ФИЗИКА

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TEMPERATURE DEPENDENCE OF THE FREQUENCY OF TWO-ELECTRON EXCHANGE BETWEEN IMPURITY NEGATIVE-U TIN-CENTERS IN LEAD SULFIDE

A Fast two_electron exchange between neutral Sn^{2+} and doubly ionized Sn^{4+} impurity negative_U tin centers in partially compensated $Pb_{0.98}Sn_{0.02}Na_{0.01}Tl_{0.01}S$ solid solutions has been found by emission Mössbauer spectroscopy on $^{119mm}Sn(^{119m}Sn)$ isotope; the lifetime of the Sn^{2+} and Sn^{4+} states changes from $\sim 6\times10^{-4}$ to $\sim 8\times10^{-9}$ s with a change in temperature from 295 to 900 K.

Keywords: Mössbauer spectroscopy, two electron exchange, U-centers.

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ТЕМПЕРАТУРНАЯ ЗАВИСИМОСТЬ ЧАСТОТЫ ДВУХЭЛЕКТРОННОГО ОБМЕНА МЕЖДУ ПРИМЕСНЫМИ U-МИНУС-ЦЕНТРАМИ ОЛОВА В СУЛЬФИДЕ СВИНЦА

Методом эмиссионной мессбауэровской спектроскопии на изотопе $^{119mm}Sn(^{119m}Sn)$ обнаружен процесс быстрого двухэлектронного обмена между нейтральными Sn^{2+} и двукратно ионизованными Sn^{4+} примесными U-минус-центрами олова в частично компенсированных твердых растворах $Pb_{0.98}Sn_{0.02}Na_{0.01}Tl_{0.01}S$, причем время жизни состояний Sn^{2+} и Sn^{4+} меняется от $\sim 6\cdot10^{-4}$ с до $\sim 8\cdot10^{-9}$ с при изменении температуры от 295 до 900 K.

Ключевые слова: мессбауэровская спектроскопия, двухэлектронный обмен, U-минус-центры.

The notion of negative-U centers was used for the first time by Anderson [1] to explain the electric and magnetic properties of glassy semiconductors. Mössbauer spectroscopy on ^{119}Sn isotope was found to be the most efficient method for identifying negative-U centers in glassy and crystalline semiconductors, as well as superconductors [2, 3]. In particular, it was shown that impurity tin atoms in lead chalcogenides (PbS and PbSe) are located in regular sites of cationic sublattice and form two-electron donor centers with negative correlation energy; the parameters of the microscopic model of negative-U centers were also determined. However, the question of the existence of two-electron exchange between neutral and ionized negative-U centers in semiconductors remains open. In this article, we report on the uncovering of this process and determining the temperature dependence of the frequency of two-electron exchange between neutral and ionized tin centers in partially compensated solid solutions based on lead sulfide by emission Mössbauer spectroscopy on $^{119mm}Sn(^{119m}Sn)$ isotope in the temperature range of 80–900 K.

$Pb_{0.98}Sn_{0.02}Na_{0.01}Tl_{0.01}S$ solid solutions were prepared by alloying the initial components of semiconductor purity grade in evacuated quartz ampoules with subsequent annealing ingots and then pressed powders at 650°C for 120 h. All samples were single-phase and had a NaCl-type structure. The samples had p-type conductivity and were nondegenerate (the hole concentration varied from $\sim 5 \times 10^{13}$ at 80 K to $\sim 10^{17}$ cm^{-3} at 295 K). $Pb_{0.98}{}^{119mm}Sn_{0.02}Na_{0.01}Tl_{0.01}S$ Mössbauer sources were prepared using a ^{118}Sn preparation irradiated by a neutron flux of $\sim 10^{15}$ cm^{-2} s^{-1} for 6 months.

In figure 1 Emission Mössbauer spectra of $^{119mm}Sn(^{119m}Sn)$ isotope in $Pb_{0.98}Sn_{0.02}Na_{0.01}Tl_{0.01}S$ solid solutions recorded at 80 and 295 K are shown. They are superpositions of two lines of instrumental width ($G_{Sn^{2+}} = G_{Sn^{4+}} = 0.80(1)$ mm/sm), isomeric shifts δ of which correspond to the Sn^{2+} ($\delta_{Sn^{2+}} = 3.69(1)$ mm/s) and Sn^{4+} ($\delta_{Sn^{4+}} = 1.26(1)$ mm/s) centers.
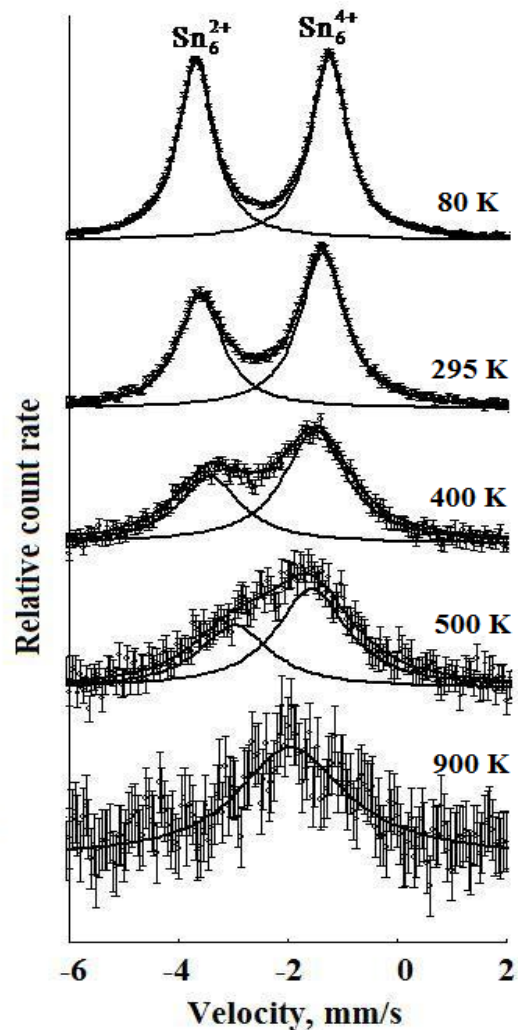

Fig. 1. Emission Mössbauer spectra of $^{119mm}Sn(^{119m}Sn)$ isotope in $Pb_{0.98}Sn_{0.02}Na_{0.01}Tl_{0.01}S$ solid solutions recorded by a resonant detector at source temperatures of 80, 295, 400, 500, and 900 K. The lines corresponding to the Sn^{2+} and Sn^{4+} centers are shown. The spectrum recorded at 900 K corresponds to the averaged state of tin centers

An increase in temperature from 80 to 295 K is accompanied by a decrease in relative intensity R of the Sn^{2+} line (R = 0.49(1) at 80 K and R = 0.41(2) at 295 K), which can be explained by a sharper temperature dependence of the fraction of recoilless processes for divalent tin compounds, as compared with four-valence tin compounds. The Sn^{2+} and Sn^{4+} lines are somewhat

broadened ($G_{Sn^{2+}} = G_{Sn^{4+}} = 0.90(1)$ mm/s) and located closer to each other ($\delta_{Sn^{2+}} = 3.62(1)$ mm/s) and Sn^{4+} ($\delta_{Sn^{4+}} = 1.36(1)$ mm/s).

At 500 K (figure 1), the relative intensity of the Sn^{2+} line further decreases (R = 0.31(3)) and the Sn^{2+} and Sn^{4+} lines are significantly broadened ($G_{Sn^{2+}} = G_{Sn^{4+}} = 1.6(1)$ mm/s) and even closer to each other ($\delta_{Sn^{2+}} = 1.5(1)$ mm/s and $\delta_{Sn^{4+}} = 3.2(1)$ mm/s). Finally, at 900 K (figure 1), the lines are merged into one broadened line (G = 2.4(1) mm/s), the isomeric shift of which ($\delta = 2.0(2)$ mm/s) is intermediate between those for the Sn^{2+} and Sn^{4+} centers.

The spectra in figure 1 illustrate a typical process of electron exchange between two Sn^{2+} and Sn^{4+} states; the frequency of electron exchange increases with an increase in temperature. The spectrum recorded at 900 K corresponds to the averaged state of tin centers, which arises due to the fast electron exchange between Sn^{2+} and Sn^{4+}. The absence of the intermediate charge state of tin centers (Sn^{3+}) in the spectra indicates that the exchange occurs via simultaneous transfer of two electrons.

To determine the frequency of electron exchange, the experimental spectra were processed by the least-squares method on the assumption that the shape of the spectral line is determined by the relation

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

where:

$$A = J_{Sn^{2+}}\left(G_{Sn^{4+}} + \tau_{Sn^{4+}}^{-1} + \tau_{Sn^{2+}}^{-1}\right),$$
$$B = J_{Sn^{2+}}\left(\delta_{Sn^{4+}} - V\right) + J_{Sn^{4+}}\left(\delta_{Sn^{2+}} - V\right),$$
$$C = \left(G_{Sn^{2+}} + \tau_{Sn^{2+}}^{-1}\right)\left(G_{Sn^{4+}} + \tau_{Sn^{4+}}^{-1}\right) - \left(\delta_{Sn^{2+}} - V\right)\left(\delta_{Sn^{4+}} - V\right) - \tau_{Sn^{2+}}^{-1}\tau_{Sn^{4+}}^{-1},$$
$$D = \left(\delta_{Sn^{2+}} - V\right)\left(G_{Sn^{4+}} + \tau_{Sn^{4+}}^{-1}\right) + \left(\delta_{Sn^{4+}} - V\right)\left(G_{Sn^{2+}} + \tau_{Sn^{2+}}^{-1}\right),$$

$J_{Sn^{2+}}$ and $J_{Sn^{4+}}$ — are the amplitudes of the Sn^{2+} and Sn^{4+} lines, respectively; and $\tau_{Sn^{2+}}$ and $\tau_{Sn^{4+}}$ are the lifetimes of the Sn^{2+} and Sn^{4+} centers, respectively (we assume that $\tau_{Sn^{2+}} = \tau_{Sn^{4+}} = \tau$ because of the lack of experimental parameters).

The temperature dependence of the frequency of electron exchange $\nu = \tau^{-1}$ between the centers of the Sn^{2+} and Sn^{4+} is shown in figure 2.

Fig. 2. Temperature dependence of the frequency of the electron exchange between the centers of Sn^{2+} and Sn^{4+}
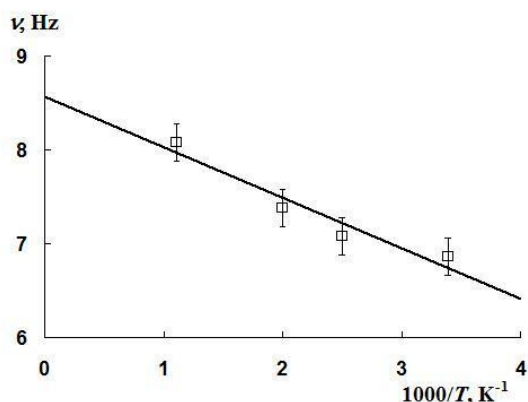
The activation energy of exchange is 0.11(2) eV. This corresponds to the distance of the Fermi level from the valence band to the hole partially-compensated solid solutions Pb_{1-x-}

ySnx(Na,Tl)yS [2], and indicates that the electron exchange between the centers of Sn^{2+} and Sn^{4+} is implemented using state of the valence band. In favor of such a mechanism is evidenced by the fact that the exchange is observed at low concentrations of tin, when the process can not be a direct exchange of electrons between the centers of the tin.

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CORRELATIONS OF THE ^{63}Cu NMR DATA WITH THE ^{67}Cu (^{67}Zn) AND THE ^{61}Cu (^{61}Ni) EMISSION MÖSSBAUER DATA FOR CERAMIC SUPERCONDUCTORS

A linear correlation between the quadrupole coupling constant C_{Cu} measured by the ^{63}Cu NMR technique on the one hand and the quadrupole coupling constants C_{Zn} and C_{Ni} measured by the ^{67}Cu(^{67}Zn) and ^{61}Cu(^{61}Ni) emission Mössbauer spectroscopy on the other hand has been found for ceramic superconductors.

Keywords: Mössbauer spectroscopy, NMR, electric field gradient.

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КОРРЕЛЯЦИОННЫЕ СООТНОШЕНИЯ МЕЖДУ ДАННЫМИ ЯМР ^{63}Cu И ЭМИССИОННОЙ МЕССБАУЭРОВСКОЙ СПЕКТРОСКОПИИ ^{67}Cu(^{67}Zn) И ^{61}Cu(^{61}Ni) ДЛЯ КЕРАМИЧЕСКИХ СВЕРХПРОВОДНИКОВ

Установлена линейная корреляция между постоянной квадрупольного расщепления C_{Cu}, измеренной методом ЯМР ^{63}Cu и постоянными квадрупольного расщепления C_{Zn} и C_{Ni}, измеренные методом эмиссионной мессбауэровской спектроскопии ^{67}Cu(^{67}Zn) и ^{61}Cu(^{61}Ni) для керамических сверхпроводников.

Ключевые слова: мессбауэровская спектроскопия, ЯКР, градиент электрического поля.

1. Introduction

One of the main problems in physics of high-temperature (high-T_c) superconductors is the determination of the spatial distribution of electronic defects in the lattices of copper metal oxides. A potentially effective method to solve this problem is to compare the experimentally determined and calculated parameters of the electric field gradient (EFG) tensor for specific lattice sites [2]. Copper sites are of utmost interest in such work because these atoms are found in the