"Softening" of phonon spectrum in semiconductors of the $Pb_{1-x}Sn_xTe$ system on going to the gapless state

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A decrease of about 30% was observed in the Mössbauer-effect probability in the region of the gapless state in narrow-band semiconductors of the $Pb_{1-x}Sn_xTe$ system. This is attributed to the "softening" of the phonon spectrum as a result of a decrease in the optical-branch frequencies, and points to a strong electron-phonon interaction.

The narrow-band semiconductors of the $Pb_{1-x}Sn_xTe$ system have a gapless state in the interval $0.6 < x < 0.7$; band inversion takes place in this case at points L of the Brillouin zone.[1] It was proposed in[2] that a strong electron-phonon interaction is produced in this system. We report here experimental results favoring this assumption.

The idea of our experiments is the following: If the aforementioned assumption is valid, then a change of the electron spectrum in the region of the gapless state should give rise to a change in the phonon spectrum. Information on the phonon spectrum can be obtained by measuring the Mössbauer-effect probability.

We measured the Mössbauer effect on Sn^{119} in polycrystalline samples of $Pb_{1-x}Sn_xTe$ alloys with different tin contents at room temperature. The γ-quantum source was tin dioxide with activity ~10 μCi. The alloys were synthesized by the procedure described in[3]. For the "thin" absorbers used by us, the Mössbauer probability f' was calculated from the formula $f' = AS_0/d$, where A is a normalization constant, S_0 is the area under the spectral curve, and d is the absorber thickness in terms of tin. With decreasing x, the ratio of the number of resonant atoms (Sn) to the nonresonant ones (Pb, Te) decreases. This can lead to a side effect, viz., a decrease of S_0 as a result of the nonresonant absorption. Our control experiments have shown that this effect can be neglected at the chosen absorber thickness. The Mössbauer spectra of the samples consisted of single lines. The areas S_0 under the spectral curves and the isomeric shifts ϵ (the positions of the gravity centers of the spectra) were calculated with a computer.

Figure 1a shows the probabilities f' at various tin

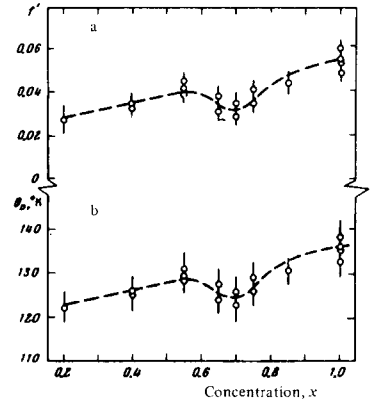

FIG. 1. a) Dependence of the probability of the Mössbauer effect at the Sn^{119} nuclei on x in $Pb_{1-x}Sn_xTe$ alloys. b) Dependence of the Debye temperatures on the tin content x for the same alloys. The values of θ_D were calculated in the high-temperature limit ($T \gg \theta_D$).

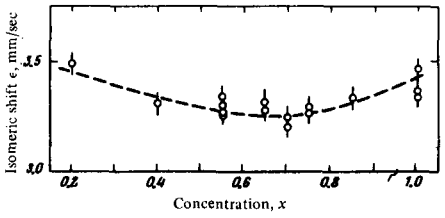

FIG. 2. Dependence of the isomeric shifts of the Sn^{119} nuclei in $Pb_{1-x}Sn_xTe$ alloys on x. Source-$Sn^{119m}O_2$ at room temperature.

contents x. The scatter of the points at fixed x illustrates the degree of reproducibility of the results. As seen from the figure, f' decreases by ~30% in the region $x=0.7$. It should be noted that such large values of f' (~20%) are observed usually in phase transitions that are accompanied by a jumplike change of either the crystal lattice parameter or the type of lattice structure. This raises the question whether the observed anomaly of f' at $x=0.7$ is the consequence of analogous causes. According to our measurements and the data of[5], the alloy lattice parameters, measured with accuracy ~0.003 Å, decrease linearly with increasing x. We observed no anomaly whatever in this dependence in the vicinity of the point $x=0.7$. In addition, both PbTe and SnTe have a structure of the NaCl type. Consequently, the transition to the gapless state is not accompanied by an appreciable realignment of the crystal lattice.

The fact itself that f' decreases at $x=0.7$ shows unequivocally that the elastic constants of the crystal lattice of the alloy become weaker and that the rms displacements of the tin atoms from their equilibrium positions are increased. This means also that the oscillation frequencies of the tin atom decrease. Since the tin atom can oscillate in optical modes, one can suggest the following possible explanation of anomaly of $f'(x)$: the optical-branch frequencies decrease in the the gapless state; in other words, the phonon spectrum becomes "softer." This can lead to instability of the crystal lattice relative to certain oscillation modes.

Figure 1b shows the $f'(x)$ plot in terms of the characteristic Debye temperatures θ_D, calculated for the case $T \gg \theta_D$ from the formula $f' = \exp(-6RT/k\theta_D^2)$, where R is the recoil energy of the nucleus and k is the Boltzmann constant. In the case considered here θ_D is only an approximate characteristic of the phonon spectrum, inasmuch as the unit cell of the alloy contains more than one atom.

Thus, the observed relation between the changes of the electron and phonon spectrum indicates, in our opinion, a strong electron-phonon interaction in the semiconductors of the $Pb_{1-x}Sn_xTe$ system.

We also obtained from the Mössbauer spectra information on the state of the s electrons of the tin atom. It is known that the change $\Delta\epsilon$ of the isomeric shift is proportional to the change of the total density of the s electrons at the nuclei. Figure 2 shows a plot of $\epsilon(x)$, from which it is seen that the s-electron density at the Sn^{119} nuclei is minimal at $x=0.7$. It was suggested in[5] that the sign of the tin-ion changes on going to the gapless state. In pure ionic compounds of tin, a unity change in the ion charge corresponds to $\Delta\epsilon \approx 2.6$ mm/sec. Although the $Pb_{1-x}Sn_xTe$ ions are not pure ionic, our results nevertheless contradict this assumption, since the depth of the $\epsilon(x)$ minimum is only ~0.15 mm/sec. It appears that $\epsilon(x)$ reflects the dependence of the concentration of the s-like electrons in the conduction band of the alloys on the tin content.

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