. The asymmetric profile of this peak can be decomposed into two doublets which cannot be attributed to impurities such as SnS_2 and Sn_2S_3. The similarity between the quadrupolar splitting values corresponding to the first and third, and the second and fourth sites makes evident the presence of environments for the Sn^{4+} ions that are close to those of Sn^{2+}. These results would allow us to assume the occurrence of electron-transfer phenomena between sublattices.

In summary, ^{119}Sn Mössbauer spectroscopy of some misfit layer sulfides has shown the occurrence of interactions between SnS and TS_2 sublattices. This fact gives rise to an extended coordination number (5 + 2) and (5 + 3) for tin atoms by long bonding with sulfur atoms of the neighboring layer. Concerning the electron charge transfer between layers, the weak signals corresponding to Sn^{4+} ions, which have been observed for $(SnS)_{1.20}TiS_2$ and $(SnS)_{1.16}TaS_2$, demonstrate that Mössbauer spectroscopy is a reliable technique to study this phenomenon. To solve this problem, a group of experiments, consisting of the modification of the conditions of synthesis and the complementary use of ^{119}Sn Mössbauer spectroscopy and X-ray absorption of the L and M edges of the transition metals and L edge of Sn atoms, are being developed.

Acknowledgment. The authors acknowledge the financial support of Action 13F of the Picasso program. The spanish group wants to acknowledge to CICYT (MAT 93-1204) for financial support.

CM9405281

---

(19) Ettema A. R. H. F. *The Electronic Structure of the Misfit Layer Compounds $(MX)_\delta TX_2$*; Ph.D. Dissertation, Groningen Univeristy, 1993.