Zero-gap state and phonon spectrum of the systen of narrow-band compounds $Pb_{1-x}Sn_xSe$

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Using the method of inelastic scattering of slow neutrons we have obtained, for the first time, the phonon spectrum of the solid-solution system $Pb_{1-x}Sn_xSe$ ($x = 0.07$ and $x = 0.2$). For the crystal with $x = 0.2$, which undergoes a band inversion at $T = 100$ K, a softening of the TO ($q \to 0$) phonon was observed, due to realization of a zero-gap state in the system.

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The influence of the electron system on the phonon spectrum of crystals is most conveniently investigated in narrow-band semiconducting compounds of the IV–VI type. In some of these compounds, under certain conditions, a zero-gap state is realized, followed by band inversion.

It was shown in [1,2] that in the system $Pb_{1-x}Sn_xFe$, at the band-inversion point, the effectiveness of the Mössbauer effect decreases by approximately 30%. In a measurement[3] of the magnetoplasma reflection of the same system, an anomalous increase was observed in the static dielectric constant following the collapse of the bands.

The purpose of the present study was to study the influence of the zero-gap state in the solid-solution system $Pb_{1-x}Sn_xSe$ on its phonon spectrum. The experimental method was chosen to be that of inelastic scattering of slow neutrons, since it yields the most complete information on the dispersion dependence of the vibrational modes in the entire Brillouin zone.

The transition to the zero-gap state can be accomplished in several ways, say by varying the composition of the solid solution x or by changing the temperature or by applying hydrostatic pressure. We used the first two methods.

Single crystals of $Pb_{1-x}Sn_xSe$ with homogeneous composition were grown by us by directed crystallization from the vapor phase. We chose for the measurements samples with a volume not less than 1 cm^3.

Experiments on inelastic scattering of slow neutrons were carried out with an IN3 three-axis spectrometer and the strong-current reactor of the Laue–Langevin Joint Institute in Grenoble. The scanning was carried out at a constant momentum transferred to the lattice by the neutrons, and at a fixed energy of the scattered neutrons.

The measurements have shown that the experimental maxima of the energy distribution of the inelastic scattering of the neutrons by phonons are well resolved against the background of the more intense elastic-scattering maxima.

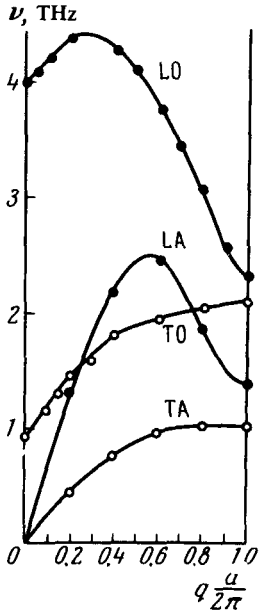

FIG. 1. Dispersion dependences of the normal modes propagating in the (100) direction in the $Pb_{0.8}Sn_{0.2}Se$ crystal at $T=80$ K.

An analysis of the obtained data has made it possible to trace the dispersion relation $\nu(q)$ for all the vibrational modes predicted by the symmetry theory for a cubic structure of the NaCl type (Fig. 1). The largest amount of information on the dynamics of the crystal lattice can be obtained from an analysis of the behavior of the TO mode. On the other hand, the frequency of the LO mode is greatly influenced by the screening by the free carriers, which are inevitably present in narrow-band semiconductors. As seen from Fig. 1, in the region $q\to 0$ the TO mode becomes noticably softer. To determine the nature of this softening, we plotted the temperature depen

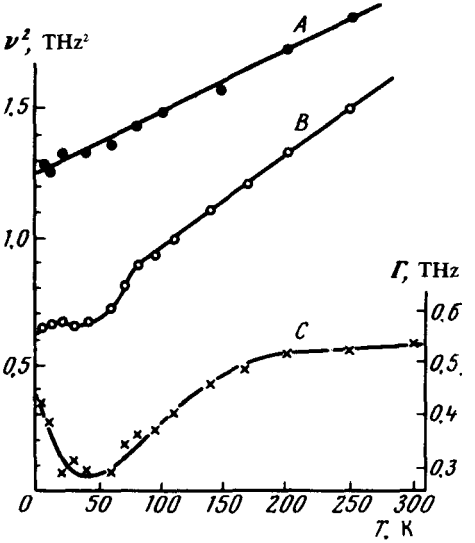

FIG. 2. Temperature dependences of the frequenc squared of the TO ($q\to 0$) phonons for crystals wi $x=0.07$ (A) and $x=0.2$ (B), as well as of the phonc attenuation coefficient $\Gamma(C)$.

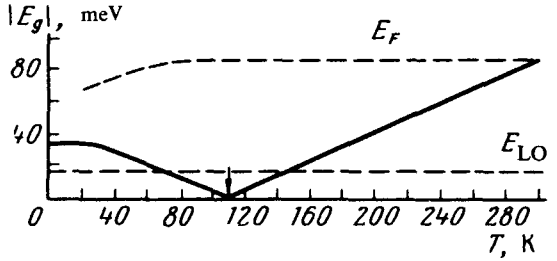

FIG. 3. Calculated dependences of the modulus of the width of the forbidden band E_g and of the Fermi energy E_F for the crystal with $x=0.2$ on the temperature. E_{LO} is the average LO-phonon energy.

dence of the square of the TO frequency (as $q\to 0$ of the phonon in the range $T=4.5$–300 K, for crystals with $x=0.07$ and $x=0.2$. These two crystals differ qualitatively from each other in that there is no band inversion in the former (at any temperature), while in the latter the inversion takes place at $T=100$ K. An analysis of the temperature dependence (Fig. 2) has revealed two effects: a linear decrease of ν_{TO}^2 with decreasing temperature, observed for both crystals, and an additional softening of the TO frequency of the phonon in the region ~ 50 K, which manifests itself only in the case of a sample with $x=0.2$. The first effect proves the existence of a temperature-dependent soft mode that attests to the tendency of the system to a structural phase transition into the ferroelectric state.[4] Extrapolation of the obtained dependences to the intercept with the horizontal axis (Fig. 2) has made it possible to estimate the phase-transition temperatures, namely $T_c=500$ K for $x=0.07$ and 175 K for $x=0.2$. It is seen that the temperature of the phase transition increases substantially with increasing tin content in the $Pb_{1-x}Sn_xSe$ solid solution.

The second effect is attributed by us to the influence of the transition of the crystal to the zero-gap state on the character of its vibrational excitations. The observed additional softening is evidence of a strong electron-phonon interaction at the band-inversion point.

However, an examination of the energy state of the crystal with $x=0.2$ has shown that in this case direct resonant interaction of the phonon and electron systems is excluded even at the band-collapse point. The point is that this crystal has a hole density $p=6\times 10^{18}$ cm^{-3}, at which degeneracy takes place. As a result, the Fermi energy E_F lies much higher than the characteristic energies of the LO and particularly of the TO phonons. The corresponding temperature dependences of E_g, E_F, and E_{LO} are shown in Fig. 3. It should be noted that the center of the experimentally observed minimum of $\nu_{TO}^2(T)$ lies at a lower temperature (~ 60 K) than the band-inversion point (~ 110 K). This may be due to the decrease in the Fermi energy as a result of the growth of the state density beyond the band-inversion point.[5]

It should be noted that in the region of the additional softening there is also observed a clearly pronounced minimum in the temperature dependence of the inelastic-scattering line (Γ) (Fig. 2c).

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