

Charge exchange of tin atoms in $Pb_{1-x}Sn_xS$ solid solutions

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It was established by using the Mössbauer spectroscopy method that tin atoms can be ionized to Sn^{+4} by introducing a sodium acceptor impurity into $Pb_{1-x}Sn_xS$ solid solutions.

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The PbS and SnS compounds form solid solutions on a PbS base ($Pb_{1-x}Sn_xS$, $x \leq 0.1$) with an NaCl lattice.¹ The authors² mentioned that if the introduction of a fine sodium acceptor impurity into PbS is accompanied by an increase of hole density, then the introduction of sodium into $Pb_{1-x}Sn_xS$ leads to a strong compensation of the carriers. It was assumed that tin in a solid solution of $Pb_{1-x}Sn_xS$ plays the role of a deep donor center, so that it becomes ionized with the capture of holes in the Sn^{+2} tin centers and produces Sn^{+4} centers. We investigated the ionization of the impurity centers of tin by using the Mössbauer method, since the parameters of Mössbauer spectra make it possible to identify the charge state of tin atoms and to verify the correctness of the authors' assumption.²

The solid solutions of $Pb_{0.99}Sn_{0.01}S$ and $Pb_{0.98}Sn_{0.01}Na_{0.01}S$ were synthesized by using the method described in Ref. 1. We used 92% enriched ^{119}Sn . The Mössbauer spectra were recorded at 80 K and 295 K with a $CaSnO_3$ source. The spectra were analyzed according to a standard program on a BESM-4 computer. The isomeric shifts are given for SnO_2 . Typical spectra are shown in Fig. 1.

Two types of Mössbauer spectra are possible for the solid solution of $Pb_{0.98}Sn_{0.01}Na_{0.01}S$, depending on the ratio of the lifetime (τ) of the Sn^{+2} and Sn^{+4} states in $Pb_{0.98}Sn_{0.01}Na_{0.01}S$ to that of the Mössbauer level of ^{119}Sn ($\tau_0 \sim 10^{-8}$ sec):

- 1) A spectrum representing a superposition of two lines corresponding to Sn^{+2} and Sn^{+4} ($\tau \gg \tau_0$);
- 2) a spectrum of a single line corresponding to an "averaged" state of tin ($\tau \ll \tau_0$).

We can see in Fig. 1 that the Mössbauer spectrum of a solid solution $Pb_{0.99}Sn_{0.01}S$ is a single line whose isomeric shift corresponds to a bivalent tin Sn^{+2} ($\delta = 3.94 \pm 0.02$ mm/sec, line width $\Gamma = 0.81 \pm 0.03$ mm/sec). Doping of the solid solution by sodium impurity atoms gives rise to the appearance of a $Pb_{0.98}Sn_{0.01}Na_{0.01}S$ sample in the Mössbauer spectrum, in addition to an Sn^{+2} line (its location coincides with that of the $Pb_{0.99}Sn_{0.01}S$ spectrum) and a line of tetravalent tin Sn^{+4} ($\delta = 1.35 \pm 0.02$ mm/sec, $\Gamma = 0.88 \pm 0.03$ mm/sec). This indicates that the introduction of a sodium acceptor impurity into solid solutions of $Pb_{1-x}Sn_xS$ ionizes Sn^{+2} tin to Sn^{+4} .

The appearance of two lines in the Mössbauer spectrum of $Pb_{0.98}Sn_{0.01}Na_{0.01}S$ at 80 K and the coincidence of the isomeric shift of the lines corresponding to Sn^{+2} in

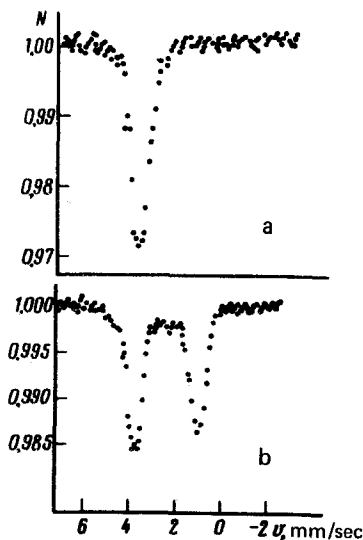


FIG. 1. Mössbauer ^{119}Sn spectra of (a) $\text{Pb}_{0.99}\text{Sn}_{0.01}\text{S}$ and (b) $\text{Pb}_{0.98}\text{Sn}_{0.01}\text{Na}_{0.01}\text{S}$ at 80 K. The fine structure of the spectra does not vary at 295 K, but the Sn^{+2} and Sn^{+4} lines converge (the spacing between them is equal to 2.58 ± 0.03 mm/sec at 80 K and 2.28 ± 0.03 mm/sec at 295 K for the (b) spectrum.

$\text{Pb}_{0.99}\text{Sn}_{0.01}\text{S}$ and $\text{Pb}_{0.98}\text{Sn}_{0.01}\text{Na}_{0.01}\text{S}$ indicates that there is no electron exchange between the Sn^{+2} and Sn^{+4} states ($\tau \gg \tau_0$) at 80 K. However, a measurement of the spectra at 295 K clearly shows that the Sn^{+2} and Sn^{+4} lines converge for $\text{Pb}_{0.98}\text{Sn}_{0.01}\text{Na}_{0.01}\text{S}$. This convergence can be the consequence of the initiated electron exchange between the Sn^{+2} and Sn^{+4} centers (the electron exchange between neutral and ionized iron impurity centers in gallium arsenide was observed by using the Mössbauer method³).

In conclusion, we emphasize that the charge exchange of one of the atoms that forms the lattice of a solid solution, depending on the location of the Fermi level in the forbidden band of a semiconductor, is an anomalous effect, which was observed for the first time by using a direct experimental method. The difficulty of this problem is compounded by the fact that the charge exchange of a tin atom is achieved either by a simultaneous transfer of two electrons or through the intermediate, unstable charge state of tin; hence this process cannot be analyzed in terms of a single-electron approximation.

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