

MÖSSBAUER EMISSION SPECTRA OF STANNUM DAUGHTER ISOTOPES MEASURED UNDER CONDITION OF A DYNAMIC RADIOACTIVE EQUILIBRIUM OF TELLURIUM PARENT ISOTOPES AND ANTIMONIUM DAUGHTER ONES

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The information on a valence and a coordination states of the ^{119m}Sn daughter atoms formed in the cationic and anionic lattice sites of the crystalline lead telluride PbTe and the glassy arsenic telluride As_2Te_3 from the ^{119}Sb and ^{119m}Te parent isotopes has been obtained using the emission Mössbauer spectroscopy with the ^{119m}Te parent isotopes being in a dynamic radioactive equilibrium with the ^{119}Sb daughter ones. It was found by calculation and experimentally that the proportion of various valent and coordinate states of tin atoms in the crystal and the glass depended on the preparation moment of Mössbauer sources. Moreover, the displacement of a part of the ^{119}Sb daughter atoms from lattice sites of the ^{119m}Te parent isotopes as a result of a radioactive decay was established when bringing into agreement with experimental data.

Key words: dynamic radioactive equilibrium; Mössbauer emission spectroscopy; isotope; telluride; lead; arsenic

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Introduction

Mössbauer emission spectroscopy on the ^{119m}Sn tin isotope with parent ^{119}Sb antimony and ^{119m}Te tellurium nuclei is widely used to study the state of impurity atoms in crystalline lead chalcogenides and glassy chalcogenides of arsenic and germanium [1 – 11]. Depending on the chemical nature of the parent isotope, daughter tin atoms can stabilize either at chalcogen sublattice sites (if the ^{119m}Te isotope is used) [2, 3, 5, 7, 8], or at sites not determined in advance (if the ^{119}Sb isotope is used) [1, 4, 6 – 11].

In this paper we have measured the ^{119m}Sn Mössbauer emission spectra for sources based on crystalline lead telluride PbTe and glassy arsenic telluride As_2Te_3 , containing simultaneously parent ^{119m}Te and ^{119}Sb isotopes. The spectra allowed to obtain data on the state of parent impurity atoms of tellurium and antimony, and daughter impurity atoms of tin.

Experimental samples and procedure

It follows from Fig. 1 that the decay of par-

ent ^{119m}Te atoms occurs with the formation of radioactive daughter ^{119}Sb nuclei. By the time dynamic equilibrium (the maximum concentration of the ^{119}Sb isotope) is established, a mixture of radioactive atoms of tellurium (denoted as $^{119m}\text{Te-1}$) and antimony (denoted as $^{119}\text{Sb-1}$) is formed.

The fraction of $^{119m}\text{Te-1}$ atoms in the initial content of ^{119m}Te is 0.575, while the fraction of $^{119}\text{Sb-1}$ atoms is 0.195. This mixture was fused with glassy arsenic telluride As_2Te_3 or crystalline lead telluride PbTe in vacuum-sealed quartz tubes. The estimated concentration of impurity atoms did not exceed 10^{17} cm^{-3} . The As_2Te_3 melt was air-quenched; the glassy state was assessed by such criteria as conchoidal fracture, the absence of lines on the X-ray powder patterns, the absence of inclusions and inhomogeneities on polished surfaces observed under an MIM-7 metallographic microscope and an MIK-1 IR microscope. The initial PbTe samples were *n*-type (with an excess of lead, $n \approx 5 \cdot 10^{18} \text{ cm}^{-3}$) and *p*-type (with an excess of tellurium, $p \approx 10^{18} \text{ cm}^{-3}$). The quantitative composition of glasses and crystals was moni-

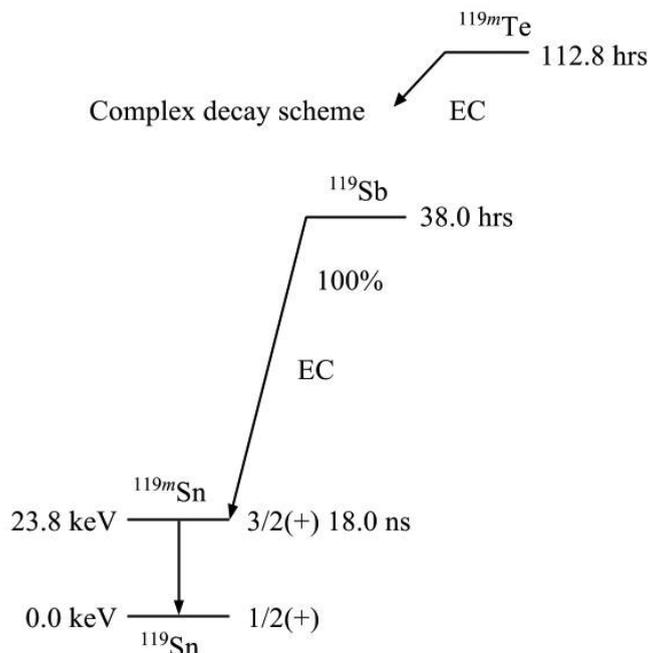


Fig. 1. Diagram of decay of parent ^{119m}Te and ^{119}Sb isotopes.

The decay periods and the energy released are indicated. The decay is accompanied by electron capture (EC)

tored by X-ray fluorescence analysis.

The ^{119m}Te isotope was obtained by the reaction



The anion exchange procedure was used to separate the carrier-free ^{119m}Te sample [5].

The ^{119m}Sn Mössbauer spectra were measured with an SM-2201 spectrometer at a temperature of 80 K with calcium stannate CaSnO_3 (tin density of 5 mg/cm²) as an absorber. The typical Mössbauer spectra of $\text{PbTe} : (^{119}\text{Sb} + ^{119m}\text{Te})$ and $\text{As}_2\text{Te}_3 : (^{119}\text{Sb} + ^{119m}\text{Te})$ samples are shown in the figures below.

A series of emission spectra of ^{119m}Sn was recorded for each source with the acquisition lasting for 9.5 h in the interval from the end of sample alloying to 190.5 h. Evidently, parent ^{119}Sb -1 atoms (the decay constant $\lambda_{\text{Sb}} = 5.05 \cdot 10^{-6} \text{ s}^{-1}$) make the main contribution to the Mössbauer spectra of $\text{PbTe} : (^{119}\text{Sb} + ^{119m}\text{Te})$ and $\text{As}_2\text{Te}_3 : (^{119}\text{Sb} + ^{119m}\text{Te})$ samples in the initial period of measurements, whereas the intensity of the spectrum from parent ^{119}Sb -2 atoms increases with the accumulation of second antimony ^{119}Sb -2 formed during the decay of ^{119m}Te -1 ($\lambda_{\text{Te}} = 1.70 \cdot 10^{-6} \text{ s}^{-1}$).

Experimental results and discussion

Lead telluride. The experimental Mössbauer spectra of the ^{119m}Sn isotope for n - $\text{PbTe} : (^{119}\text{Sb} + ^{119m}\text{Te})$ (n -type lead telluride) and p - $\text{PbTe} : (^{119}\text{Sb} + ^{119m}\text{Te})$ (p -type lead telluride) samples are a superposition of two lines (Fig. 2).

One of these lines has an isomer shift of 2.31(2) mm/s; it is typical for isomer shifts of the ^{119}Sn Mössbauer spectra of intermetallic tin compounds, and, accordingly, this line should be attributed to $^{119m}\text{Sn}^0$ centers formed after the chain of decays



at tellurium sublattice sites (spectrum I).

The second line has an isomer shift of 3.42(2) mm/s; it corresponds to tin telluride and, consequently, this line can be attributed to divalent $^{119m}\text{Sn}^{2+}$ centers formed after the decay of ^{119}Sb -1 atoms at lead sublattice sites (spectrum II).

The intensity of the $^{119m}\text{Sn}^0$ spectrum in the tellurium sublattice for the p -type sample increases with time that has elapsed since the synthesis of Mössbauer sources (this time variable shall be referred to as the source age

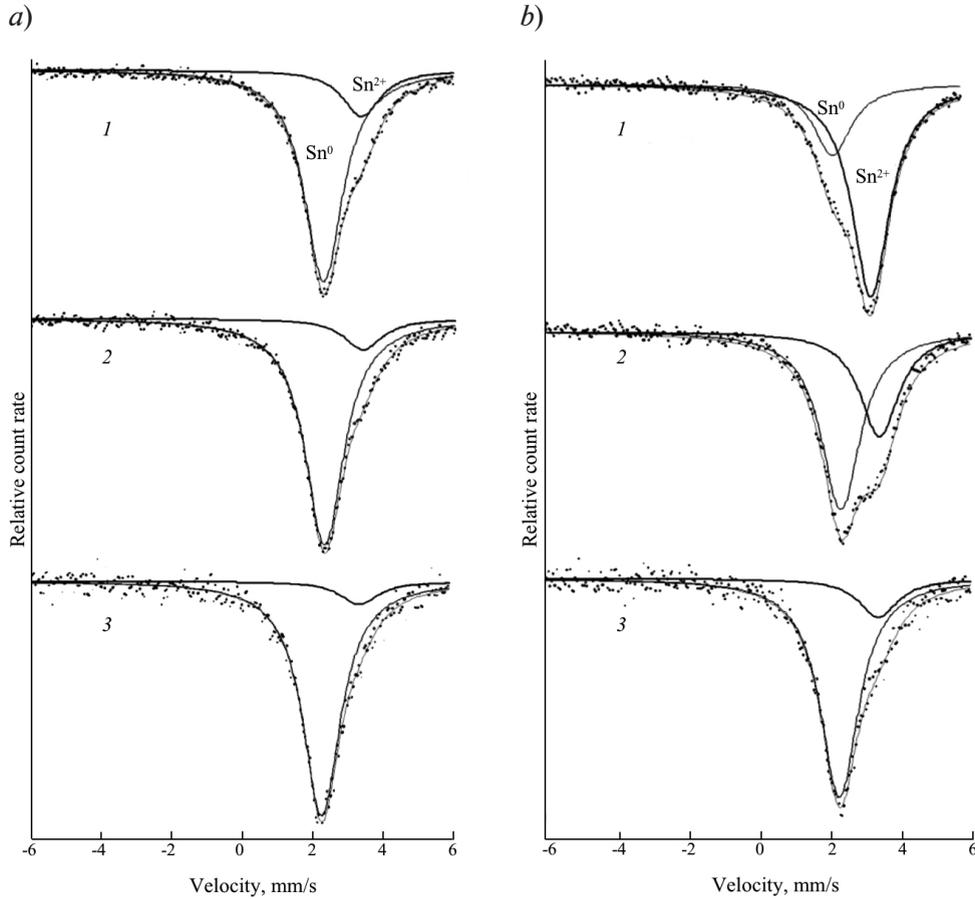


Fig. 2. ^{119m}Sn Mössbauer emission spectra in $n\text{-PbTe}$ (a) and $p\text{-PbTe}$ (b). The spectra were obtained at 80 K in the time intervals of 0 – 9.5 h (1), 66.7 – 76.2 h (2) and 152.4 – 190.5 h (3) after the preparation of the Mössbauer source. Emission lines corresponding to the Sn^0 and Sn^{2+} centers are shown.

from now on), while the ratio of the areas under the two lines varies only slightly for the n -type sample. Since tin impurity atoms in lead telluride are electrically inactive [4, 5], the differing behavior of the ^{119m}Sn Mössbauer spectra for the hole and electron lead telluride samples needs an explanation.

To quantitatively describe the change in the structure of the ^{119m}Sn Mössbauer spectra in lead telluride, the experimental ratios

$$P = \frac{SI}{SI + SII}$$

were calculated for different source age values (here SI and SII are the areas under the normalized Mössbauer spectra I and II, respectively).

The area S under the ^{119m}Sn spectrum is

proportional to the concentration of antimony atoms N_{Sb} and the Mössbauer factor f in the corresponding sublattice:

$$S \sim f N_{\text{Sb}}.$$

Antimony atoms ^{119}Sb are direct radioactive precursors of the ^{119m}Sn isotope.

The dependence of the N_{Sb} concentration on the time t can be obtained from the balance equation:

$$N_{\text{Sb}} = \frac{\lambda_{\text{Te}}}{\lambda_{\text{Sb}} - \lambda_{\text{Te}}} N_{\text{Te}}^0 [\exp(-\lambda_{\text{Te}}t) - \exp(-\lambda_{\text{Sb}}t)] + N_{\text{Sb}}^0 \exp(-\lambda_{\text{Sb}}t),$$

where λ_{Te} , λ_{Sb} are the decay constants of the corresponding parent isotopes; N_{Te}^0 , and N_{Sb}^0 are the concentrations of ^{119m}Te and ^{119}Sb atoms at the initial time; the subscript Te indicates

that the ^{119m}Te concentration is taken in the same sublattice as Sb.

Since the N_{Te}^0 concentration in the lead sublattice can be neglected, instead of expression (1) we obtain:

$$N_{\text{Sb in Pb}} = N_{\text{Sb in Pb}}^0 \exp(-\lambda_{\text{Sb}}t), \quad (2)$$

where $N_{\text{Sb in Pb}}^0$ is the concentration of Sb-1 atoms at lead sites.

Similarly, we obtain for the tellurium sublattice:

$$N_{\text{Sb in Te}} = \frac{\lambda_{\text{Te}}}{\lambda_{\text{Sb}} - \lambda_{\text{Te}}} N_{\text{Te}}^0 [\exp(-\lambda_{\text{Te}}t) - \exp(-\lambda_{\text{Sb}}t)] + N_{\text{Sb}}^0 \exp(-\lambda_{\text{Sb}}t), \quad (3)$$

with the total concentration of Sb-1 determined as

$$N_{\text{Sb}}^0 = N_{\text{Sb in Pb}}^0 + N_{\text{Sb in Te}}^0.$$

Thus, the ratio of the areas under the normalized spectra can be written in the following form:

$$P = \left[\frac{\lambda_{\text{Te}}}{\lambda_{\text{Sb}} - \lambda_{\text{Te}}} N_{\text{Te}}^0 [\exp(-\lambda_{\text{Te}}t) - \exp(-\lambda_{\text{Sb}}t)] + \right.$$

$$\left. + N_{\text{Sb in Te}}^0 \exp(-\lambda_{\text{Sb}}t) \right] \cdot f_{\text{Te}} \times \left[\frac{\lambda_{\text{Te}}}{\lambda_{\text{Sb}} - \lambda_{\text{Te}}} N_{\text{Te}}^0 [\exp(-\lambda_{\text{Te}}t) - \exp(-\lambda_{\text{Sb}}t)] + N_{\text{Sb in Te}}^0 \exp(-\lambda_{\text{Sb}}t) \right] \cdot f_{\text{Te}} + \left[N_{\text{Sb in Pb}}^0 \exp(-\lambda_{\text{Sb}}t) \cdot f_{\text{Pb}} \right]^{-1}. \quad (4)$$

Ratio (4) allows to extrapolate the curves in Fig. 3 to obtain the values

$$q = \frac{N_{\text{Sb in Te}}^0 f_{\text{Te}}}{N_{\text{Sb in Te}}^0 f_{\text{Te}} + N_{\text{Sb in Pb}}^0 f_{\text{Pb}}},$$

equal to 0.2 for p -PbTe and 0.8 for n -PbTe.

If we disregard the difference in the Mössbauer factors at tellurium sublattice sites f_{Te} and at lead sublattice sites f_{Pb} (which is valid at 80 K), then these quantities indicate the fraction of Sb-1 that got into the tellurium sublattice during synthesis. Sb-1 atoms in the

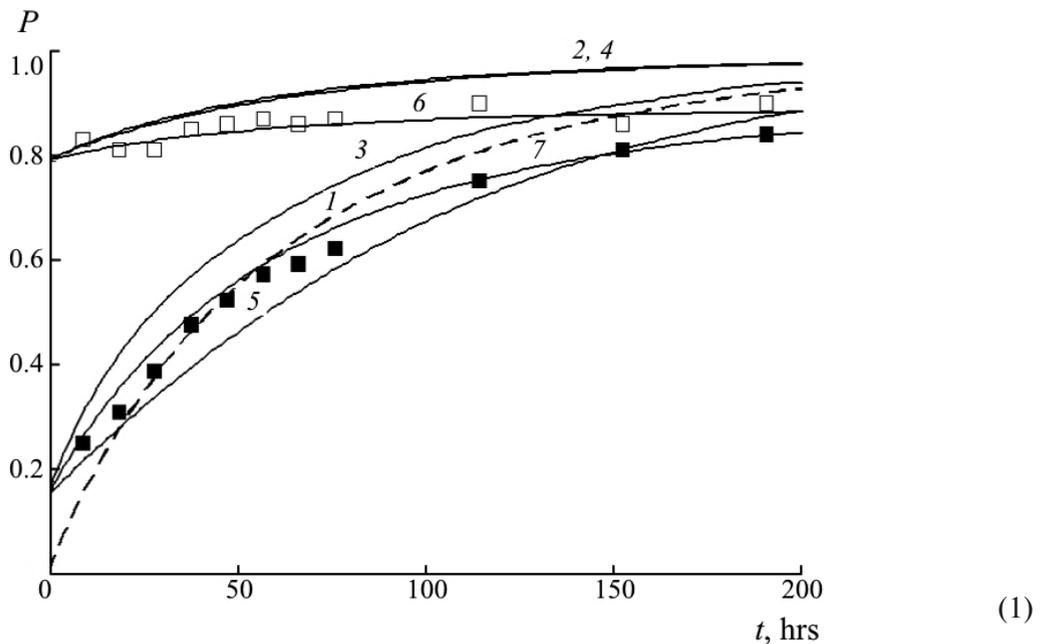


Fig. 3. Experimental (symbols) and calculated (curves 1–7) dependences of the ratio P on source ages for electron (shaded squares, curves 2, 4, 6) and hole (open squares, curves 3, 5, 7) of $\text{PbTe}:(^{119}\text{Sb}+^{119m}\text{Te})$ samples; the calculated curves were obtained under different assumptions, for varying contents of ^{119}Sb atoms in the lead sublattice (also curve 1) (see description in the text)

n -PbTe sample (with an excess of lead atoms and tellurium vacancies) fill tellurium vacancies with a probability of about 0.8, while most of the antimony atoms in the p -PbTe sample appear at lead lattice sites.

The time dependences $P(t)$ of the ratio of the areas for the electron and hole lead tellurides, calculated by formula (4) with the above distribution of Sb-1 over the sublattices and taking into account the value

$$m = \frac{N_{\text{Te}}^0}{N_{\text{Sb}}^0} = 2.949,$$

are shown in Fig. 3 together with the experimental values of P .

Curve 1, calculated with the assumption that all $^{119}\text{Sb-1}$ atoms are located in the lead sublattice, and all $^{119m}\text{Te-1}$ atoms in the tellurium sublattice, deviates significantly from the behavior of the experimental values for both hole and (in particular) electron lead telluride. With above assumption that part of $^{119}\text{Sb-1}$ is displaced into the tellurium sublattice, the calculated $P(t)$ curves are in satisfactory agreement with the experimental data for a small source age but yield overestimated values for the spectra measured a considerable time after source preparation (curves 2 and 3 in Fig. 3). The reasons for this discrepancy might be, firstly, the smaller value of the Mössbauer factor f_{Te} for the structural sites of tellurium in comparison with that for the lead sites (f_{Pb}), and, secondly, the displacement of a part of the $^{119}\text{Sb-2}$ atoms of the tellurium sublattice into the lead sublattice that can occur due to the recoil energy obtained by the daughter $^{119}\text{Sb-2}$ atoms during radioactive decay of the parent $^{119m}\text{Te-1}$ atoms [5].

Curves 4 and 5 in Fig. 3 show the behavior of $P(t)$ calculated for the hole and electron lead tellurides under the assumption that $f_{\text{Te}}/f_{\text{Pb}} = 0.5$. This assumption significantly improves agreement with the experiment for the hole sample, but hardly changes the form of the $P(t)$ curve for the electron sample. Consequently, the difference in the Mössbauer factors cannot explain the lower values of $P(t)$ for the spectra of sources with an older age. In further calculations, it was assumed that $f_{\text{Te}}/f_{\text{Pb}} = 0.5$.

Curves 6 and 7 in Fig. 3 show the behav-

ior of $P(t)$ calculated for the hole and electron lead tellurides under the assumption that some of the total population of $^{119}\text{Sb-2}$ atoms (the fraction $\alpha = 0.1$) is displaced into to the lead sublattice. In this case, ratio (4) can be transformed into

$$P = 1 - \alpha - (1 - q - \alpha) \times \left(m \frac{\lambda_{\text{Te}}}{\lambda_{\text{Sb}} - \lambda_{\text{Te}}} \{ \exp[(\lambda_{\text{Sb}} - \lambda_{\text{Te}})t] - 1 \} + 1 \right)^{-1} \quad (5)$$

A satisfactory agreement with the measured values of P is observed for both types of samples. This result also confirms the conclusion of Ref. [5] on the displacement of $^{119}\text{Sb-2}$ atoms

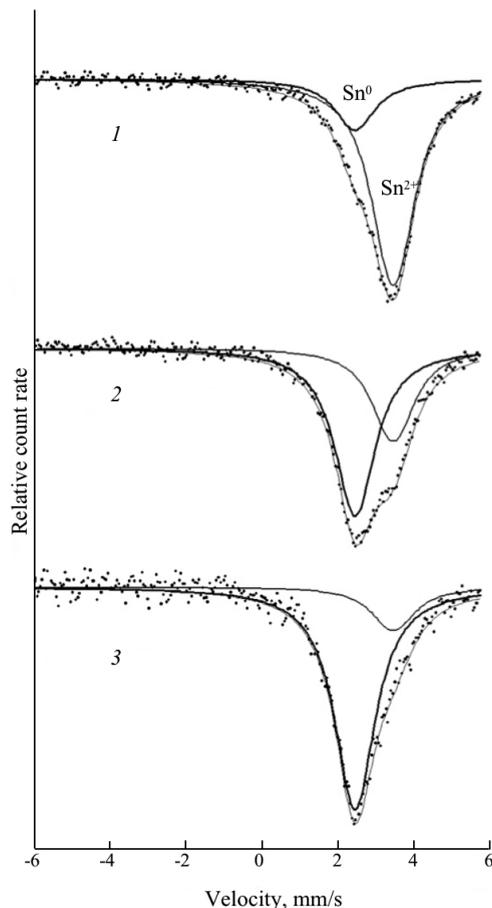


Fig. 4. ^{119m}Sn Mössbauer emission spectra in a glassy As_2Te_3 : ($^{119}\text{Sb} + ^{119m}\text{Te}$) sample. The conditions in which the spectra were recorded and the notations are identical to those shown in Fig. 2. Emission lines corresponding to the Sn^0 and Sn^{2+} centers are also shown

during the decay of the parent ^{119m}Te isotopes.

Arsenic telluride. According to the data of Ref. [12], impurity tin atoms in glassy arsenic telluride As_2Te_3 are electrically inactive (in accordance with the general principle that chalcogenide glassy semiconductors are unable to form solid solutions with dopants). The experimental Mössbauer spectra of the ^{119m}Sn isotope in the $\text{As}_2\text{Te}_3 : (^{119}\text{Sb} + ^{119m}\text{Te})$ alloy that we have obtained are a superposition of two lines (Fig. 4).

A less intense line for the spectrum measured in the time range of 0 – 19.05 h has an isomer shift of 2.61 (2) mm/s; it is close to the isomer shift of the ^{119}Sn Mössbauer spectrum in the semimetallic compound of tin arsenide SnAs and, consequently, this line can be attributed to $^{119m}\text{Sn}^0$ tin impurity centers formed after the decay of ^{119m}Te -1 atoms at tellurium sublattice sites (spectrum I). The relative intensity of this line increases with the source age, which also indicates its origin from ^{119m}Te -1 at tellurium structural sites.

The isomer shift of the line whose intensity decreases with the source age is 3.65 (2) mm/s; it is close to the isomer shift of the ^{119}Sn Mössbauer spectrum for the SnTe compound

and, consequently, this line can be attributed to divalent $^{119m}\text{Sn}^{2+}$ tin impurity centers formed after the decay of ^{119}Sb -1 atoms in arsenic sites (spectrum II). Evidently, the relative intensity of the $^{119m}\text{Sn}^0$ Mössbauer spectrum at tellurium sites increases with the source age.

To quantitatively describe the changes in the structure of the ^{119m}Sn Mössbauer spectra shown in Fig. 4, we have calculated the dependences of the ratio

$$P = \frac{SI}{SI + SII}$$

on the age of the source $(\text{As}, ^{119}\text{Sb})_2^{119m}\text{Te}_3$.

The calculated $P(t)$ dependences are shown in Fig. 5 together with the corresponding experimental values of P . If P is calculated under the assumption that ^{119}Sb -1 atoms are located in arsenic sublattice sites, and the ^{119}Sb -2 atoms in tellurium sublattice sites during Mössbauer spectra measurements, the calculation yields overestimated values of the P ratio. To fit these data, we should assume that a fraction of ^{119m}Te -1 atoms ($\alpha = 0.15(2)$) is displaced from tellurium structural sites into arsenic sublattice sites during the measurement of the spectra

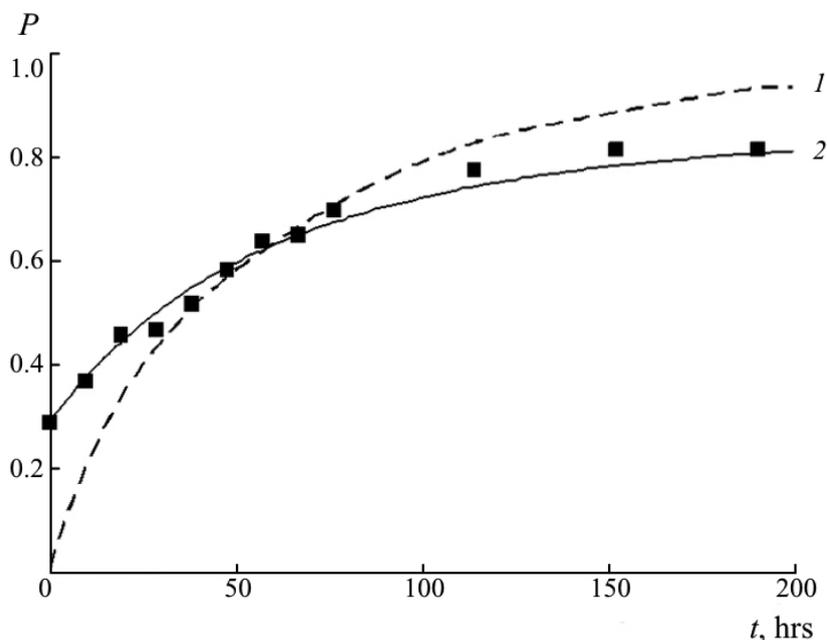


Fig. 5. Experimental (symbols) and calculated (curves 1, 2) dependences of the ratio P on the source age for samples of glassy As_2Te_3 ($^{119}\text{Sb} + ^{119m}\text{Te}$); the calculated curves were obtained under different assumptions, for varying contents of ^{119}Sb atoms in the arsenic sublattice (see description in the text)



(this value is obtained by extrapolating the experimental $P(t)$ dependence to $t \rightarrow \infty$) (solid line 1 in Fig. 5). This displacement can occur due to the recoil energy obtained by the daughter ^{119}Sb -2 atoms during the radioactive decay of $^{119\text{m}}\text{Te}$ -1 atoms. In addition, the local environment of the formed ^{119}Sb -2 atoms can be restructured during the lifetime of ^{119}Sb (55 h).

Conclusion

It is shown that data on the location of

antimony and tellurium atoms in the crystal lattice of lead telluride (or at the structural lattice sites of glassy arsenic telluride) and the valence state of tin daughter atoms formed from parent ^{119}Sb atoms can be obtained from a series of Mössbauer emission spectra of a single $^{119}\text{Sb} + ^{119\text{m}}\text{Te}$ source. We have also established that some of the ^{119}Sb daughter atoms are displaced from the structural positions of the $^{119\text{m}}\text{Te}$ parent atoms as a result of the decay of the latter.

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