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BRIEF REPORTS

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Local environment of tin in layered $SnSe_{2x}S_{2(1-x)}$ compounds by ^{119}Sn Mössbauer spectroscopy

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The local environment of tin atoms in $SnSe_{2x}S_{2(1-x)}$ $(x=0-1)$ solid solutions has been studied by ^{119}Sn Mössbauer spectroscopy. A linear increase of the Mössbauer isomer shift δ as a function of x is observed. First, we show that this result is in good agreement with a tight-binding evaluation of the Mössbauer isomer shift which takes into account the experimental values of the lattice parameters. Then, we propose a molecular calculation which provides a rather simple explanation of the linear relationship of δ and x based on the description of the local Sn environment. [S0163-1829(97)07336-0]

INTRODUCTION

The compounds of $SnSe_{2x}S_{2(1-x)}$ stoichiometry with $x=0-1$ have a CdI_2-related crystal structure.[1] It consists of two layers of hexagonal closed packed chalcogenide anions with sandwiched tin cations, which are octahedrally coordinated by six nearest-neighbor chalcogen atoms. Each S or Se atom is nested at the top of a triangle of Sn atoms. Adjacent X-Sn-X (X=S,Se) layers are bound by weak van der Waals interactions. The different stacking sequence of these layers along the c axis defines an extended polytypism in these solids. The most common polytype of $Sn(S,Se)_2$ involves only one sandwich layer per unit cell and is commonly referred to as 1T.[2]

Because of the strong anisotropy of their physical properties, $SnSe_{2x}S_{2(1-x)}$ compounds have been extensively studied, including synthesis conditions[3–5] and optical properties.[6–8] One interesting application concerns their aptitude as host materials for intercalation reactions by both chemical (solvated[9,10] and unsolvated[11,12] alkaline ions, $CoCp_2$,[13] amines,[14] etc.) and electrochemical procedures [Li and Na (Refs. 12 and 15)]. ^{119}Sn Mössbauer spectroscopy is a very efficient tool for probing the local environment of tin atoms in the as-prepared chalcogenides and their intercalation products. Baggio *et al.*[16] have reported isomer shift values of −0.66, −0.86, and 0.88 mm/s (reference Mg_2Sn) for SnS_2, SnSeS, and $SnSe_2$, respectively, which suggest similar environments of tin atoms in SnSeS and $SnSe_2$. Herbert *et al.*[17] carried out a systematic study of the solid solution $SnSe_{2x}S_{2(1-x)}$ focused on the lattice dynamics of these materials, in which an increase in the Mössbauer isomer shift δ with the selenium content x was reported. The observed correlation between δ and x was not strictly linear and no information was given on the lattice parameter variations with x. Mössbauer studies of $(CoCp_2)_xSnS_2$ have shown a peak ascribable to a partial reduction of tin atoms from Sn(IV) to Sn(II), maintaining the octahedral coordination. Recently, Mössbauer spectra of lithiated phases Li_xSnS_2 revealed two new signals, which were interpreted in terms of a partial reduction from Sn(IV) to Sn(II) and tetrahedral coordinated Sn(0).[18]

In this paper, a systematic study of the local environment of tin atoms in $SnSe_{2x}S_{2(1-x)}$ solid solutions is carried out by using x-ray diffraction and Mössbauer spectroscopy data. We focus our interest on the variations of the Mössbauer isomer shift δ as a function of x. The variations of the Mössbauer isomer shift with the electron charge density at the nucleus are evaluated from the numbers of tin valence electrons. First, the number of electrons are calculated from a tight-binding calculation which takes into account the real and periodic structure of the materials. Then, a simple molecular calculation based on the local environment of the tin atoms is proposed. Finally, the results and related to some parameters commonly used in solid state chemistry.

EXPERIMENTAL

$SnSe_{2x}S_{2(1-x)}$ samples were obtained by direct synthesis from pure elements. Stoichiometric mixtures of tin metal powder (99.5%, Stream Chemicals), selenium powder (99.7%, Stream Chemicals), and sulfur powder (99.5%, Merck) were prepared in the $0 \leqslant x \leqslant 1$ range (step, $\Delta x = \frac{1}{8}$) and placed inside a silica tube and vacuum sealed. The ampoules were heated to 500 °C over a period of 2 h. This temperature was maintained for 48 h and then allowed to cool to room temperature. The products were ground, vacuum sealed, and heated under the same conditions, and this process was repeated a second time. The final products were crushed to reduce the particle size and stored under inert atmosphere in order to avoid oxidation reactions.

X-ray diffraction patterns were recorded at room temperature on a Siemens D500 diffractometer using CuK_α radiation and a graphite monochromator. ^{119}Sn Mössbauer spectra were recorded at room temperature in the constant-acceleration mode on a ELSCINT-AME40 spectrometer. The γ-ray source was $Ba^{119m}SnO_3$. The velocity scale was calibrated with the magnetic sextet spectrum of a high purity iron foil absorber. The source was ^{57}Co(Rh). Recorded spectra were fitted to Lorentzian profiles by least square method[19] and the fit quality was controlled by the classical χ^2 and misfit test. The origin of the isomer shift was determined from the center of the $BaSnO_3$ spectrum also recorded at room temperature.

RESULTS AND DISCUSSION

The x-ray diffraction patterns of all the stannic dichalcogenide samples prepared by the procedure described above were characteristic of a single phase product and were indexed in the hexagonal system, $P\text{-}\bar{3}m1$space group of polytype 1 T.[2] The unit cell parameters of $SnSe_{2x}S_{2(1-x)}$ are in good agreement with previously reported data.[6] As expected, they increase with the selenium content (Fig. 1) due to the expansion required for locating the selenium atoms, which are larger than sulfur atoms. The smooth variation of the unit cell parameters with the composition is in agreement with Vegard's law.[20] The lattice constant a increases linearly with x, in contrast with the c parameter which exhibits a weakly nonlinear increase. Linear and quadratic regressions for a and c, respectively, give the following results (in Å):

$$a = 3.644 + 0.162x, \tag{1}$$

$$c = 5.901 + 0.347x - 0.106x^2. \tag{2}$$

The c/a ratio is close to 1.633, the theoretical value for a perfect hexagonal closed packed.

The ^{119}Sn Mössbauer spectra exhibit one peak and are fitted to one equivalent site, as shown in Fig. 2. Table I summarizes the experimental values of the isomer shift δ and the linewidth Γ, the quadrupole splitting Δ being equal to 0. The observed small values of Γ (0.83–1.01 mm/s) are in good agreement with a statistical distribution of the chalcogenide atoms on their crystallographic sites rather than a mixture of sulfur and selenium rich domains. Small values of Γ also confirm the weak quadrupole hyperfine interactions due to an almost spherical charge distribution around tin atoms and the octahedral coordination not to be distorted. This

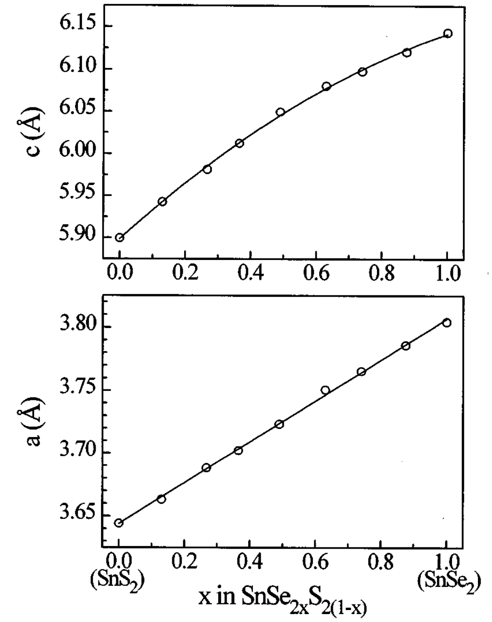

FIG. 1. Evolution of the lattice constant a and c of $SnSe_{2x}S_{2(1-x)}$ as a function of Se content.

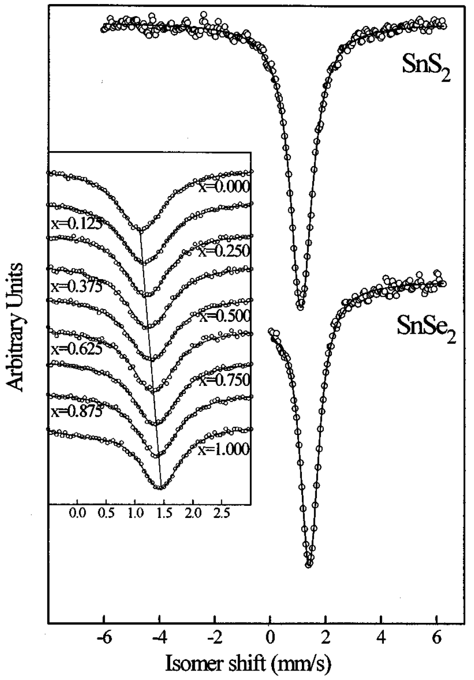

FIG. 2. Mössbauer spectra of $SnSe_{2x}S_{2(1-x)}$ recorded at room temperature (in circles) and the proposed fitting (full line) to one site.

TABLE I. Isomer shift (δ) and full width at half maximum (Γ) values obtained from the fitting of the Mössbauer spectra of Fig. 2.

x in $SnSe_{2x}S_{2(1-x)}$	δ (mm/s)	$\Delta\delta$ (mm/s)	Γ (mm/s)	$\Delta\Gamma$ (mm/s)
0.000	1.018	0.003	0.985	0.009
0.125	1.081	0.003	1.013	0.008
0.250	1.111	0.004	0.933	0.012
0.375	1.148	0.004	0.962	0.013
0.500	1.185	0.003	0.962	0.009
0.625	1.226	0.005	0.914	0.016
0.750	1.263	0.003	0.916	0.009
0.875	1.300	0.004	0.886	0.012
1.000	1.343	0.005	0.831	0.016

in turn, inhibits the Goldanski-Karyagin effect usually found for other polycrystalline samples.[21,22] The evolution of Γ values as a function of the composition x shows a linear variation from about 1.01 mm/s at $x=0$ to 0.85 mm/s at $x=1$. This evolution is directly related to the decrease of the amount of ^{119}Sn from SnS_2 to $SnSe_2$, since the used amount of sample was a constant of ≈ 100 mg. Thus, the effective thickness to the Mössbauer effect decrease from $x=0$ to $x=1$.

Variations of the Mössbauer isomer shift δ as a function of x clearly show a linear increase (Fig. 3). This results is somewhat different of that of Herber *et al.*[17] obtained at 78 K. A shift in the δ values is observed, due to a thermal effect. However, as shown in Fig. 3 the values of δ reported by Herber *et al.*[17] exhibit a nonlinear variation with x. This could be tentatively explained by the different synthesis conditions, since their samples were annealed and some ordering of S and Se anions may be present.

We now propose an analysis of the observed variations of δ with x from the well-known relation of the Mössbauer isomer shift (in velocity units):[23]

$$\delta = (4\pi Z e^2 c R^2)/5E_0\ (\Delta R/R)[\rho_a(0) - \rho_s(0)], \tag{3}$$

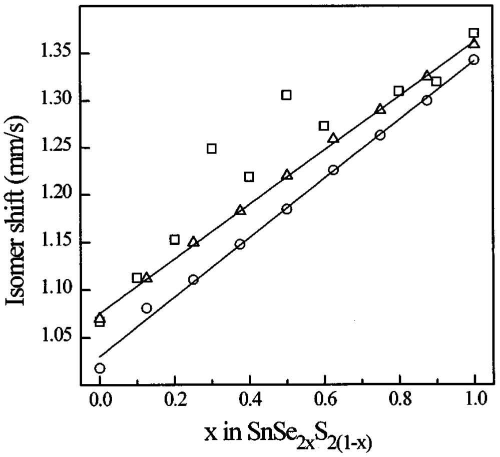

FIG. 3. Variations of the ^{119}Sn Mössbauer isomer shift in $SnSe_{2x}S_{2(1-x)}$ compounds as a function of x. Experimental values obtained in this work (at room temperature, circles) from Ref. 10 (at 78 K, squares), and calculated values (triangle) are shown.

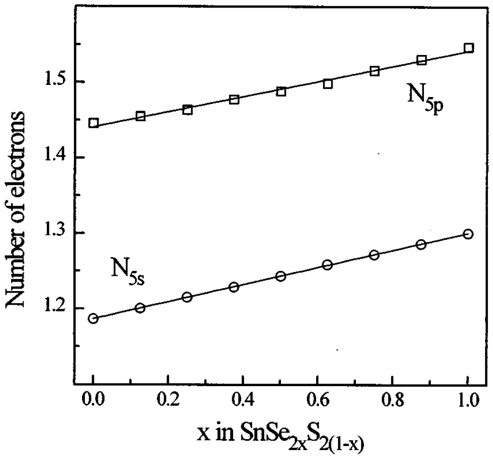

FIG. 4. Variations of the calculated numbers of $5s(N_{5s})$ and $5p(N_{5p})$ electrons of the Sn atoms in $SnSe_{2x}S_{2(1-x)}$ as a function of x.

where e is the electronic charge, c is the velocity of light, Z is the electron number, and R the effective nuclear radius of the Mössbauer atom, E_0 is the energy of the nuclear transition, $\Delta R/R$ is the variation of the nuclear radius, $\rho_a(0)$ and $\rho_s(0)$ are the electron densities in atomic units at the nucleus of the absorber and source, respectively. This relation predicts a linear correlation between the Mössbauer isomer shift δ and the electronic density at the nucleus of the absorbing material $\rho_a(0)$. Following the approach of Ruby and Shenoy[23] the electron density at the nucleus $\rho(0)$ can be written as a linear function of the numbers of tin valence electrons. Values of $\rho(0)$ for different electronic configurations of the Sn-free atom have been calculated by Ellis[23] and the linear expression of $\rho(0)$ is obtained by a linear regression from those values. This gives for the difference between the electron densities at the nucleus of the absorber and source materials

$$\rho_a(0) - \rho_s(0) \approx 40.7\Delta N_{5s} - 4.5\Delta N_{5p}, \tag{4}$$

where ΔN_{5s} (ΔN_{5p}) is the difference between the Sn $5s$ ($5p$) electron number in the absorbing and source materials. This relation clearly shows the dominant influence of the Sn $5s$ electrons on the electron density at the tin nucleus and thus, on the Mössbauer isomer shift.

We first evaluate the numbers of tin valence electrons by a tight-binding calculation[24] following a procedure similar to that of Lefebvre *et al.*[25] Previous results[26] obtained for numerous tin compounds have provided a value of $\Delta R/R = 1.3\times 10^{-4}$ in agreement with other previously published values.[23] The number of Sn $5s$ electrons, N_{5s}(Sn), and Sn $5p$ electrons, N_{5p}(Sn), in $SnSe_{2x}S_{2(1-x)}$ were obtained within the virtual crystal approximation considering an averaged value of the intra-atomic energies. Experimental values of the cell parameters (Fig. 1) have been considered. The variations of N_{5s}(Sn) and N_{5p}(Sn) as a function of x are shown in Fig. 4. We have evaluated δ from relations (3) and (4) and for the calculated numbers of tin valence electrons. The values of δ for SnO_2 and $BaSnO_3$ are very close and the electron density at the nucleus of the source material $\rho_s(0)$ has been calculated for SnO_2. Comparison between the experimental and calculated values of δ shows good agreement (Fig. 3). The observed linear correlation between the calculated values of δ and x can be related to the expressions (3) and (4) and to the results of Fig. 4. It is worth noting that variations of δ are mainly influenced by changes in the number of Sn 5s electrons. Thus, the linear correlation between δ and x can be explained by the linear variations between N_{5s} and x.

A molecular calculation based on the local environment of the Sn atom has also been performed in order to derive an analytical expression of δ as a function of x. This calculation is based on the following assumptions: (i) the Sn 5s and 5p orbitals and the S 3p and Se 4p orbitals pointing toward the Sn atoms are considered, neglecting the effect of the anion s valence electrons because of their deep energetic levels and (ii) only the main $sp\sigma$ and $pp\sigma$ interactions are taken into account. A simple calculation on isolated SnA_6 (A=S,Se) molecules is then possible considering a Hamiltonian matrix 10×10 which can be analytically diagonalized because of the octahedral symmetry of the molecules. From the expressions of the molecular wave functions it is possible to evaluate the number of Sn 5s and 5p electrons. As a first approximation, the influence of the 5p electrons on δ can be neglected. We obtain

$$N_{5s}(\mathrm{Sn}) = 1 - \frac{\gamma}{\sqrt{6+\gamma^2}}; \quad \gamma = \frac{E_{5s}(\mathrm{Sn}) - E_p(A)}{2\beta}, \tag{5}$$

where $E_{5s}(\mathrm{Sn}) = -12.5$ eV is the Sn 5s free-atom level.[27] Considering $E_{3p}(\mathrm{S}) = -10.27$ eV and $E_{4p}(\mathrm{Se}) = -9.53$ eV (Ref. 27) the valence p level of the virtual anions is given by

$$E_p(x) = (1-x)E_{3p}(\mathrm{S}) + xE_{4p}(\mathrm{Se}) \approx -10.27 + 0.74x \ \text{eV}. \tag{6}$$

The hopping integral β (in eV) between Sn 5s and chalcogen valence p orbitals is evaluated from the Harrison rule:[28] $\beta = 10.82/d^2$, where d is the Sn-S distance. The Sn-S distance d can be calculated from the interpolated values of the lattice parameters given by relations (1) and (2), the chalcogen position being $(\frac{1}{3}, \frac{2}{3}, z=\frac{1}{4})$. Neglecting the term in x^3, we obtain

$$d^2 = \frac{a^2}{3} + \frac{c^2}{12} \approx 6.603 + 6.650x - 0.062x^2. \tag{7}$$

Relations (6) and (7) show that variations of $E_p(A)$ and d as a function of x are lower than 0.74 eV and 0.11 Å, respectively. These small variations suggest a Taylor expansion of γ and N_{5s} which, at the second order, leads to the simple expression

$$N_{5s}(\mathrm{Sn}) \approx 1.38 - 0.11x + 0.005x^2. \tag{8}$$

This expression shows that variations of N_{5s} are lower than 0.11 electron in excellent agreement with the previous tight-binding calculation although the absolute value of N_{5s} is slightly overestimated with the molecular calculation by 0.07 electron. Expression (8) also shows that the second-order term can be neglected confirming the linear relationship of N_{5s} and x. This can be related to small variations of the chalcogen p valence electron energy level $E_p(A)$ [given by Eq. (6)] and of the Sn-A bond length d [given by Eq. (7)].

Finally, it is interesting to relate the previous results with the commonly used notions of covalent radius and electronegativity. The increase of N_{5s} from SnS_2 to $SnSe_2$ can be related to the increase of the Sn-A bond length of about 0.11 Å [Eq. (7)] which can be compared to the difference between the anion average covalent radius of S (1.04 Å) and Se (1.17 Å).[28] This increase of N_{5s} can also be explained by the decrease of the energy difference $E_{5s} - E_p(A)$ of about 0.7 eV which can be correlated to the decrease of the Pauling electronegativity[29] difference for Sn-A from 0.7 (Sn-S) to 0.6 (Sn-Se). Considering a constant value for d in the evaluation of N_{5s}, given by Eq. (5) leads to variations of about 0.07 electron instead of 0.11 electron. Thus, the increase of N_{5s} from SnS_2 to $SnSe_2$ with x is mainly influenced by the decrease of $E_{5s} - E_p(A)$. This provides a rather simple and qualitative explanation of the linear relationship of the ^{119}Sn Mössbauer isomer shift in $SnSe_{2x}S_{2(1-x)}$ as a function of x.

CONCLUSION

We have measured the ^{119}Sn Mössbauer isomer shift δ in $SnSe_{2x}S_{2(1-x)}$ ($x = 0-1$). The observed linear correlation between δ and x is in good quantitative agreement with the results of a tight-binding calculation and can be related to linear variations of the number of Sn 5s electrons $N_{5s}(\mathrm{Sn})$ with x. Then, a simple molecular calculation has been used to derive an approximate analytical expression of $N_{5s}(\mathrm{Sn})$ which is found to be linear with x because of the close values of the energy levels of the chalcogen p valence electrons.

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