

Identification of neutral and ionized tin donor states and the observation of two-electron exchange between tin centers in solid solutions based on PbS and PbSe

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It is shown by ^{119}Sn Mössbauer spectroscopy that the charge state of tin atoms in $\text{Pb}_{1-x}\text{Sn}_x\text{S}$ and $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ solid solutions depends on the position of the Fermi level, and that in these materials the tin atoms form deep donor levels. Neutral (Sn^{2+}) and ionized (Sn^{4+}) states of the tin centers are identified. The process of two-electron exchange between neutral and ionized tin centers is observed for a partially compensated $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ solid solution doped with sodium and thallium acceptor impurities.

According to electrical measurements, tin atoms in $\text{Pb}_{1-x}\text{Sn}_x\text{S}$ and $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ solid solutions take on the role of deep donor centers.¹ Such a behavior of the atoms of one of the components of a semiconducting solid solution lies outside the framework of traditional ideas, and it seemed to us advisable to try to identify the neutral and ionized states of the tin donor center in these solid solutions (in particular by the method of Mössbauer spectroscopy). As will be shown below (see also our preliminary publication²), tin in a partially compensated material is present in two charge states and electron exchange should, in principle, occur, enabling the establishment of equilibrium between these states. It was just for this reason that we tried, as a second stage, to observe electron exchange between the neutral and ionized states of tin in $\text{Pb}_{1-x}\text{Sn}_x\text{S}$ and $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ solid solutions partially compensated by sodium and thallium, with the help of Mössbauer spectroscopy. Preliminary results have been published.³

1. EXPERIMENTAL METHOD

The solid solutions were obtained by melting the starting components in evacuated quartz ampoules. Preliminary studies showed that the parameters of the Mössbauer spectra depend on the thermal treatment of the specimens, and reproducible results are obtained if the specimens are annealed after synthesis in the form of large blocks and then in the form of pressed powders at 600 °C for 320 h.

Mössbauer spectra of ^{119}Sn were taken at 80 and 295 K, using an electrodynamic-type spectrometer with a $\text{Ca}^{119m}\text{SnO}_3$ source. The isomer shifts are quoted relative to SnO_2 .

2. EXPERIMENTAL RESULTS AND DISCUSSION. IDENTIFICATION OF THE NEUTRAL AND IONIZED STATES OF THE TIN CENTER

According to electrical measurements, tin in PbS produces a donor level which lies in the forbidden band. The neutral state of tin centers should therefore be observed in electronic specimens. The Mössbauer spectrum of one such specimen ($\text{Pb}_{99}\text{SnS}_{100}$) is shown in Fig. 1, a; it forms a single line with a weakly temperature dependent isomer shift and corresponds to divalent Sn^{2+} (see Table I). This spectrum must be ascribed to isolated neutral tin donor centers.

Ionized tin centers should be observed in hole specimens, containing acceptor impurities (for example, sodium or thallium). As can be seen from Fig. 1b, alloying a $\text{Pb}_{1-x}\text{Sn}_x\text{S}$ solid solution with sodium leads to the appearance of an additional line in the Mössbauer spectrum, together with the Sn^{2+} line, with an isomer shift characteristic for tetravalent tin Sn^{4+} (see Table I). This line corresponds to isolated tin donor centers.

It is tempting to ascribe this line, corresponding to ionized tin centers, not to the Sn^{4+} state (as follows from the value of the isomer shift), but to the Sn^{3+} state (this state is not observed in tin compounds, but might be realized for impurity atoms). However, such an interpretation does not accord with the observed acceptor concentration dependence of the relative intensity of the lines in the Mössbauer spectra of $\text{Pb}_{1-x}\text{Sn}_x\text{S}$ specimens (Fig. 1, b, c, d). In fact, the ratio of intensities of lines in Mössbauer spectra is described in the general case by the expression

$$R = \frac{I_N}{I_I} = \frac{f_N N_N}{f_I N_I} = \frac{f_N N}{f_I} - \frac{f_N}{f_I}, \quad (1)$$

where I_N and I_I are the line intensities, f_N and f_I the Mössbauer factors, N_N and N_I the concentrations of neutral and ionized states of the tin center respectively, and N the total concentration of tin in the solid solution.

If the additional line is associated with Sn^{3+} , then the equation of electrical neutrality is of the form

$$N_I = N_a - p, \quad (2)$$

and we have, instead of Eq. (1)

$$R = \frac{f_N N}{f_I (N_a - p)} - \frac{f_N}{f_I}, \quad (3)$$

where N_a and p are the concentrations of acceptors and holes.

If the additional line corresponds to Sn^{4+} , then the equation of electrical neutrality has the form

$$2N_I = N_a - p, \quad (4)$$

and instead of Eq. (1) we have

$$R = 2 \frac{f_N N}{f_I (N_a - p)} - \frac{f_N}{f_I}. \quad (5)$$

The experimental dependences of R on $N/(N_a - p)$ for

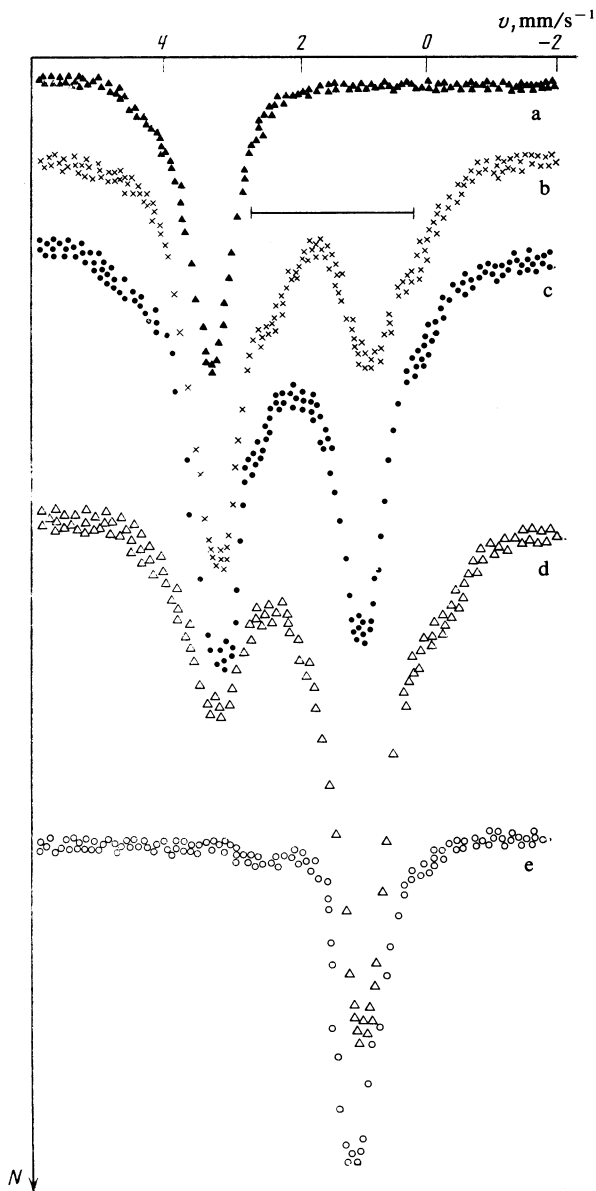


FIG. 1. Mössbauer spectra of ^{119}Sn at 80 K for the specimens: $\text{Pb}_{99}\text{SnS}_{100}$ (a), $\text{Pb}_{98.5}\text{SnNa}_{0.5}\text{S}_{100}$ (b), $\text{Pb}_{98}\text{SnNaS}_{100}$ (c), $\text{Pb}_{96.75}\text{Sn}_{1.25}\text{NaTlS}_{100}$ (d), $\text{Pb}_{98.5}\text{Sn}_{0.5}\text{NaS}_{100}$ (e). In spectra (b–e) the position of the quadrupole doublet is shown, corresponding to the associations of Sn^{4+} with ionized acceptors.

TABLE I. Parameters of the Mössbauer spectra of isolated tin centers in solid solutions based on Pbs and Pbse.

Solid solution composition	T, K	carrier concentration		δ_N , mm/s $^{-1}$	δ_I , mm/s $^{-1}$
		n , 10^{18}cm^{-3}	p , cm^{-3}		
$\text{Pb}_{99}\text{SnS}_{100}$	80	3	—	3,70	—
	295	3	—	3,68	—
$\text{Pb}_{98.5}\text{Sn}_{0.5}\text{S}_{100}$	30	—	$6 \cdot 10^{13}$	—	1,25
	295	—	$1 \cdot 10^{17}$	—	1,23
$\text{Pb}_{98}\text{Sn}_2\text{NaTlS}_{100}$	80	—	$6 \cdot 10^{13}$	3,70	1,25
	295	—	$6 \cdot 10^{16}$	3,60	1,37
$\text{Pb}_{99}\text{SnSe}_{100}$	80	2	—	3,65	—
	295	2	—	3,63	—
$\text{Pb}_{97.5}\text{Sn}_{0.5}\text{NaTlSe}_{100}$	80	—	$4 \cdot 10^{19}$	—	1,52
	295	—	$4 \cdot 10^{19}$	—	1,50
$\text{Pb}_{96.5}\text{Sn}_{1.7}\text{NaTlSe}_{100}$	80	—	$3 \cdot 10^{19}$	3,53	1,58
	295	—	$3 \cdot 10^{19}$	3,13	2,05

Note: δ_N and δ_I are the isomer shifts in the Mössbauer spectra, corresponding to the neutral Sn^{2+} and ionized Sn^{4+} states; the measurement error is ± 0.02 .

$\text{Pb}_{1-x}\text{Sn}_x\text{S}$ solid solutions doped with sodium and thallium are shown in Fig. 2. It can be seen that the experimental results agree well with Eq. (5) for doubly ionized tin centers and the value of p can be neglected, since $p \ll N_a$. For comparison, the straight line corresponding to singly ionized tin centers [Eq. (3)] is shown dashed in Fig. 2. The difference between experiment and Eq. (3) is most noticeable for $N/N_a = 1$: Eq. (3) predicts a zero intensity for the Sn^{2+} line, while experiment, in agreement with Eq. (5), gives a value of R near to unity.

The line observed in Mössbauer spectra of $\text{Pb}_{1-x}\text{Sn}_x\text{S}$ specimens doped with acceptor impurities has thus to be ascribed to Sn^{4+} . The absence of a Sn^{3+} line in the Mössbauer spectra indicates that tin forms doubly charged donor centers in PbS with negative Hubbard energy, i.e., the energy of single ionization of this center is greater than half the energy of ionizing it doubly.

Apart from the Sn^{4+} line, corresponding to isolated ionized tin centers, there is observed in Mössbauer spectra of $\text{Pb}_{1-x}\text{Sn}_x\text{S}$ specimens doped with an acceptor impurity, a quadrupole doublet which must be ascribed to associations of Sn^{4+} with an ionized acceptor (see Fig. 1, b–e). The intensity of the additional doublet depends to a large extent on the thermal history of the specimen.

The neutral state of tin donor centers in PbSe, as also in PbS, is only observed in electronic (not doped with an acceptor impurity) specimens. In particular, the spectra of $\text{Pb}_{99}\text{SnSe}_{100}$ specimens at 80 and 295 K consist of single lines (Fig. 3, a) with a weakly temperature dependent isomeric shift, and correspond to divalent tin Sn^{2+} (see Table I). This spectrum corresponds to isolated neutral tin donor centers.

The introduction of an acceptor impurity into $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ leads to the appearance of an additional line in the Mössbauer spectrum (Fig. 3, b). Since p -type specimens were used (see Table I), this line must be ascribed to isolated tin centers. Its isomer shift corresponds to tetravalent tin Sn^{4+} (see Table I), i.e., a doubly ionized state of the tin center in PbSe as in PbS. This conclusion is confirmed by the dependence of R on $N/(N_a - p)$ (see Fig. 2). However, in $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ solid solutions, unlike $\text{Pb}_{1-x}\text{Sn}_x\text{S}$, the hole concentration has to be taken into account to describe this dependence. This is associated with the fact that the tin level in

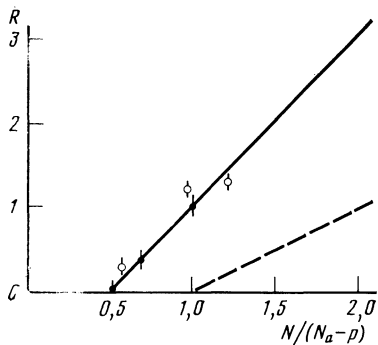


FIG. 2. The dependence of $R = I_N/I_I$ on $N/(N_a - p)$ for $Pb_{1-x}Sn_xS$ (●) and $Pb_{1-x}Sn_xSe$ (○). The dashed line shows the relation for the case of tin forming a singly ionized center. The values of I_N , I_I , and p are taken at 80 K.

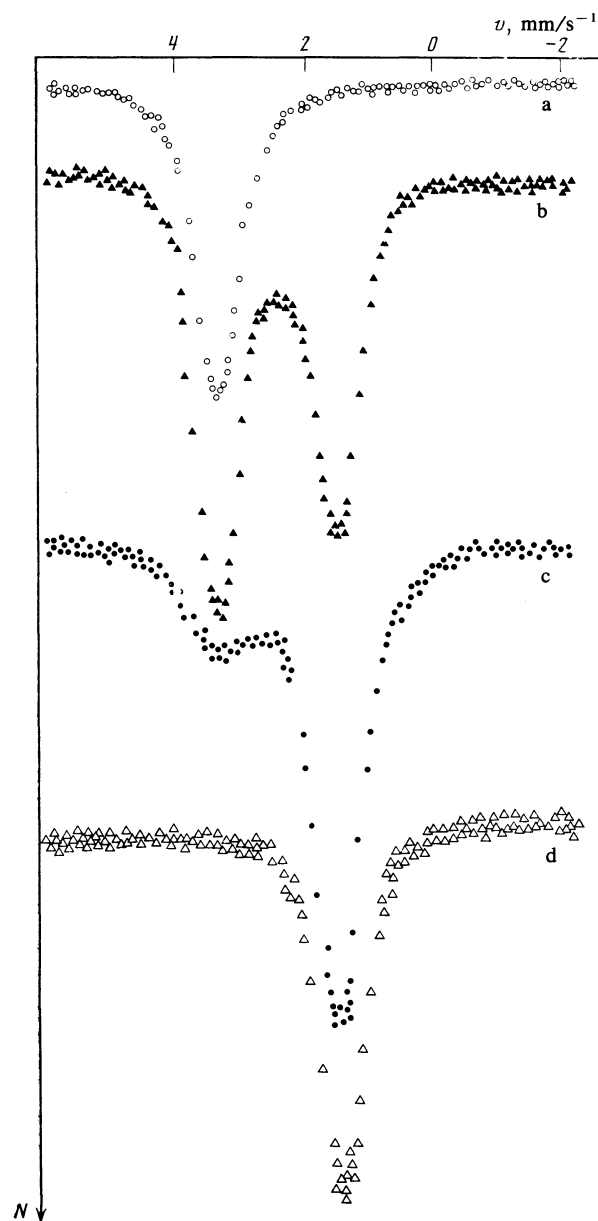


FIG. 3. Mössbauer spectra of ^{119}Sn at 80 K for the specimens: $Pb_{99}SnSe_{100}$ (a), $Pb_{98}SnNaSe_{10}O$ (b), $Pb_{97}SnNaTlSe_{100}$ (c), $Pb_{97.5}Sn_{0.5}NaTlSe_{100}$ (d).

$PbSe$ does not occur in the forbidden band but on the valence band background, and the Fermi level is attached to the partially filled tin levels, i.e., it is also in the valence band. As a result, the concentration of holes in $Pb_{1-x}Sn_xSe$ specimens, doped with acceptor impurities, is comparable with the acceptor concentration (see Table I). It is for this reason that the Mössbauer spectrum of a $Pb_{97}SnNaTlSe_{100}$ specimen (in which the acceptor concentration is equal to double the tin concentration) is a superposition of the Sn^{2+} and Sn^{4+} lines (Fig. 3,c). Completely ionized tin centers can only be obtained in $Pb_{1-x}Sn_xSe$ specimens with acceptor concentration much greater than half the tin concentration (Fig. 3,d).

A quadrupole doublet, corresponding to association of Sn^{4+} with ionized acceptors, was not found for a $Pb_{1-x}Sn_xSe$ solid solution, which is possibly connected with insufficient resolving power of Mössbauer spectroscopy.

3. TWO-ELECTRON EXCHANGE BETWEEN NEUTRAL AND IONIZED CENTERS

The electron exchange between tin centers in $Pb_{1-x}Sn_xS$ and $Pb_{1-x}Sn_xSe$ solid solutions was studied with specimens doped with sodium and thallium, containing equal Sn^{2+} and Sn^{4+} concentrations (see Table I). For such specimens part of the tin centers are in the neutral and part in the ionized state, and this means that in the presence of electron exchange between them, each tin center spends part of the time in the neutral, and part of the time in the ionized state. If the lifetime of tin centers in each of the states (τ_N, τ_I) is much greater than the lifetime for the Mössbauer level of the ^{119}Sn nucleus ($\tau_0 \approx 20$ ns), then the Mössbauer spectrum will be a superposition of the Sn^{2+} and Sn^{4+} spectra, with the ratio of line intensities determined as

$$R = f_N \tau_N / f_I \tau_I. \quad (6)$$

If, however, the times τ_N and τ_I become less than τ_0 , then the Sn^{2+} and Sn^{4+} lines must approach one another, and in the limit of fast electron exchange ($\tau_N \sim \tau_I \ll \tau_0$) a single line will be observed in the spectrum corresponding to an "averaged" state of the tin center, and the isomer shift of this line is determined by the relation

$$\delta = (\delta_I - R\delta_N) / (1 + R), \quad (7)$$

where δ_N and δ_I are the isomer shifts of the Mössbauer spectra of the Sn^{2+} and Sn^{4+} states.

Only those lines which were in the spectra of specimens with composition $Pb_{99}SnS_{100}$ (Fig. 1,a) and $Pb_{98.5}Sn_{0.5}NaS_{100}$ (Fig. 1,e), discussed above, were observed in the spectrum of $Pb_{96}Sn_2NaTlS_{100}$ specimen at 80 and 295 K, while the Sn^{2+} and Sn^{4+} lines only get insignificantly nearer one another as the temperature is raised (see Fig. 4, a, b and Table I). Consequently, equilibrium between Sn^{2+} and Sn^{4+} in PbS at 80 K is established in a time appreciably exceeding 20 ns (i.e., $\tau_N \sim \tau_I \gg \tau_0$), but at 295 K the two-electron exchange process already affects the position of the Sn^{2+} and Sn^{4+} lines (i.e., $\tau_N \sim \tau_I > \tau_0$). Although $Pb_{1-x}Sn_xS$ solid solutions are narrow-band materials, slow exchange is not surprising in view of the fact that we are considering the transfer of two electrons.

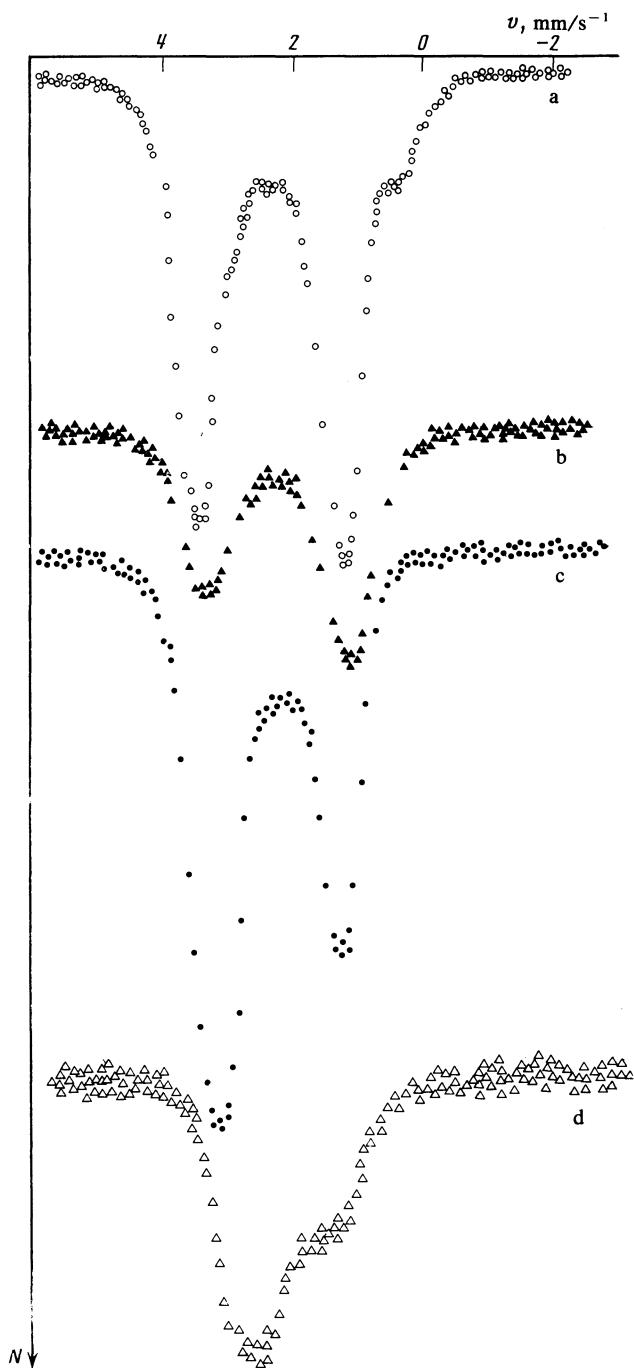


FIG. 4. Mössbauer spectra of ^{119}Sn in the specimens $\text{Pb}_{96}\text{Sn}_2\text{NaTlSe}_{100}$ (a,b) and $\text{Pb}_{96.3}\text{Sn}_{1.7}\text{NaTlSe}_{100}$ (c,d) at 80 (a,c) and 295 K (b,d).

The Mössbauer spectra of a specimen of composition $\text{Pb}_{96.3}\text{Sn}_{1.7}\text{NaTlSe}_{100}$ at 80 and 295 K are a superposition of two single lines corresponding to Sn^{2+} and Sn^{4+} (Fig. 4,c,d), but the isomer shifts of these lines depend on temperature (see Table I). The isomer shifts of the Sn^{2+} and Sn^{4+} lines at 80 K for this specimen are close to the isomer shifts of the corresponding lines in the spectra of the specimens $\text{Pb}_{99}\text{SnSe}_{100}$ (Fig. 3,a) and $\text{Pb}_{97.5}\text{Sn}_{0.5}\text{NaTlSe}_{100}$ (Fig. 3,d), although an insignificant moving together of the Sn^{2+} and Sn^{4+} lines is also observed (see Table I). This is evidence that

at 80 K the situation of slow electron exchange between Sn^{2+} and Sn^{4+} centers is realized in PbSe ($\tau_N \sim \tau_I > \tau_0$). Increasing the temperature from 80 to 295 K is accompanied by a sharp approach of the Sn^{2+} and Sn^{4+} lines (see Table I). This fact indicates unambiguously the occurrence of electron exchange between the Sn^{2+} and Sn^{4+} states. The characteristic time for exchange between the states then turns out to be of the order of τ_0 , since a single line of an "average" state is not observed in the spectrum, but the separate Sn^{2+} and Sn^{4+} lines are preserved (Fig. 4,d). We note that the isomer shifts in the Sn^{2+} and Sn^{4+} spectra are weakly temperature dependent for $\text{Pb}_{99}\text{SnSe}_{100}$ and $\text{Pb}_{97.5}\text{Sn}_{0.5}\text{NaTlSe}_{100}$ specimens (see Table I), so that the observed approach of the lines for $\text{Pb}_{96.3}\text{Sn}_{1.7}\text{NaTlSe}_{100}$ on raising the temperature cannot be explained by a temperature dependence of the isomer shift of each of the states. We tried to observe a further approach of the lines in the spectrum of the last specimen by raising the temperature to 350 K. However, the sharp decrease in amplitude of the experimental spectrum made it impossible to observe reliably an "averaged" state of the tin impurity centers.

It is noteworthy that the process of two-electron exchange between neutral and ionized tin centers at 295 K is observed in the solid solution $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ and is practically unobservable in $\text{Pb}_{1-x}\text{Sn}_x\text{S}$. To explain this it must be borne in mind that two mechanisms are possible in principle, for bringing about electron exchange between tin centers. The first mechanism is direct tunneling transfer of electrons between tin ions. In this case, the degree of localization of the tin 5s-electrons plays the main role in the exchange rate. The larger value of the isomer shift in the Sn^{2+} spectrum in $\text{Pb}_{1-x}\text{Sn}_x\text{S}$ (see Table I) indicates the large degree of localization of the tin 5s-electrons in PbS and, consequently, the rate of exchange between tin centers should be smaller in PbS . The second mechanism is exchange between tin centers using states of the valence band. The process of electron exchange in PbSe is evidently facilitated because the levels of the tin 5s-electrons are disposed on a background of the valence band. Finally, if one of the stages in the charge transfer of tin centers is connected with hole capture, then the most favorable conditions of exchange are realized in $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ solid solutions, since the hole concentration is appreciably greater for them than for $\text{Pb}_{1-x}\text{Sn}_x\text{S}$ solid solutions (see Table I).

4. CONCLUSIONS

It has been shown that in $\text{Pb}_{1-x}\text{Sn}_x\text{S}$ and $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ solid solutions the charge state of tin atoms is determined by the presence of an acceptor impurity. A neutral and ionized state of the tin donor center has been identified. The change in the charge state of atoms of one of the components of the solid solution on alloying of the latter is a new effect and has not been observed by a direct experimental method.

Two-electron exchange between neutral and ionized tin donor centers was observed for a partially compensated $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ solid solution, alloyed with acceptor impurities. Single-electron exchange between structurally equivalent atoms which are in different charge states, was observed

several times by the Mössbauer spectroscopy method [for example, between Fe^{2+} and Fe^{3+} in Fe_3O_4 (Ref. 4) and in amorphous GeSe (Ref. 5), between Eu^{2+} and Eu^{3+} in Eu_3S_4 (Ref. 6), between neutral and ionized iron centers in GaP (Ref. 7)]. The two-electron exchange process between impurity centers in a semiconductor is, however, also a new effect and was not observed before our work by a direct experimental method. Such exchange is a relatively slow process and the results for the $\text{Pb}_{1-x}\text{Sn}_x\text{S}$ solid solution are evidence of this.

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