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S. Zaynabiddinov

National University of Uzbekistan, prof_sirojiddin@mail.ru

K. Bobokhujaev

National University of Uzbekistan, qudratman@mail.ru

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ELECTRON EXCHANGE BETWEEN IMPURITY CENTERS OF TIN IN PbS AND PbSe

ZAYNABIDDINOV S., BOBOKHUJAEV K. U.

National University of Uzbekistan, Tashkent, Uzbekistan e-mail:

prof_sirojiddin@mail.ru, qudratman@mail.ru

Abstract

Electron exchange between neutral and doubly ionized U -minus centers of tin in partially compensated solid solutions $Pb_{1-x}Sn_xS$ and $Pb_{1-x}Sn_xSe$ has been investigated using $^{119m}Sn(^{119m}Sn)$ emission Mössbauer spectroscopy. The activation energy of the process for $Pb_{1-x}Sn_xS$ solid solutions is 0.11 ± 0.02 eV and is comparable to the depth of energy levels of tin in the PbS band gap, while the activation energy of this process for $Pb_{1-x}Sn_xSe$ solid solutions is comparable to the activation energy of donor U -minus centers of tin in PbSe being 0.05 ± 0.01 eV. The exchange has been performed by the simultaneous transfer of two electrons with the use of the valence band states.

Keywords: Mössbauer spectroscopy, U -centers, electron exchange

Physics and Astronomy Classification Scheme: 61.82.Fk, 77.22.-d

1 Introduction

Hubbard [1] was the first to theoretically analyze the behavior of point defects able to be a donor (acceptor) of two electrons when interacting with the crystal lattice. Two bands of localized states separated by the interatomic energy (Hubbard energy or correlation energy) $U = E_2 - E_1$, where E_1 and E_2 are the first and second ionization energies of the center, are formed in the semiconductor band gap. If $U < 0$, there appears the level scheme, which is termed “two-electron centers with negative correlation energy” (U -minus centers).

Donor U -minus centers of tin in lead chalcogenides were determined using emission Mössbauer spectroscopy [2-4] and parameters of the microscopic model of U -minus centers of tin were determined [5, 6]. However, the question on the possibility of electron exchange with neutral and ionized U -minus centers in semiconductors remains open. This study is devoted to the investigation of the electron exchange between the neutral and ionized donor U -minus tin centers in lead sulfide and selenide by the $^{119m}Sn(^{119m}Sn)$ emission Mössbauer spectroscopy using the resonant detector.

2 Main results

Solid solutions $Pb_{0.96}Sn_{0.02}Na_{0.01}Tl_{0.01}S$, $Pb_{0.99}Sn_{0.005}Na_{0.005}S$, $Pb_{0.965}Sn_{0.015}Na_{0.01}Tl_{0.01}Se$, and $Pb_{0.988}Sn_{0.005}Na_{0.007}Se$ were prepared by alloying the initial components of semiconductor purity in evacuated quartz ampules with subsequent annealing initially the ingots and then compacted powders at $650^\circ C$ for 120 h. All the samples were singlephase and had the structure of the

NaCl type. The $\text{Pb}_{0.965}\text{Sn}_{0.015}\text{Na}_{0.01}\text{Tl}_{0.01}\text{Se}$, and $\text{Pb}_{0.988}\text{Sn}_{0.005}\text{Na}_{0.007}\text{Se}$ samples were p -type degenerate (the hole concentration at 80 and 295 K was $\sim 3 \times 10^{19} \text{ cm}^{-3}$), and the $\text{Pb}_{0.96}\text{Sn}_{0.02}\text{Na}_{0.01}\text{Tl}_{0.01}\text{S}$ and $\text{Pb}_{0.99}\text{Sn}_{0.005}\text{Na}_{0.005}\text{S}$ samples were p -type nondegenerate (the hole concentration varied from $\sim 5 \times 10^{13} \text{ cm}^{-3}$ at 80 K to $\sim 10^{17} \text{ cm}^{-3}$ at 295 K). Such concentration behavior of charge carriers in solid solutions is explained by the fact that over-stoichiometric lead in lead sulfide forms shallow single-electron donor states against the background of the conduction band, whereas impurity atoms of sodium and thallium form shallow single-electron acceptor states against the background of the valence band, while energy levels of tin impurity atoms lie in the lower half of the PbS band gap and against the background of the states of the PbSe valence band [5, 6].

The Mössbauer sources were prepared using metallic ^{118}Sn irradiated with a neutron flux of $\sim 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ for six months. The Mössbauer spectra were measured using a CM 4201 TerLab spectrometer with a resonant scintillation detector, which makes it possible to increase the detection efficiency of the spectra (we used a plastic scintillator with particles of the SnO_2 converter uniformly distributed over the bulk; the converter was prepared from isotope ^{119}Sn enriched to 96%). The spectral shifts are given relative to the SnO_2 absorber.

As the first stage, we investigated the temperature dependencies of the central shift of the Mössbauer spectra of the samples containing either only neutral or only ionized state of impurity tin atoms.

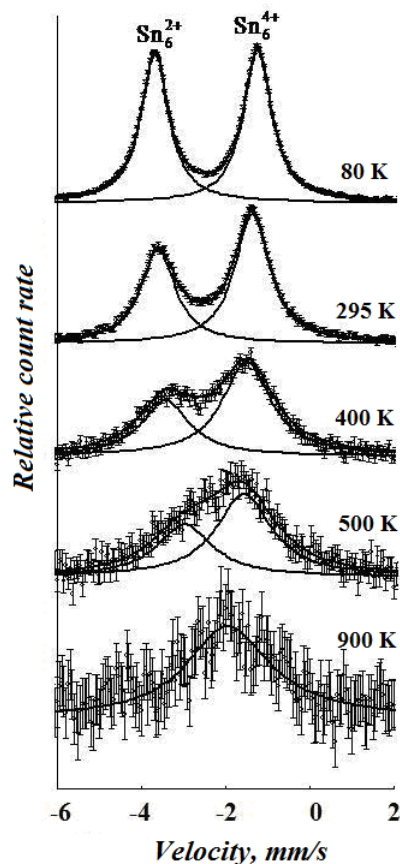


Fig. 1. $^{119m}\text{Sn}^{119m}\text{Sn}$ emission Mössbauer spectra of $\text{Pb}_{0.96}\text{Sn}_{0.02}\text{Na}_{0.01}\text{Tl}_{0.01}\text{S}$ solid solutions at different temperatures. The position of lines corresponding to and centers is shown

We investigated the temperature dependencies of the central shift of the Mössbauer spectra of the sample containing the neutral and ionized states of impurity tin atoms simultaneously. As such materials, we selected compositions $\text{Pb}_{0.96}\text{Sn}_{0.02}\text{Na}_{0.01}\text{Tl}_{0.01}\text{S}$, $\text{Pb}_{0.99}\text{Sn}_{0.005}\text{Na}_{0.005}\text{S}$, $\text{Pb}_{0.965}\text{Sn}_{0.015}\text{Na}_{0.01}\text{Tl}_{0.01}\text{Se}$, and $\text{Pb}_{0.988}\text{Sn}_{0.005}\text{Na}_{0.007}\text{Se}$. The $^{119m}\text{Sn}^{119m}\text{Sn}$ emission Mössbauer spectra of mentioned solid solutions at 80 K are the superposition of two lines of the aperture width, the central shifts of which correspond to Sn_6^{2+} (the centers of divalent six-coordinated tin in the PbS and PbSe cation sublattice, which correspond to the neutral state of the donor U -minus tin center) and Sn_6^{4+} centers (the centers of tetravalent six-coordinated tin in the PbS and PbSe cation sublattice and correspond to the doubly ionized state of the donor U -minus tin center) (spectra of $\text{Pb}_{0.96}\text{Sn}_{0.02}\text{Na}_{0.01}\text{Tl}_{0.01}\text{S}$ solid solutions are presented in Fig. 1 as an example). The spectra in Fig. 1 illustrate a typical pattern of the electron exchange between the Sn_6^{2+} and Sn_6^{4+} states. The absence of the intermediate charge state of Sn_6^{3+} tin centers evidences that the exchange is performed by the simultaneous transfer of two electrons.

To determine the frequency of the electron exchange, we processed the experimental spectra (i.e., dependencies of detector counting rate N on source motion velocity V) by least-squares method under the assumption that the shape of the spectral line is determined by relationship [7]

$$N(V) = -\frac{AC + BD}{C^2 + D^2},$$

where

$$\begin{aligned} A &= J_{\text{Sn}_6^{2+}} \left(G_{\text{Sn}_6^{4+}} + \tau_{\text{Sn}_6^{4+}}^{-1} + \tau_{\text{Sn}_6^{2+}}^{-1} \right), \quad B = J_{\text{Sn}_6^{2+}} \left(\delta_{\text{Sn}_6^{4+}} - V \right) + J_{\text{Sn}_6^{4+}} \left(\delta_{\text{Sn}_6^{2+}} - V \right), \\ C &= \left(G_{\text{Sn}_6^{2+}} + \tau_{\text{Sn}_6^{2+}}^{-1} \right) \left(G_{\text{Sn}_6^{4+}} + \tau_{\text{Sn}_6^{4+}}^{-1} \right) - \left(\delta_{\text{Sn}_6^{2+}} - V \right) \left(\delta_{\text{Sn}_6^{4+}} - V \right) - \tau_{\text{Sn}_6^{2+}}^{-1} \tau_{\text{Sn}_6^{4+}}^{-1}, \\ D &= \left(\delta_{\text{Sn}_6^{2+}} - V \right) \left(G_{\text{Sn}_6^{4+}} + \tau_{\text{Sn}_6^{4+}}^{-1} \right) + \left(\delta_{\text{Sn}_6^{4+}} - V \right) \left(G_{\text{Sn}_6^{2+}} + \tau_{\text{Sn}_6^{2+}}^{-1} \right), \end{aligned}$$

$J_{\text{Sn}_6^{2+}}$ and $J_{\text{Sn}_6^{4+}}$ are the widths of lines of Sn_6^{2+} and Sn_6^{4+} centers, respectively; are the widths of lines of and centers, respectively; $G_{\text{Sn}_6^{2+}}$ and $G_{\text{Sn}_6^{4+}}$ and are lifetimes of Sn_6^{2+} and Sn_6^{4+} centers, respectively; and $\tau_{\text{Sn}_6^{2+}}$ and $\tau_{\text{Sn}_6^{4+}}$ are lifetimes Sn_6^{2+} and Sn_6^{4+} centers, respectively. We accepted that $G_{\text{Sn}_6^{2+}} = G_{\text{Sn}_6^{4+}} = G$ and $\tau_{\text{Sn}_6^{2+}} = \tau_{\text{Sn}_6^{4+}} = \tau$ because of the lack of experimental data.

The results of processing the spectra are summarized in Figs. 2a and 2b in the form of the temperature dependence of electron exchange frequency $\nu = \tau^{-1}$ between the Sn_6^{2+} and Sn_6^{4+} centers. The exchange activation energy for the $\text{Pb}_{0.96}\text{Sn}_{0.02}\text{Na}_{0.01}\text{Tl}_{0.01}\text{S}$ and $\text{Pb}_{0.99}\text{Sn}_{0.005}\text{Na}_{0.005}\text{S}$ nondegenerate solid solutions is 0.11(2) eV, which corresponds to the distance from the Fermi level μ to the valence band top in partially compensated $\text{Pb}_{1-x-y}\text{Sn}_x\text{Na}_y\text{S}$ hole solid solutions in the low-temperature region (Fig. 2c) [5].

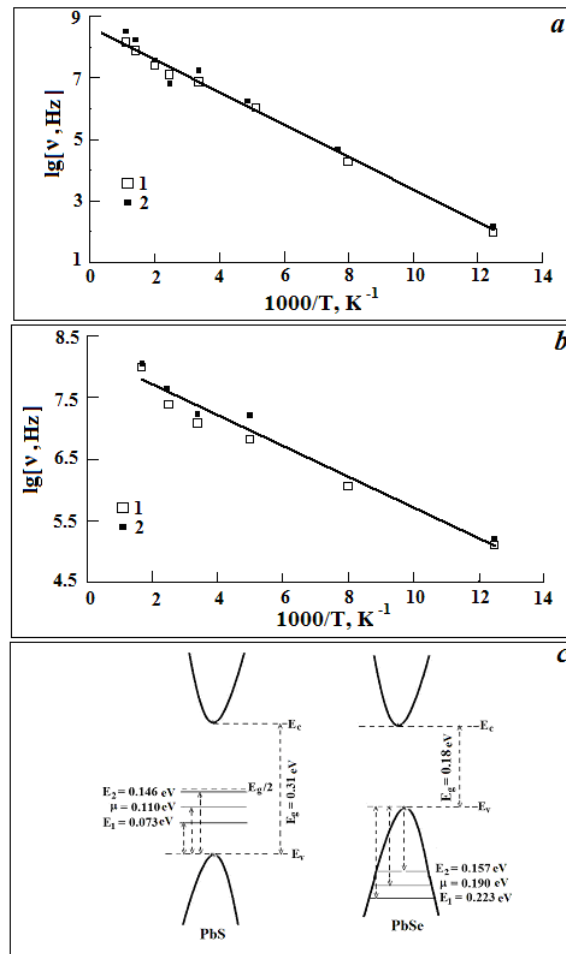


Fig. 2. Temperature dependencies of the electron exchange frequency between the $^{119\text{mm}}\text{Sn}$ and centers (a) for the $^{119\text{mm}}\text{Sn}$ containing (1) $\text{Pb}_{0.96}\text{Sn}_{0.02}\text{Na}_{0.01}\text{Tl}_{0.01}\text{S}$ and (2) $\text{Pb}_{0.99}\text{Sn}_{0.005}\text{Na}_{0.005}\text{S}$ solid solutions and (b) for the $^{119\text{mm}}\text{Sn}$ containing $\text{Pb}_{0.965}\text{Sn}_{0.015}\text{N}_{0.01}\text{Tl}_{0.01}\text{Se}$ and $\text{Pb}_{0.988}\text{Sn}_{0.005}\text{Na}_{0.007}\text{Se}$ solid solutions. (c) Energy level diagrams of donor U -minus tin centers in PbS and PbSe at 100 K

The exchange activation energy for the $\text{Pb}_{0.965}\text{Sn}_{0.015}\text{Na}_{0.01}\text{Tl}_{0.01}\text{Se}$ and $\text{Pb}_{0.988}\text{Sn}_{0.005}\text{Na}_{0.007}\text{Se}$ solid solutions is 0.05(1) eV, which corresponds to the correlation energy of donor U -minus tin centers in lead selenide (Fig. 4c) [6]. Taking into account the low concentration of the tin impurity (when the direct electron exchange between the tin centers is impossible), we can conclude that the electron exchange between the Sn_6^{2+} and centers in PbS and PbSe is implemented using the valence band states. The fact that the temperature dependence of the electron exchange frequency is independent of the tin concentration also evidences in favor of the mentioned mechanisms (Figs. 2a, 2b).

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