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## Antistructural defects in lead chalcogenides

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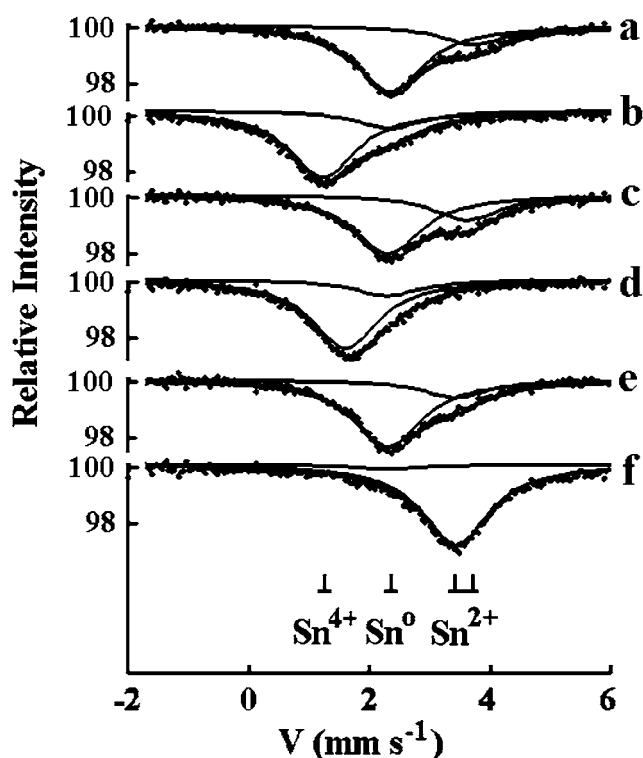
### Abstract

It is shown by means of emission Mössbauer spectroscopy on  $^{119}\text{Sb}(^{119\text{m}}\text{Sn})$  and  $^{119\text{m}}\text{Te}(^{119\text{m}}\text{Sn})$  isotopes that the charge state of the  $^{119\text{m}}\text{Sn}$  antistructural defect arising in the anion sublattice after radioactive conversion of  $^{119}\text{Sb}$  and  $^{119\text{m}}\text{Te}$  does not depend on the Fermi level position. In contrast, the  $^{119\text{m}}\text{Sn}$  centre in the cation sublattice of PbS and PbSe acts like an electrically active substitutional impurity: in n-type samples the spectrum corresponds to the neutral state of a donor centre ( $^{119\text{m}}\text{Sn}^{2+}$ ), while in p-type samples it corresponds to the twice ionized state of this centre ( $^{119\text{m}}\text{Sn}^{4+}$ ). In the case of PbTe the tin centres in the cation sublattice are electrically neutral and are stabilized as  $^{119\text{m}}\text{Sn}^{2+}$  ions. The localization of antimony impurity atoms in the PbS, PbSe and PbTe lattices depends on the conductivity type of the material: in n-type samples the antimony is mainly localized in the anion sublattice, while in p-type samples it is mainly in the cation sublattice.

### 1. Introduction

This paper demonstrates the results of an experimental study of tin atoms being part of the antistructural defects in lead chalcogenides. For this purpose the emission variant of Mössbauer spectroscopy on the  $^{119}\text{Sb}(^{119\text{m}}\text{Sn})$  and  $^{119\text{m}}\text{Te}(^{119\text{m}}\text{Sn})$  isotopes was used that allowed the tin impurity atoms to be stabilized at foreign sites after a maternal nuclei radioactive decay sequence.

The emission Mössbauer spectroscopy on the  $^{119}\text{Sb}(^{119\text{m}}\text{Sn})$  isotope also allows us to resolve a problem of the nature of states formed by antimony impurity atoms in PbX (X = S, Se, Te). There are practically no papers related to the impurities from group-V elements (As, Sb, and Bi) in lead chalcogenides. It is only known that these impurities act as donors, although the fraction of electrically active atoms is considerably less than one [1]. This fact can be explained in two ways: either a significant number of impurity atoms form electrically inactive complexes (e.g.  $\text{Sb}_2\text{Te}_3$ ) in the lattice, or the impurity is distributed between the cation sublattice (where it acts as a donor) and the anion sublattice (in this case the nature of the impurity states is not obvious). The choice between these alternative models is possible if the position of the antimony atoms in the lead chalcogenide lattices is determined.



**Figure 1.**  $^{119}\text{Sb}(^{119\text{m}}\text{Sn})$  Mössbauer emission spectra at 80 K in n-PbS (a), p-PbS (b), n-PbSe (c), p-PbSe (d), n-PbTe (e), and p-PbTe (f). The experimental spectra are split into components corresponding to  $^{119\text{m}}\text{Sn}^0$ ,  $^{119\text{m}}\text{Sn}^{2+}$  and  $^{119\text{m}}\text{Sn}^{4+}$ .

## 2. Experimental procedure

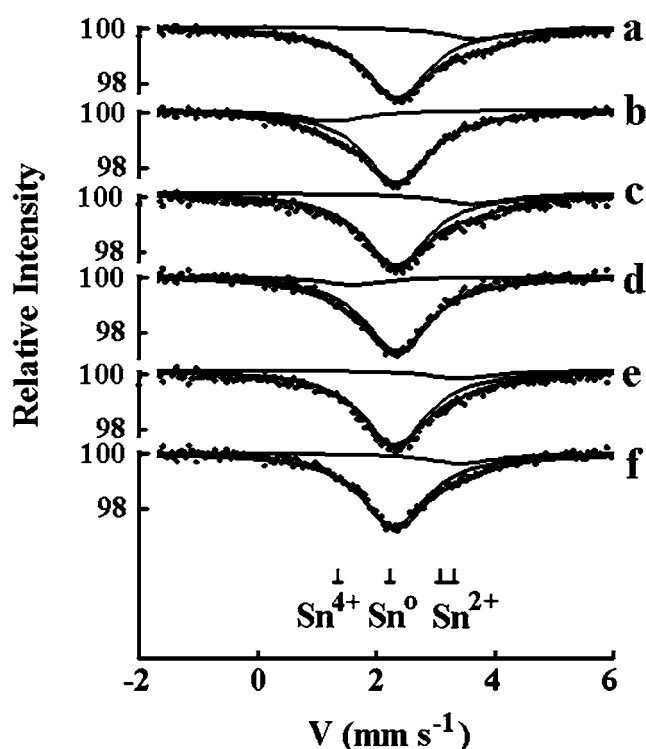
The  $^{119\text{m}}\text{Te}$  and  $^{119}\text{Sb}$  isotopes were obtained using the  $^{117}\text{Sn}(\alpha, 2n)^{119\text{m}}\text{Te}$  and  $^{120}\text{Sn}(p, 2n)^{119}\text{Sb}$  reactions. The procedure of anion exchange was used to separate the carrier-free  $^{119\text{m}}\text{Te}$  and  $^{119}\text{Sb}$  samples. Mössbauer sources were prepared by alloying the PbS or PbTe samples with the carrier-free  $^{119\text{m}}\text{Te}$  samples so that the estimated concentration of impurity atoms did not exceed  $10^{17}$  atoms  $\text{cm}^{-3}$ . The initial PbX samples were n-type (with an excess of lead,  $n = 5 \times 10^{18}$   $\text{cm}^{-3}$ ) and p-type (with an excess of chalcogen,  $p = 10^{18}$   $\text{cm}^{-3}$ ).

The measurements of the  $^{119}\text{Sb}(^{119\text{m}}\text{Sn})$  and  $^{119\text{m}}\text{Te}(^{119\text{m}}\text{Sn})$  Mössbauer spectra were performed on an industrial SM-2201 spectrometer at 80 K with a  $\text{CaSnO}_3$  absorber (the surface density with respect to tin was  $5 \text{ mg cm}^{-2}$ ). The spectrum with this absorber and the  $\text{Ca}^{119\text{m}}\text{SnO}_3$  was a single line, with a FWHM  $\Gamma = 0.79 \pm 0.01 \text{ mm s}^{-1}$ , that was accepted as an instrumental width of the spectral line. Typical spectra of the PbX: $^{119}\text{Sb}$  and PbX: $^{119\text{m}}\text{Te}$  samples are shown in figures 1 and 2, and the results of their processing are presented in table 1.

## 3. Experimental results and discussion

### 3.1. Isotope $^{119}\text{Sb}$

A diagram of the  $^{119\text{m}}\text{Sn}$  Mössbauer level formation using the parent isotope  $^{119}\text{Sb}$  (half-decay period is 38 h) is shown in figure 3(a). Taking into consideration that the recoil energy of



**Figure 2.**  $^{119m}\text{Te}(^{119m}\text{Sn})$  Mössbauer emission spectra at 80 K in n-PbS (a), p-PbS (b), n-PbSe (c), p-PbSe (d), n-PbTe (e), and p-PbTe (f). The experimental spectra are split into components corresponding to  $^{119m}\text{Sn}^0$ ,  $^{119m}\text{Sn}^{2+}$  and  $^{119m}\text{Sn}^{4+}$ .

the daughter  $^{119m}\text{Sn}$  atoms arising from the electron capture (EC) in  $^{119}\text{Sb}$  with emission of a neutrino does not exceed 1.4 eV, it is possible to conclude that the radioactive transformation does not lead to a displacement of the tin atoms from the normal sites within the crystal lattice. Then the parameters of the emission  $^{119}\text{Sb}(^{119m}\text{Sn})$  Mössbauer spectra should reflect the valence (charge) state of the  $^{119m}\text{Sn}$  atoms located at sites occupied by the antimony atoms.

The spectra of the  $\text{PbX}:\text{Sb}$  n-type samples are a superposition of two lines (figures 1(a), (c), (e)). The widths of both lines considerably exceed the instrumental width, which indicates the distortion of the cubic symmetry in the local environment of the  $^{119m}\text{Sn}$  daughter atoms. The reason for this distortion can be a non-central position of the impurity atom caused by the difference in the sizes of a replaced ( $\text{Pb}^{2+}$ ,  $\text{X}^{2-}$ ) and a replacing (tin) ion.

One of these lines (which dominates in n-type samples, and is referred to as spectrum I) has an isomeric shift typical for intermetallic tin compounds, so it should be assigned to the  $^{119m}\text{Sn}^0$  centres in the anion sublattice of  $\text{PbX}$  (lead atoms located in the immediate vicinity of these centres interact with them, leading to an isomeric shift typical for metallic tin alloys). It is obvious that  $^{119m}\text{Sn}^0$  atoms are formed from the  $^{119}\text{Sb}$  atoms located in the  $\text{PbX}$  anion sublattice.

The second line (spectrum II) has an isomeric shift typical for divalent tin compounds, so it should be assigned to the  $^{119m}\text{Sn}^{2+}$  centres in the cation sublattice of  $\text{PbX}$  (chalcogenide atoms located in the immediate vicinity of these centres interact with them, leading to an isomeric shift that is close to the isomeric shift of the  $^{119}\text{Sn}$  spectrum in the  $\text{SnX}$  compounds).

**Table 1.** Parameters of the  $^{119}\text{Sb}(^{119\text{m}}\text{Sn})$  emission Mössbauer spectra in PbS, PbSe and PbTe at 80 K. (Note: IS stands for isomeric shift relative to  $\text{CaSnO}_3$ ,  $G$  is the spectral width at half-height (FWHM), and  $S$  is the relative area under the spectrum.)

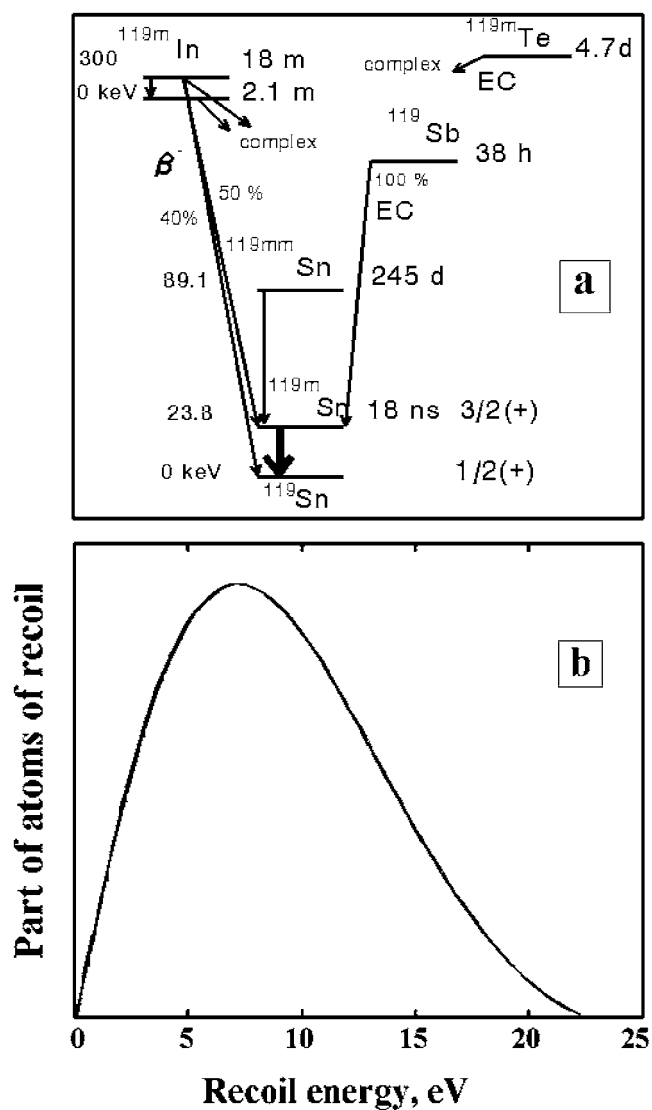
Compound	Parent	Type	Centre	IS	$G$	$S$
conductivity type	isotope	of spectrum		( $\text{mm s}^{-1}$ )	( $\text{mm s}^{-1}$ )	
n-PbS	$^{119}\text{Sb}$	I	$^{119\text{m}}\text{Sn}^0$	2.34	1.34	0.78
		II	$^{119\text{m}}\text{Sn}^{2+}$	3.73	1.33	0.22
	$^{119\text{m}}\text{Te}$	I	$^{119\text{m}}\text{Sn}^0$	2.35	1.34	0.85
		II	$^{119\text{m}}\text{Sn}^{2+}$	3.72	1.45	0.15
p-PbS	$^{119}\text{Sb}$	I	$^{119\text{m}}\text{Sn}^0$	2.33	1.33	0.21
		III	$^{119\text{m}}\text{Sn}^{4+}$	1.23	1.32	0.79
	$^{119\text{m}}\text{Te}$	I	$^{119\text{m}}\text{Sn}^0$	2.34	1.36	0.87
		III	$^{119\text{m}}\text{Sn}^{4+}$	1.25	1.46	0.13
n-PbSe	$^{119}\text{Sb}$	I	$^{119\text{m}}\text{Sn}^0$	2.30	1.33	0.70
		II	$^{119\text{m}}\text{Sn}^{2+}$	3.61	1.35	0.30
	$^{119\text{m}}\text{Te}$	I	$^{119\text{m}}\text{Sn}^0$	2.33	1.32	0.87
		II	$^{119\text{m}}\text{Sn}^{2+}$	3.62	1.46	0.13
p-PbSe	$^{119}\text{Sb}$	I	$^{119\text{m}}\text{Sn}^0$	2.29	1.34	0.19
		III	$^{119\text{m}}\text{Sn}^{4+}$	1.60	1.33	0.81
	$^{119\text{m}}\text{Te}$	I	$^{119\text{m}}\text{Sn}^0$	2.35	1.33	0.90
		III	$^{119\text{m}}\text{Sn}^{4+}$	1.62	1.47	0.10
n-PbTe	$^{119}\text{Sb}$	I	$^{119\text{m}}\text{Sn}^0$	2.31	1.30	0.79
		II	$^{119\text{m}}\text{Sn}^{2+}$	3.41	1.32	0.21
	$^{119\text{m}}\text{Te}$	I	$^{119\text{m}}\text{Sn}^0$	2.31	1.32	0.90
		II	$^{119\text{m}}\text{Sn}^{2+}$	3.42	1.41	0.10
p-PbTe	$^{119}\text{Sb}$	I	$^{119\text{m}}\text{Sn}^0$	2.33	1.32	0.05
		II	$^{119\text{m}}\text{Sn}^{2+}$	3.43	1.31	0.95
	$^{119\text{m}}\text{Te}$	I	$^{119\text{m}}\text{Sn}^0$	2.30	1.33	0.88
		II	$^{119\text{m}}\text{Sn}^{2+}$	3.41	1.40	0.12
Errors				$\pm 0.01$	$\pm 0.01$	$\pm 0.02$

It is obvious that  $^{119\text{m}}\text{Sn}^{2+}$  atoms are formed from the  $^{119}\text{Sb}$  atoms located in the PbX cation sublattice.

The spectra of the p-type samples are also a superposition of two broad lines (figures 1(b), (d), (f)). For PbTe the specified lines are identical to spectra I and II according to the value of an isomeric shift and width, but in the p-type samples the spectrum of type II dominates.

For PbS and PbSe one of these lines has parameters close to those of the type-I spectrum (it dominated in the case of n-type samples, although its intensity in p-type samples is considerably decreased). This spectrum should be assigned to the  $^{119\text{m}}\text{Sn}^0$  centres formed from the  $^{119}\text{Sb}$  atoms located in the anion sublattice of PbS. The second line (spectrum III) has an isomeric shift typical for the quadrivalent tin compounds, and it should be assigned to the  $^{119\text{m}}\text{Sn}^{4+}$  centres formed from the  $^{119}\text{Sb}$  atoms located in the cation sublattice of PbS.

Thus the place of localization of antimony impurity atoms in the PbX lattices depends on the character of the loss in the stoichiometry of the material: in samples with excess lead the antimony is localized mainly in the anion sublattice, while in the samples with excess chalcogenides the antimony is mainly in the cation sublattice (and plays the donor role). The fraction of antimony electrically active atoms depends on the distribution of antimony between



**Figure 3.** A decay diagram of  $^{119m}\text{Te}$  and  $^{119}\text{Sb}$  (a) and spectrum of the recoil of the  $^{119}\text{Sb}$  atoms (b).

the sublattices, but it is always less than one (this follows from the fact that even in the p-type samples a considerable number of antimony atoms are located in the anion sublattice).

### 3.2. Isotope $^{119m}\text{Te}$

The source of the Mössbauer gamma quanta while measuring  $^{119m}\text{Te}(^{119m}\text{Sn})$  spectra was the  $^{119m}\text{Sn}$  nucleus formed after the EC first at the  $^{119m}\text{Te}$  nucleus, and then at the  $^{119}\text{Sb}$  nucleus (see figure 3(a)). It is considered that the maternal  $^{119m}\text{Te}$  atoms substitute chalcogen atoms in  $\text{PbX}$  lattices.

As can be seen from figure 2, the Mössbauer spectra of the n-type samples are a superposition of two lines: an intense one (spectrum I; the isomeric shift corresponds to  $^{119\text{m}}\text{Sn}^0$ ) and a less intense one (spectrum II; the isomeric shift corresponds to  $^{119\text{m}}\text{Sn}^{2+}$ ). The emission spectra of the p-type samples are also a superposition of two lines. For p-PbTe the experimental spectrum is identical to the spectrum for n-PbTe whereas spectra for p-PbS and p-PbSe, in addition to the intense line I, also contain a less intense line III (the isomeric shift corresponds to  $^{119\text{m}}\text{Sn}^{4+}$ ).

If we take into account the isomeric shifts values, then spectrum I corresponds to tin daughter atoms having only metal (lead) atoms in their immediate environment so it should be assigned to the  $^{119\text{m}}\text{Sn}^0$  centres formed after the decay of the  $^{119\text{m}}\text{Te}^{2-}$  maternal atoms remaining at the anion lattice. The isomeric shifts of spectra II and III are typical for chalcogenides of bivalent and tetravalent tin, where the immediate vicinity of the tin atoms contains only chalcogenide atoms, so these spectra correspond to tin daughter atoms  $^{119\text{m}}\text{Sn}^{2+}$  (spectrum II) and  $^{119\text{m}}\text{Sn}^{4+}$  (spectrum III), arising after the decay of the  $^{119\text{m}}\text{Te}^{2-}$  maternal atoms in the cation lattice sites.

To explain the data obtained it should be taken into consideration that an excited daughter atom is formed as a result of EC from the inner shell of the maternal atom. Its excitation is removed either by radioactive transitions or by emission of Auger electrons, leading to a spectrum of charges of the tin daughter ions. The ionized atom can be displaced from the normal lattice site, and the emission of an antineutrino during an EC transfers a recoil energy to the atom, also leading to the appearance of the displaced tin atoms. An analysis of numerous Mössbauer studies of after-effects of nuclear conversions shows that the daughter atom undergoes a transition to a stable charge state in a time less than several picoseconds. In other words, only the final shapes of the daughter atoms stabilization appear in the Mössbauer emission spectra. The probability for the appearance of displaced atoms depends on the ratio of the recoil energy of the daughter nucleus  $E_R$  to the threshold energy of the atom displacement  $E_d \sim 25$  eV. To estimate the possibility of displacement of daughter atoms from their normal lattice sites due to the recoil energy, the maximum recoil energy for the probe nucleus  $^{119\text{m}}\text{Sn}$  was calculated: the  $^{119\text{m}}\text{Te} \rightarrow ^{119}\text{Sb}$  decay is accompanied by a recoil energy  $E_R \sim 24$  eV. A spectrum of the recoil of the  $^{119}\text{Sb}$  atoms is shown in figure 3(b). The significant value of  $E_R$  explains the appearance of lines corresponding to the  $^{119\text{m}}\text{Sn}$  atoms displaced from the cation lattice sites in the  $^{119\text{m}}\text{Te}(^{119\text{m}}\text{Sn})$  Mössbauer emission spectra in PbX samples.

#### 4. Conclusions

The  $^{119\text{m}}\text{Sn}$  centre in the cation PbS sublattice (corresponding to type-II and type-III spectra) is an isoelectronic substitutional impurity. According to data from [2] the isoelectronic tin impurity in PbS and PbSe is electrically active, acting as a two-electron donor with negative correlation energy. It explains the observed dependence of the isomeric shift in the spectra of such centres on the conductivity type of the PbS and PbSe: in n-type samples the spectrum corresponds to the neutral state of the donor centre ( $^{119\text{m}}\text{Sn}^{2+}$ ), while in p-type samples it corresponds to the twice ionized state ( $^{119\text{m}}\text{Sn}^{4+}$ ). According to [2], the isoelectronic tin impurity in PbTe is electrically inactive, thus explaining the independence of the isomeric shift of the type-II spectrum in PbTe from the conductivity type of the material.

The  $^{119\text{m}}\text{Sn}$  centre in the anion sublattice of PbX (corresponding to a type-I spectrum) is an antistructural defect, so the independence of the isomeric shift of spectrum I from the conductivity type of the material means that the charge state of the antistructural defect does not depend on the position of the Fermi level.

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