Observation of two-electron exchange between tin centers in solid $Pb_{1-x}Sn_xSe$ solutions

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Two-electron exchange between neutral and ionized tin centers in solid $Pb_{1-x}Sn_xSe$ solutions is observed for the first time using the method of Mössbauer spectroscopy.

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Prokof'eva *et al.*[1,2] discovered, using Mössbauer spectroscopy and Hall effect measurements, that tin atoms in solid solution $Pb_{1-x}Sn_xS$ and $Pb_{1-x}Sn_xSe$ play the role of deep donor centers. Introduction of acceptors (sodium, thallium) into the materials indicated leads to ionization of tin; in addition, charge transfer in tin is accompanied by simultaneous transfer of two electrons and tin is present in the partially compensated material in two charge states: Sn^{+2} (neutral center) and Sn^{+4} (ionized center).

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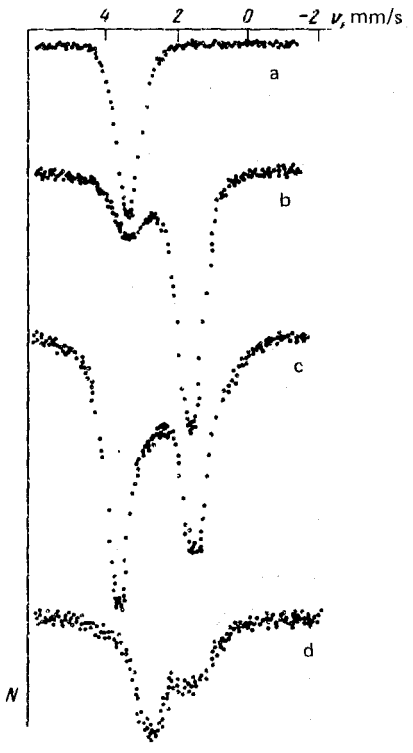

FIG. 1. Mössbauer spectra of ^{119}Sn in solid solutions $Pb_{99}SnSe_{100}$ at 80 K (a), $Pb_{97}SnNaTlSe_{100}$ at 80 K (b), and $Pb_{96.3}Sn_{1.7}NaTlSe_{100}$ at 80 (c) and 295 K (d). The isomeric shifts of the Sn^{+2} and Sn^{+4} spectra of specimens (a) and (b) depend weakly on temperature and at 80 K equal, respectively, $\sigma = 3.68 \pm 0.02$ mm/s and $\sigma = 1.59$ mm/s. The isomeric shifts of the spectra of the specimen $Pb_{96.3}Sn_{1.7}NaTlSe_{100}$ are: $\sigma = 3.71$ mm/s at 80 K for the Sn^{+2} line and $\sigma = 3.11$ mm/s at 295 K; for Sn^{+4} line $\sigma = 1.58$ mm/s at 80 K and $\sigma = 1.85$ mm/s at 295 K.

In principle, two-electron exchange is possible between the two states of tin, which can be observed by the method of Mössbauer spectroscopy. We attempted to observe electron exchange between Sn^{+2} and Sn^{+4} centers experimentally in solid solutions $Pb_{1-x}Sn_xS$ and $Pb_{1-x}Sn_xSe$ partially compensated with sodium and thallium.

The solid solutions were prepared using the technique described in Ref. 2. The Mössbauer spectra of ^{119}Sn were measured at 80 and 295 K using a $CaSnO_3$ source and were analyzed using a standard program on a BÉSM-4 computer. The isomeric shifts are presented relative to SnO_2. The typical spectra are shown in Fig. 1.

The spectrum of the specimen $Pb_{99}SnSe_{100}$ at 80 and 295 K represents an isolated line, whose isomeric shift corresponds to Sn^{+2} (neutral tin center). The spectrum of the specimen $Pb_{97}SnNaTlSe_{100}$ at 80 and 295 K represents the superposition of an intense isolated line, which corresponds to Sn^{+4} (ionized tin center), and an additional line, which corresponds to Sn^{+2} (see Figs. 1a and 1b). From electrical measurements it is known that the donor level of tin in $Pb_{1-x}Sn_xSe$ is situated in the background of the

valence band and, for this reason, total electric compensation should not be observed in the solid solution $Pb_{1-x}Sn_xSe$.

The spectrum of the specimen $Pb_{96.3}Sn_{1.7}NaTlSe_{100}$ at 80 and 295 K represents a superposition of two intense lines corresponding to Sn^{+2} and Sn^{+4} (see Figs. 1c and 1d). If electronic exchange occurs between the neutral Sn^{+2} and ionized Sn^{+4} tin centers, then as the temperature increases the lines corresponding to Sn^{+2} and Sn^{+4} must approach each other and, when the lifetime of the Sn^{+2} and Sn^{+4} states (τ) is much shorter than the lifetime of the Mössbauer level ^{119}Sn ($\tau_0 \sim 10^{-8}$), an isolated line, which corresponds to an "averaged" state of tin, should be observed in the spectrum. Indeed, as is evident from Figs. 1c and 1d, an increase in temperature from 80 to 295 K is accompanied by convergence of Sn^{+2} and Sn^{+4} lines in the spectrum. This fact uniquely indicates that thermally activated electronic exchange between the Sn^{+2} and Sn^{+4} states occurs in the system.

We attempted to observe two-electron exchange between Sn^{+2} and Sn^{+4} states in solid solutions $Pb_{96}Sn_2NaTlS_{100}$ and $Pb_{98}SnNaS_{100}$ partially compensated with sodium and thallium. However, the position of lines in the spectrum which corresponds to Sn^{+2} and Sn^{+4} depended weakly on the temperature, i.e., it turned out that for the solid solutions $Pb_{1-x}Sn_xS$ $\tau \gg \tau_0$ in the temperature range 80–295 K. This difference in the behavior of the solid solutions $Pb_{1-x}Sn_xS$ and $Pb_{1-x}Sn_xSe$ is explained by the fact that in PbS, according to electrical measurements, the donor level of tin is situated near the center of the forbidden band and two-electron exchange between Sn^{+2} and Sn^{+4} states with the average electron energy equal to the center of the forbidden band is inhibited, while in $Pb_{1-x}Sn_xSe$ the donor level of tin is situated on the background of the valence band and the presence of a finite density of band states near the tin level facilitates two-electron exchange between the two charge states of tin.

In conclusion, we note that single-electron exchange between centers in different charge states was observed repeatedly by the Mössbauer spectroscopy method, for example, between Fe^{+2} and Fe^{+3} in Fe_3O_4,[3] between Eu^{+2} and Eu^{+3} in Eu_3S_4,[4] and between neutral and ionized iron centers in GaP.[5] However, the two-electron exchange between two different charge states of an impurity center in a semiconductor, which is a new effect, was observed for the first time by a direct experimental method.

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