ISSN 1087-6596, Glass Physics and Chemistry, 2017, Vol. 43, No. 1, pp. 53–62. © Pleiades Publishing, Ltd., 2017.
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Two-Electron Exchange between Impurity Centers of Tin in PbS_zSe_{1-z} Solid Solutions

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Received April 14, 2016

Abstract—Using emission Mössbauer spectroscopy on $^{119mm}Sn(^{119m}Sn)$ and $^{119}Sb(^{119m}Sn)$ isotopes, the electron exchange process between neutral and doubly ionized U^- tin centers is studied in partially compensated PbS_zSe_{1-z} solid solutions. The activation energy of this process for compositions with $z \approx 1$ is comparable to the deposition depth of the tin energy levels in the band gap of PbS (~0.11(1) eV, and for compositions with $z \approx 1$, it is comparable with the correlation energy of donor U^- tin centers in PbSe (~0.05(1) eV). For all compositions of solid solutions, the exchange is realized by the simultaneous transfer of two electrons with the use of the delocalized states of the valence band.

Keywords: U^- centers, electronic exchange, solid solutions of lead chalcogenides

DOI: 10.1134/S1087659617010084

INTRODUCTION

Two-electron centers with negative correlation energy (U^-) are point defects, forming two energy levels in the band gap, separated by the value of the correlation energy $U = E_2 - E_1 < 0$ (here E_1 and E_2 are the first and second ionization energies of the center) [1]). EPR [1] and Mössbauer spectroscopy [2] are effective methods for studying U^- centers. In particular, donor U^- tin centers in chalcogenide glass [3–5], lead chalcogenides [6–8], and high-temperature superconductors were identified by the method of absorption Mössbauer spectroscopy [9, 10]. However, the first attempts to use Mössbauer spectroscopy for studying the electronic exchange processes between neutral and ionized U^- tin centers in lead chalcogenides have not been successful. Using the absorption variant of spectroscopy on the ^{119}Sn isotope did not allow observing the fast electron exchange process at temperatures above the ambient temperature [8, 11]. In these studies, the use of the emission variant of Mössbauer spectroscopy on ^{119}Sn is relevant with the parent isotopes of $^{119mm}Sn$ and ^{119}Sb [12, 13]. This makes it possible to significantly increase the upper limit of the temperature interval for the measurement of the Mössbauer spectra of impurity tin atoms in PbS and PbSe [14].

The present work is devoted to the study of the electron exchange process between neutral and ionized donor U^- tin centers in solid solutions of PbS_zSe_{1-z} by emission Mössbauer spectroscopy on $^{119mm}Sn(^{119m}Sn)$ and $^{119}Sb(^{119m}Sn)$ isotopes.

EXPERIMENTAL

Single phase solid solutions of $Pb_{1-x-y}Sn_x$-$(Na,Tl)_yS_zSe_{1-z}$ ($z = 0, 01, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0$; $x = 0.005, 0.01, 0.015, 0.02$; $y = 0, 0.005, 0.006, 0.01, 0.02$) with a NaCl lattice were prepared by fusing original components of semiconductor purity in evacuated quartz ampoules with further annealing at 650°C for 120 h. As a donor impurity, excessive lead relative to the stoichiometric composition lead was used, and as an acceptor impurity, excessive sodium and thallium were used. Mössbauer sources containing $^{119mm}Sn$ were prepared using the specimen of metal ^{118}Sn irradiated by the neutron flux of $\sim 10^{15}$ cm^{-2} s^{-1} for 6 months. Mössbauer sources containing ^{119}Sb were prepared by melting-hole (with an excess of chalcogen) solid solutions of PbS_zSe_{1-z} with carrier-free ^{119}Sb specimen (the antimony atom concentration was not higher than 10^{17} cm^{-3}).

Mössbauer spectra were measured on a SM 4201 TERLAB industrial spectrometer in the temperature range of 80–900 K using a resonant scintillation detector. To prevent oxidation of the samples, the Mössbauer sources were in a nitrogen flow. Central shifts were given relative to $Ca^{119mm}SnO_3$ spectrum, measured at 80 K (determination error is ±0.01 mm/s). The width of the $Ca^{119mm}SnO_3$ Mössbauer spectrum, measured at 80 K ($G = 0.78(2)$ mm/s), was taken as the instrumental spectral line width.

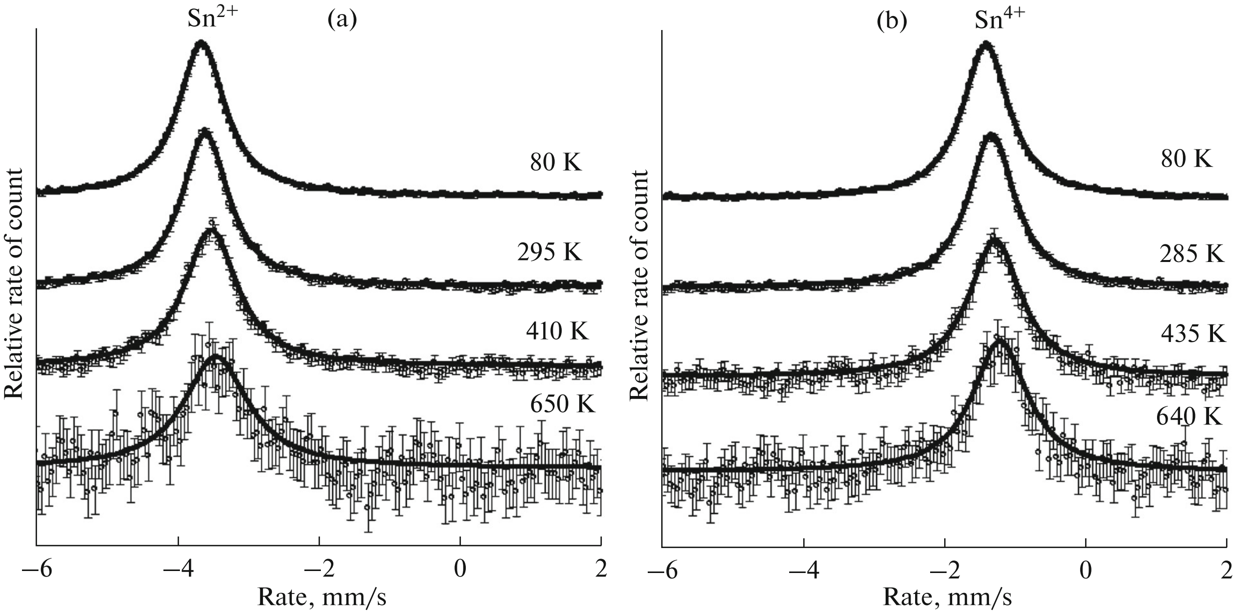

Fig. 1. Emission Mössbauer spectra of impurity atoms of ^{119mm}Sn(^{119m}Sn) in solid solutions of $Pb_{0.995}Sn_{0.005}S_{0.5}Se_{0.5}$ (a) and $Pb_{0.975}Sn_{0.005}Na_{0.01}Tl_{0.01}S_{0.5}Se_{0.5}$ (b).

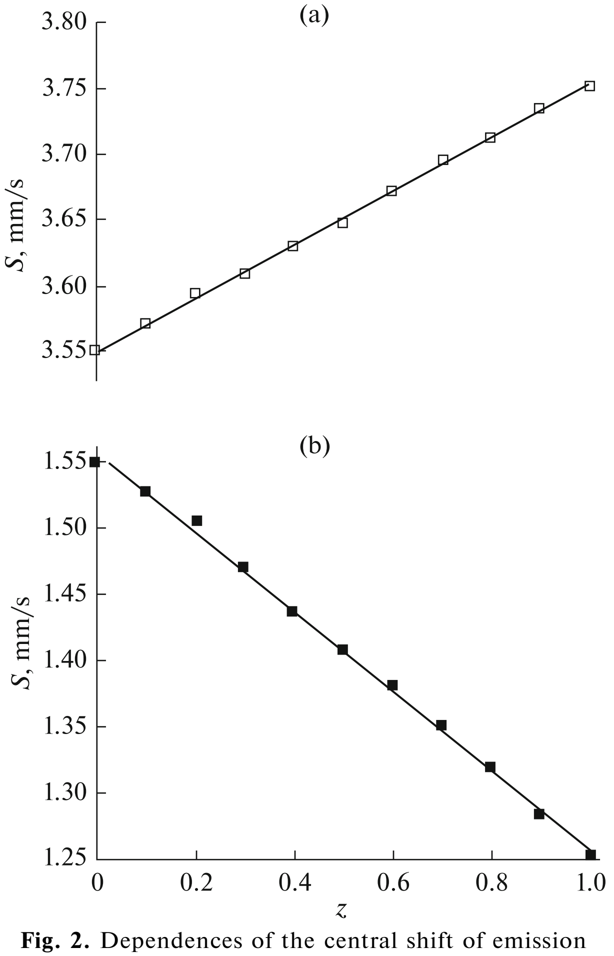

Fig. 2. Dependences of the central shift of emission Mössbauer spectra of impurity atoms of ^{119mm}Sn(^{119m}Sn) on z in $Pb_{0.995}Sn_{0.005}S_zSe_{1-z}$ (a) and $Pb_{0.975}Sn_{0.005}Na_{0.01}Tl_{0.01}S_zSe_{1-z}$ (b).

RESULTS AND DISCUSSION

Tin is a donor impurity in solid solutions of PbS_zSe_{1-z} [11], so that only a neutral state of tin centers can be seen in the electronic solid solutions of $Pb_{1-x-y}Sn_xNa_yS_{1-z}Se_z$, when the chemical potential is near the bottom of the conduction band. $Pb_{0.995}Sn_{0.005}S_zSe_{1-z}$ degenerated electronic alloys, containing superstoichiometric lead (electron concentration was $n \sim 3 \times 10^{18}$ cm^{-3} at 80 K) were selected as such samples. The Mössbauer spectra of impurity atoms of ^{119mm}Sn(^{119m}Sn) of such samples in the temperature range of 80–650 K are represented by single lines of hardware width, whose central shift depends on the temperature (Fig. 1a) and composition (Fig. 2a), and corresponds to the double-charged six-coordinated tin ion Sn^{2+}, replaced the tin atoms, in the local environment of which chalcogen atoms are located.

The ionized state of tin centers is observed in the compensated hole samples of $Pb_{1-x-y}Sn_xNa_yS_{1-z}Se_z$, when the chemical potential is near the vertex of the valence band. $Pb_{0.975}Sn_{0.005}Na_{0.01}Tl_{0.01}S_zSe_{1-z}$ were taken as such samples (they were the degenerated hole and the hole concentration $p \sim 10^{18}$–10^{19} cm^{-3} at 80 K). The Mössbauer spectra of impurity atoms of ^{119mm}Sn(^{119m}Sn) of these samples are single lines of hardware width, whose central shift depends on the temperature (Fig. 1b) and composition (Fig. 2b), and corresponds to tetravalent six-coordinated tin Sn^{4+} in a lead sublattice (in the local environment of which are chalcogen atoms).

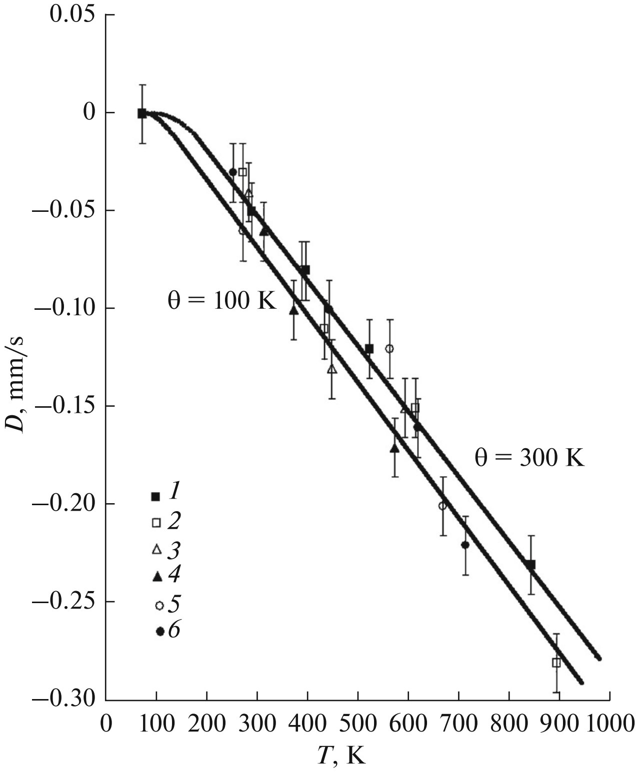

Fig. 3. The theoretical temperature dependence of the Doppler shift of the ^{119}Sn isotope for the Debye temperatures θ = 100 and 300 K (shown by the solid lines) and the experimental temperature dependences of the central shifts of the Mössbauer spectra for the Sn^{2+} and Sn^{4+} centers in solid solutions based on PbS_zSe_{1-z}: (*1*) Sn^{2+} in $Pb_{0.995}Sn_{0.005}S$, (*2*) Sn^{4+} in $Pb_{0.985}Sn_{0.005}Na_{0.01}S$, (*3*) Sn^{2+} in $Pb_{0.995}Sn_{0.005}Se$, (*4*) Sn^{4+} in $Pb_{0.975}Sn_{0.005}Na_{0.01}Tl_{0.01}Se$, (*5*) Sn^{2+} in $Pb_{0.995}Sn_{0.005}S_{0.5}Se_{0.5}$, (*6*) Sn^{4+} in $Pb_{0.975}Sn_{0.005}Na_{0.01}Tl_{0.01}S_{0.5}Se_{0.5}$.

The dependence of the central shift of the Sn^{2+} and Sn^{4+} spectra on the composition of the solid solutions can be explained by the gradual replacement of the sulfur atoms in the local environment of tin on selenium atoms with an increase of index z.

The temperature dependence of the central shift S of Sn^{2+} and Sn^{4+} spectra is explained by the fact that, in general,

$$S = \delta + D, \qquad (1)$$

where δ and D are the isomer and quadratic Doppler shifts and the temperature dependence S is determined by temperature dependence D, which can be written as

$$D = -\frac{3}{2}E_0\frac{k\Delta T}{Mc^2}F\left(\frac{\theta}{\Delta T}\right), \qquad (2)$$

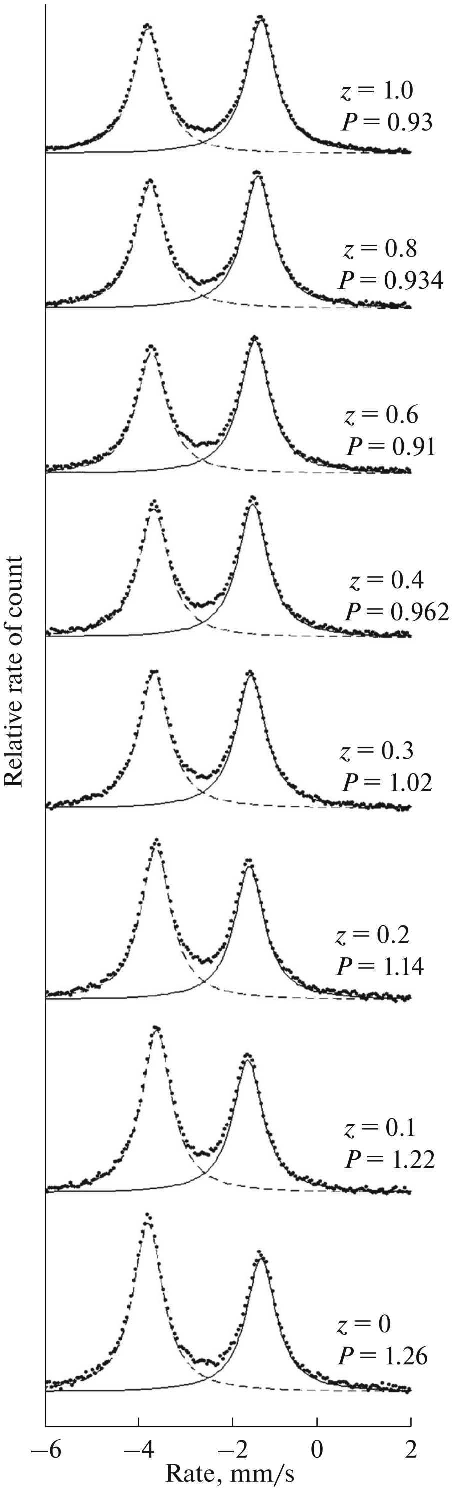

Fig. 4. Emission Mössbauer spectra at 80 K of impurity atoms of $^{119mm}Sn(^{119m}Sn)$ in solid solutions of $Pb_{0.99}Sn_{0.005}Na_{0.005}S_zSe_{1-z}$. The value of $P = \frac{S_{Sn^{2+}}}{S_{Sn^{4+}}}$ is shown for each spectrum, where $S_{Sn^{2+}}$ and $S_{Sn^{4+}}$ are the areas under the spectra corresponding to the Sn^{2+} and Sn^{4+} centers, respectively.

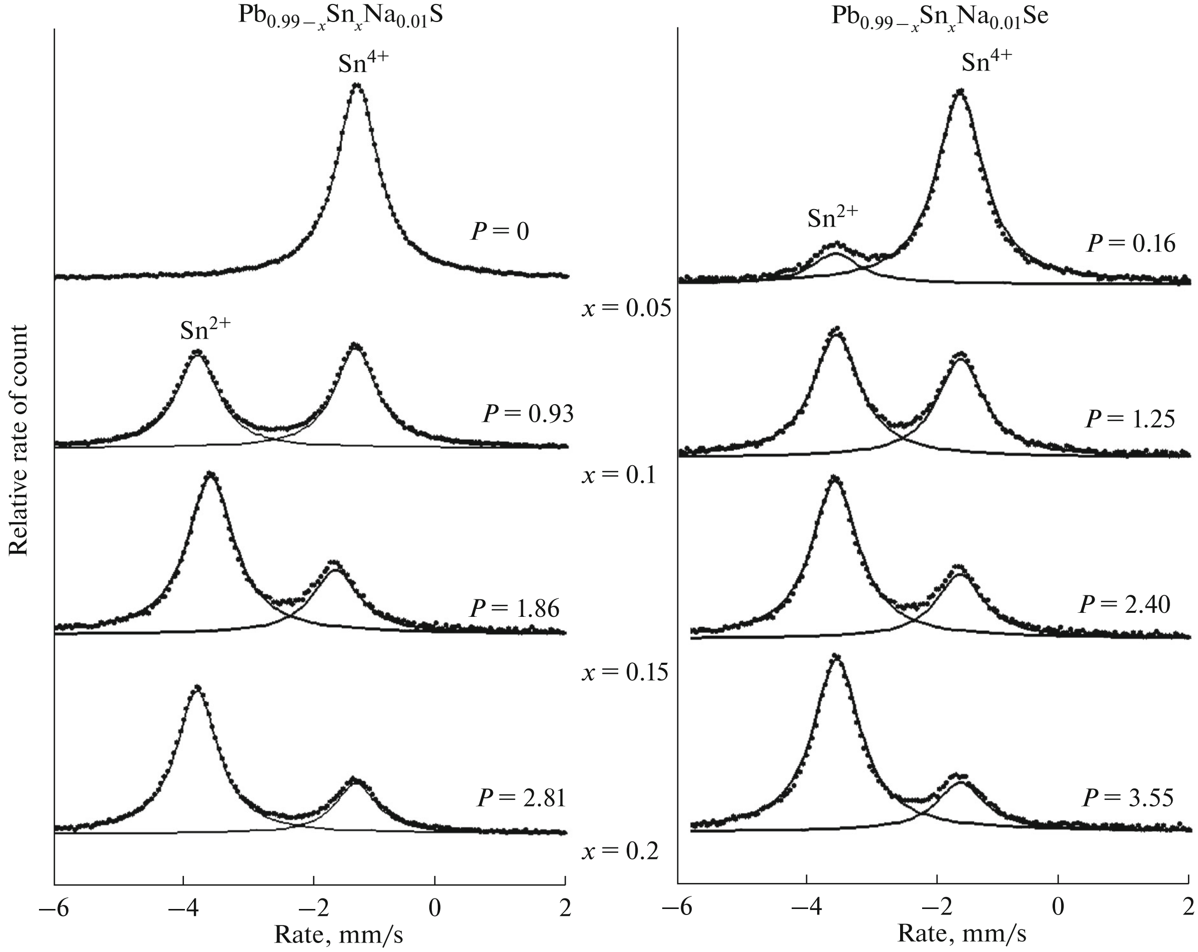

Fig. 5. Emission Mössbauer spectra at 80 K of impurity atoms of $^{119mm}Sn(^{119m}Sn)$ in solid solutions of $Pb_{0.99-x}Sn_xNa_{0.01}S$ and $Pb_{0.99-x}Sn_xNa_{0.01}Se$. The value of $P = \frac{S_{Sn^{2+}}}{S_{Sn^{4+}}}$ is shown for each spectrum, where $S_{Sn^{2+}}$ and $S_{Sn^{4+}}$ are the areas under the spectra corresponding to the Sn^{2+} and Sn^{4+} centers, respectively.

where E_0 is the isomeric transition energy for the ^{119m}Sn isotope, k is the Boltzmann constant, M is the mass of the emitter atom, c is the speed of light in vacuum, θ is the Debye temperature of the studied material, $F\left(\frac{T}{\theta}\right)$ is the Debye function, and ΔT is temperature difference at which the Mössbauer spectra of the sample are measured.

Figure 3 shows the theoretical (for Debye temperatures of 100 and 300 K, which is consistent with the values of θ for PbS and PbSe [15]) and experimental temperature dependences of the Doppler shift of the Mössbauer spectra for Sn^{2+} and Sn^{4+} centers described above. We see a satisfactory agreement of these relationships for both states of the tin impurity centers in $Pb_{0.995}Sn_{0.005}S_zSe_{1-z}$ solid solutions.

According to the results, the tin impurity atoms replace lead atoms in a cubic lattice of solid solutions of PbS_zSe_{1-z} and form energy levels in the band gap corresponding to the two-electron donor. In the Mössbauer spectra, the line of bivalent Sn^{2+} ion corresponds to neutral states, and line of the tetravalent Sn^{4+} ion corresponds to the doubly ionized states of the tin center. By varying the concentration ratio of the two-electron donor centers of tin N_{Sn} and the single-electron acceptor centers of sodium (thallium) N_A in solid solutions of PbS_zSe_{1-z}, one can obtain any controlled intensity ratio of the Sn^{2+} and Sn^{4+} lines in the Mössbauer spectrum at 80 K. In particular, Fig. 4 shows the emission Mössbauer spectra of the impurity atoms of $^{119mm}Sn(^{119m}Sn)$ at 80 K in the partially compensated $Pb_{0.99}Sn_{0.005}Na_{0.005}S_zSe_{1-z}$ samples, which

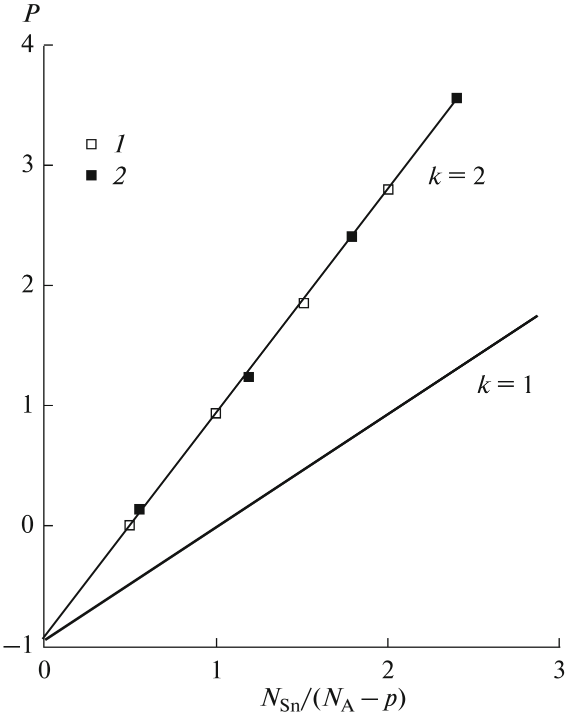

Fig. 6. The dependence of P on $N/(N_{\mathrm{A}} - p)$ for $\mathrm{Pb}_{0.99-x}\mathrm{Sn}_x\mathrm{Na}_{0.01}\mathrm{S}$ (points *1*) and $\mathrm{Pb}_{0.99-x}\mathrm{Sn}_x\mathrm{Na}_{0.01}\mathrm{Se}$ (points *2*). The straight lines show the theoretical dependences for the case when tin is a one-electron ($k = 1$) or a two-electron ($k = 2$) donor center.

are the superposition of Sn^{2+} and Sn^{4+} lines of approximately the same intensity. The absence of partially compensated samples of the trivalent tin Sn^{3+} line in the Mössbauer spectra indicates that tin forms two-electron donor centers with negative correlation energy in $\mathrm{PbS}_z\mathrm{Se}_{1-z}$.

Certainly, accounting for the predetermined ratio of $N_{\mathrm{Sn}} = N_{\mathrm{A}}$ in solid solutions of $\mathrm{Pb}_{0.99}\mathrm{Sn}_{0.005}\mathrm{Na}_{0.005}\mathrm{S}_z\mathrm{Se}_{1-z}$, one would expect the same intensity of the Sn^{2+} Sn^{4+} lines in the Mössbauer spectra; however, as seen in Fig. 4, the value of $P = \frac{S_{\mathrm{Sn}^{2+}}}{S_{\mathrm{Sn}^{4+}}}$ (where $S_{\mathrm{Sn}^{2+}}$ and $S_{\mathrm{Sn}^{4+}}$ are areas under the spectra corresponding to the Sn^{2+} and Sn^{4+} centers, respectively) depends on z. Obviously, for an explanation of this feature in the behavior of $P(z)$, one should take into account the dependence on z ratios of Mössbauer (proportions of recoilless gamma rays) for the Sn^{2+} and Sn^{4+} centers, as well as the dependence position of tin donor levels in the band gap of solid solutions of $\mathrm{PbS}_z\mathrm{Se}_{1-z}$ on z.

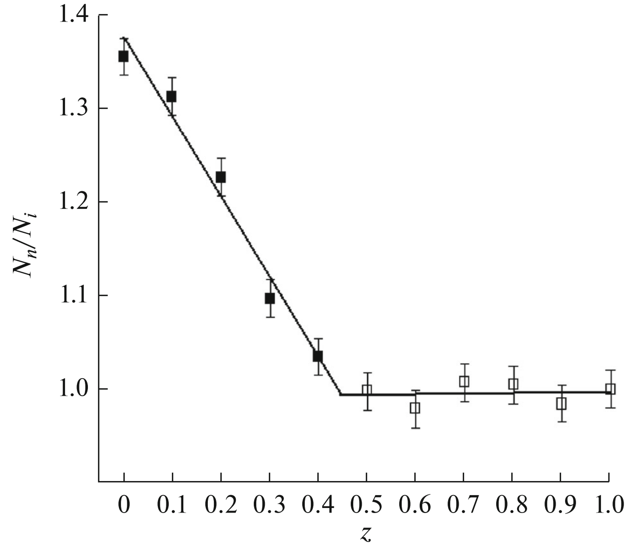

Fig. 7. Dependence of the ratio of N_n/N_i on z for solid solutions of $\mathrm{Pb}_{0.99}\mathrm{Sn}_{0.005}\mathrm{Na}_{0.005}\mathrm{S}_z\mathrm{Se}_{1-z}$. In determining from the Mössbauer spectra the concentrations of Sn^{2+} and Sn^{4+} centers, the ratio of the Mössbauer coefficients for these centers was assumed to be 0.93 (1).

The value P may be written as

$$P = k\frac{f_n}{f_i}\frac{N_n}{N_{\mathrm{A}} - p} - \frac{f_n}{f_i}, \tag{3}$$

where N_n, N_i are the concentrations of the neutral and ionized centers of tin, respectively, and f_n and f_i are the Mössbauer coefficients for these centers. In this case, $k = 1$, if tin is a one-electron donor (the electron- neutrality equation has the form $N_n = N_{\mathrm{A}} - p$), or $k = 2$, if tin is a two-electron donor (the electron-neutrality equation has the form $2N_n = N_{\mathrm{A}} - p$).

To confirm dependence (3), the emission Mössbauer spectra of the $^{119mm}\mathrm{Sn}(^{119m}\mathrm{Sn})$ impurity atoms were measured in the solid solutions of $\mathrm{Pb}_{0.99-x}\mathrm{Sn}_x\mathrm{Na}_{0.01}\mathrm{S}$ and $\mathrm{Pb}_{0.99-x}\mathrm{Sn}_x\mathrm{Na}_{0.01}\mathrm{Se}$ (Fig. 5), and the experimental dependence P on $\frac{N_n}{N_{\mathrm{A}} - p}$ for them is shown in Fig. 6. It was found that the agreement between the calculated (3) and experimental dependences can be obtained for $k = 2$ (i.e., the tin in lead chalcogenides is a two-electron donor), and extrapolation of the experimental dependence to $\frac{N_n}{N_{\mathrm{A}} - p} = 0$ allows one to determine the ratio of the Mössbauer coefficients for neutral and ionized tin centers $\frac{f_n}{f_i} = \frac{f_{\mathrm{Sn}^{2+}}}{f_{\mathrm{Sn}^{4+}}} = 0.93(1)$. Thus, the Mössbauer coefficient for the Sn^{4+} state is higher than the Mössbauer coefficient for the Sn^{2+} state, and this ratio is independent of z.

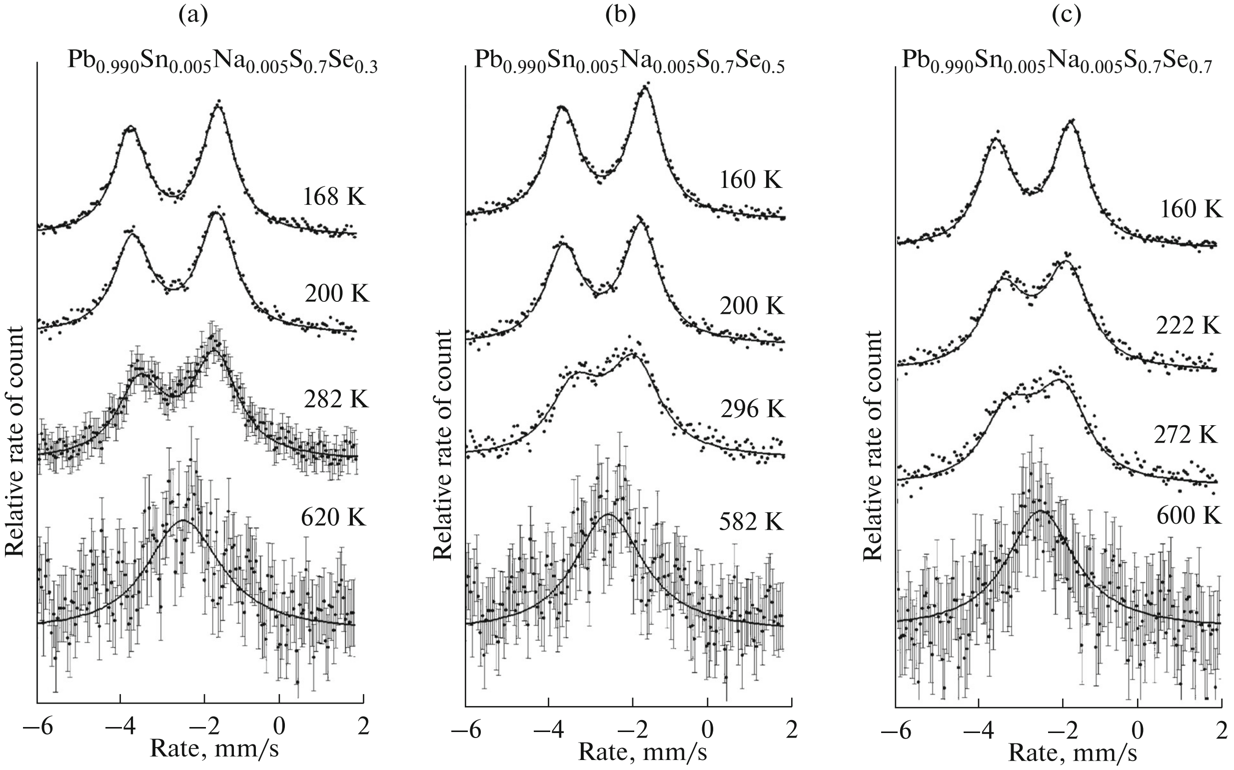

Fig. 8. Emission Mössbauer spectra of ^{119mm}Sn(^{119m}Sn) of solid solutions of $Pb_{0.99}Sn_{0.005}Na_{0.005}S_{0.7}Se_{0.3}$ (a) $Pb_{0.99}Sn_{0.005}Na_{0.005}S_{0.5}Se_{0.5}$ (b), $Pb_{0.99}Sn_{0.005}Na_{0.005}S_{0.5}Se_{0.7}$ (c) at different temperatures.
The position of the lines corresponding to the Sn^{2+} and Sn^{4+} centers is shown.

The hole-type conductivity and the absence of degeneracy for the samples of $Pb_{1-x-y}Sn_xA_yS_zSe_{1-z}$ with $z \geq 0.5$ indicates that the chemical potential associated with the system of donor tin levels is at the lower half of the band gap of the semiconductor (hence, the donor tin levels are in the lower half of the band gap), whereas for $z \leq 0.4$, the chemical potential is in the background of the valence area (hence, the donor tin levels are in the background of the valence band). This helps explain why in the solid solutions of $Pb_{0.99}Sn_{0.005}Na_{0.005}S_zSe_{1-z}$ with $z \geq 0.5$, the Mössbauer spectra match $R = \frac{N_n}{N_i} \approx 1$, whereas in solid solutions with $z \leq 0.4$, the spectra correspond to $R > 1$, and with increasing z, the R value increases (Fig. 7). Finding the chemical potential at $z \leq 0.4$ in the background of the valence band explains the cause of the appearance in the Mössbauer spectra of compensated hole samples of $Pb_{0.975}Sn_{0.005}Na_{0.01}S_zSe_{1-z}$ with $z \leq 0.4$ not a single line of Sn^{4+} but the superposition of the Sn^{4+} and Sn^{2+} lines (Fig. 5)—fully ionized tin centers in solid solutions with $z \leq 0.4$ can be obtained only at $N_A \gg 2N_{Sn}$.

To observe the process of the electron exchange between neutral and ionized tin centers in solid solutions of PbS_zSe_{1-z}, $Pb_{0.990}Sn_{0.005}Na_{0.005}S_zSe_{1-z}$ compositions were selected ($z \geq 0.5$, nondegenerate hole samples, $p \sim 3 \times 10^{16}$ cm^{-3} at 80 K) and $Pb_{0.989}Sn_{0.005}Na_{0.006}S_zSe_{1-z}$ ($z \leq 0.4$, degenerated hole samples, $p \sim 3 \times 10^{19}$ cm^{-3} at 80 K). The emission Mössbauer spectra of ^{119mm}Sn(^{119m}Sn) of these samples were a superposition of two lines of instrumental width, whose central shifts correspond to the Sn^{4+} and Sn^{2+} centers (Fig. 8). With increasing temperature, the lines of Sn^{2+} and Sn^{4+} in the spectra are broadened and approach each other. The spectra in Fig. 8 illustrate the picture of the electron exchange between the two states of Sn^{2+} and Sn^{4+}. The experimental spectra were processed as described in [14]; Fig. 9 shows the temperature dependences of the electronic exchange frequency between the Sn^{2+} and Sn^{4+} centers in solid solutions of PbS_zSe_{1-z}, and the dependence of the activation energy of the electronic exchange process on z is shown in Fig. 10. For the composition with $z =$ 1.0, the activation energy is maximum (0.11(1) eV), which is comparable to the depth of the tin energy lev-

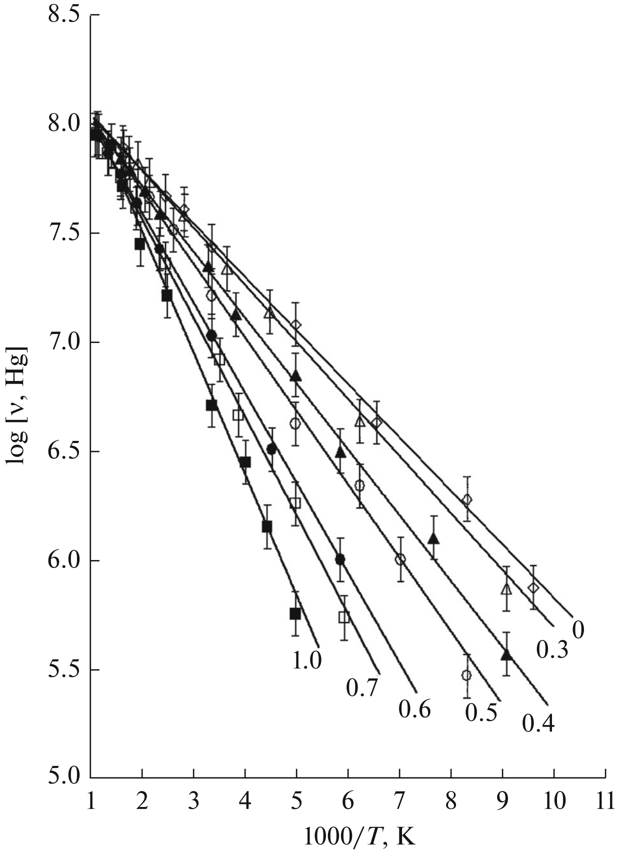

Fig. 9. Temperature dependences of the frequency of the electronic exchange between the Sn^{2+} and Sn^{4+} centers in the solid solutions of PbS_zSe_{1-z}. The values of z are listed next to the relevant lines and the compositions are marked by different icons.

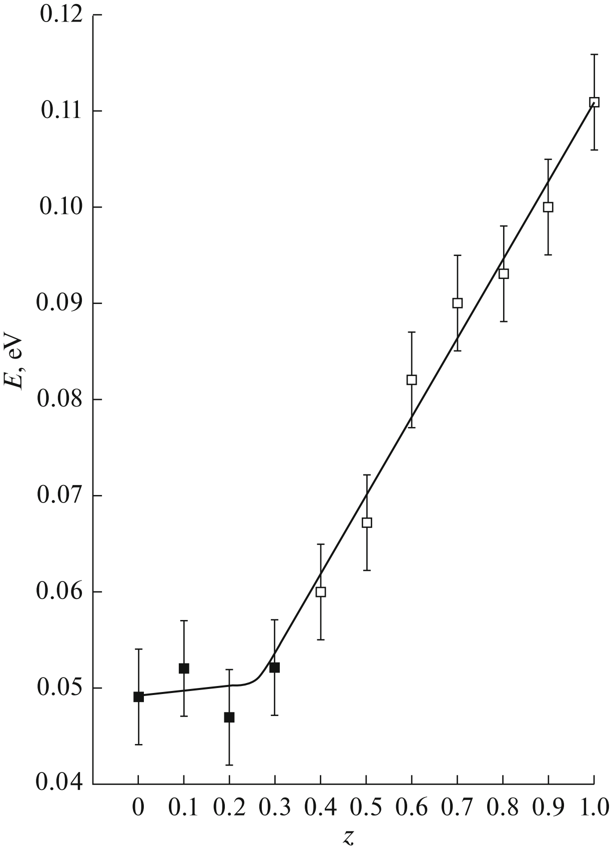

Fig. 10. The dependence of the activation energy of the electronic exchange process between U^- centers of tin in solid solutions of PbS_zSe_{1-z} on z.

els in the bandgap of PbS [16], and it monotonically decreases to 0.05(1) eV for compositions with $z = 0$ (here it is comparable to the correlation energy of the donor U^- tin centers in PbSe [17]).

To elucidate the mechanism of the electron exchange between tin centers in solid solutions of PbS_zSe_{1-z}, the dependence of the electronic exchange frequency on tin concentration is fundamentally important. That is why we have studied this process in PbS, $PbS_{0.5}Se_{0.5}$ and PbSe by emission Mössbauer spectroscopy on isotopes of $^{119}Sb(^{119m}Sn)$. To reduce the concentration of the carriers, samples, containing ^{119}Sb were subjected to thermal annealing at 650°C, so that the Mössbauer spectra in the temperature range of 80–300 K contained simultaneously the presence of centers of six-coordinated tin in the anion sublattice Sn^0 (the single line corresponds to them with a central shift of ~2.34 mm/s, typical for intermetallic tin compounds), as well as the centers of six-coordinated Sn^{2+} and Sn^{4+} in the cationic sublattice (Fig. 11). This is consistent with the data of authors [7], according to which impurity atoms of antimony in the lattices of PbS and PbSe occupy cationic and anionic sublattices. Increasing the measurement temperature of the Mössbauer spectra is accompanied by a decrease in the intensity of the Sn^0 lines and convergence of the Sn^{2+} and Sn^{4+} lines with their simultaneous broadening. The latter fact can be explained by the electron exchange processes between the centers of Sn^{2+} and Sn^{4+}. Since the temperature dependences of the frequency of the electronic exchange between the Sn^{2+} and Sn^{4+} centers, formed after the radioactive decay of $^{119mm}Sn$ (the data of emission Mössbauer spectroscopy on $^{119mm}Sn(^{119m}Sn)$ isotopes, tin concentration ~2×10^{20} cm^{-3}) and ^{119}Sb (the data of emission Mössbauer spectroscopy on $^{119}Sb(^{119m}Sn)$ isotopes, tin concentration $\leqslant 10^{17}$ cm^{-3}) are the same (Figs. 12a, 12b), then it must be concluded that the electronic exchange in both cases is implemented using the states of the valence band.

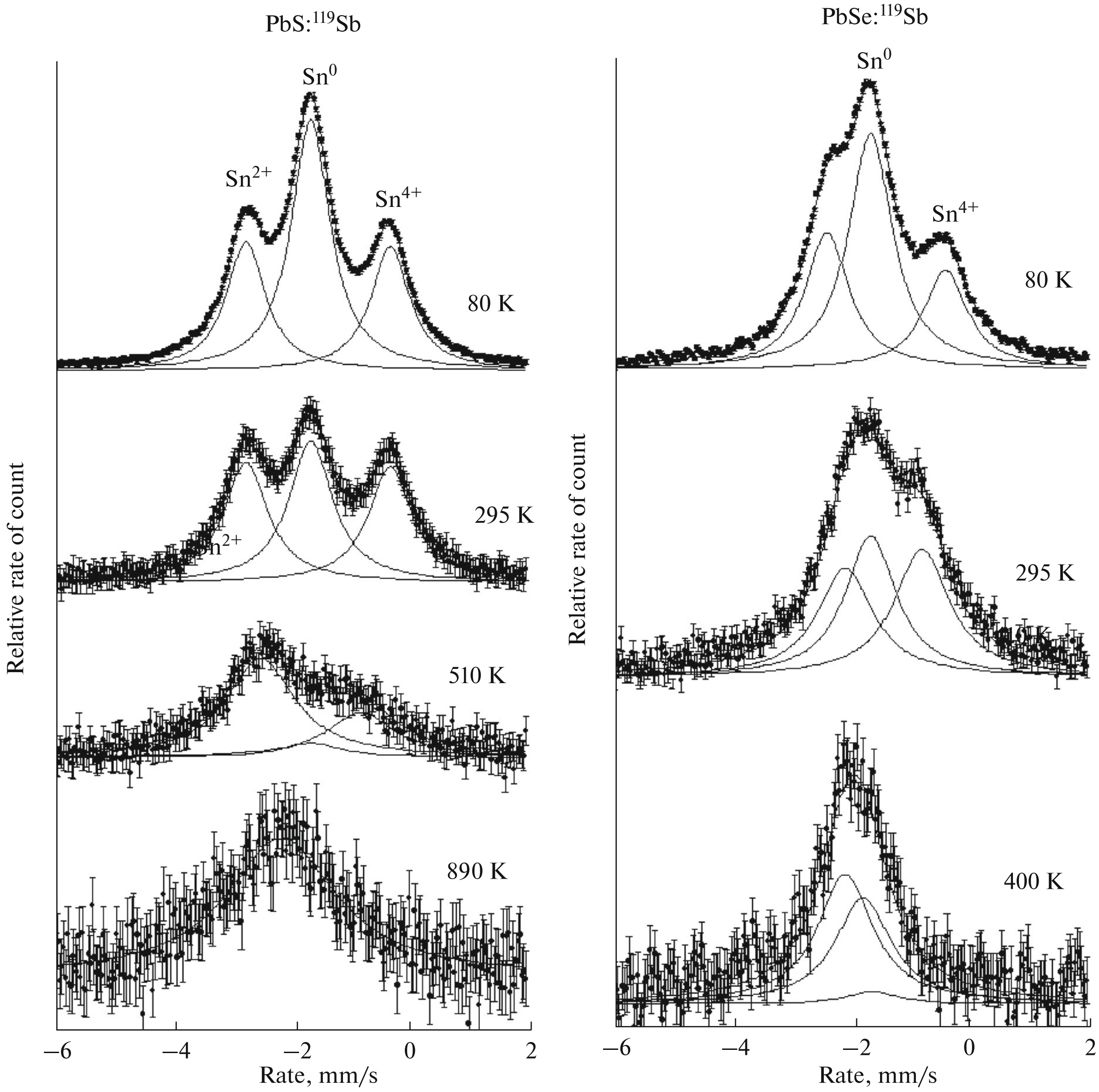

Fig. 11. Emission Mössbauer spectra of ^{119}Sb(^{119m}Sn) in PbS and PbSe at various temperatures. The position of the lines corresponding to the Sn^0, Sn^{2+}, and Sn^{4+}centers is shown.

There are three mechanisms of the electronic exchange between the U^- centers: two-electron exchange between U^- centers with the participation of the states of the valence band [1], electron transfer directly between U^- centers [18] and, finally, tunneling of single electrons between U^- centers [19]. According to the data of this study, the activation energy of two-electron exchange for nondegenerate solid solutions of PbS_zSe_{1-z} at $z \geq 0.5$ corresponds to the distance of the Fermi level from the top of the valence band. As can be seen from Fig. 12c, for the composition with $z = 1$, it is comparable to the depth of the energy levels of tin in the band gap of PbS, and the activation energy of the exchange for degenerate solid solutions of PbS_zSe_{1-z} at $z \leq 0.4$ corresponds to the correlation energy of the donor of the U^- tin centers (as seen from Fig. 12b, for the composition with $z = 0$, it is comparable to the correlation energy of donor U^- tin centers in PbSe.).

CONCLUSIONS

Tin Impurity atoms in the band gap of solid solutions of PbS_zSe_{1-z} form two energy levels, corre-

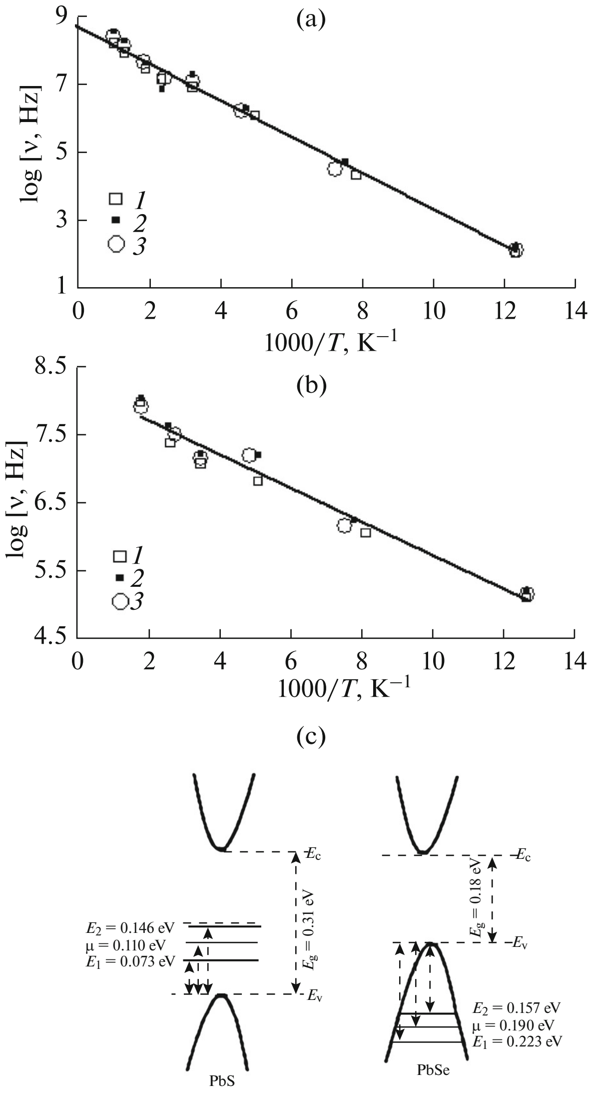

Fig. 12. Temperature dependence of the frequency of the electronic exchange between the Sn^{2+} and Sn^{4+} centers for (*1*) $Pb_{0.96}Sn_{0.02}Na_{0.01}Tl_{0.01}S$, containing $^{119mm}Sn$; (*2*) $Pb_{0.99}Sn_{0.005}Na_{0.005}S$ containing $^{119mm}Sn$; (*3*) PbS containing ^{119}Sb (a). Temperature dependence of the frequency of the electronic exchange between the Sn^{2+} and Sn^{4+} centers for (*1*) $Pb_{0.965}Sn_{0.015}Na_{0.01}Tl_{0.01}Se$ containing $^{119mm}Sn$; (*2*) $Pb_{0.988}Sn_{0.005}Na_{0.007}Se$, containing $^{119mm}Sn$.; (*3*) PbSe, containing ^{119}Sb (b). Energy diagrams of donor U^{-} tin centers in PbS and PbSe at 100 K (c) [16, 17].

sponding to two-electron donors with negative correlation energy; moreover, these levels are at the bottom half of the band gap at $z \geq 0.5$ and in the background of the allowed states of the valence band at $z \leq 0.4$. The process of two-electron exchange between neutral and doubly ionized donor U^{-} tin centers is discovered in partially compensated solid solutions of PbS_zSe_{1-z} using the states of the valence band.

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Translated by Sh. Galyaltdinov