Structural phase transition in the $Pb_{1-x}Sn_xSe$ system under the influence of temperature and hydrostatic pressure

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(Submitted 19 January 1978)
Pis'ma Zh. Eksp. Teor. Fiz. **27**, No. 7, 396–399 (5 April 1978)

A structural phase transition was observed for the first time in the crystals of the system $Pb_{1-x}Sn_xSe$ ($x = 0.41$). Measurements of the resistivity and of the Hall constant as a function of the temperature and pressure have revealed a strong change in the conductivity (by four–five orders of magnitude) in the phase-transition region. The phase-transition temperature depends on the concentration of the free carriers and ranges from 0 to 250 K when the carrier density changes from 10^{19} to 3×10^{18} cm^{-3}.

PACS numbers: 64.70.Kb, 72.60.+g

Type IV-VI semiconductors of the $Pb_{1-x}Sn_xSe$ system, in contrast to $Pb_{1-x}Sn_xTe$, do not form a continuous system of solid solutions. Crystals with tin content $x<0.43$ crystallize into a cubic lattice of the NaCl type, and those with $x>0.80$ form a phase with a lower symmetry–an orthorhombic lattice of the B29 type.[1,2] A study of the phonon spectra of the $Pb_{1-x}Sn_xSe$ crystals in the cubic phase ($x=0.07$ and $x=0.20$), carried out by the method of slow-neutron scattering, has shown a noticable "softening" of the transverse optical mode in the region of small wave vectors. However, the temperature dependence of this soft mode points to the absence of a phase transition in the entire region of positive temperature (>0 K).[3]

The absence of phase transitions in crystals with $0<x<0.30$ and with carrier density $n,p>10^{17}$ cm^{-3} is confirmed also by numerous investigations of the galvanomagnetic coefficients. The carrier density turns out to be constant in the entire tem-

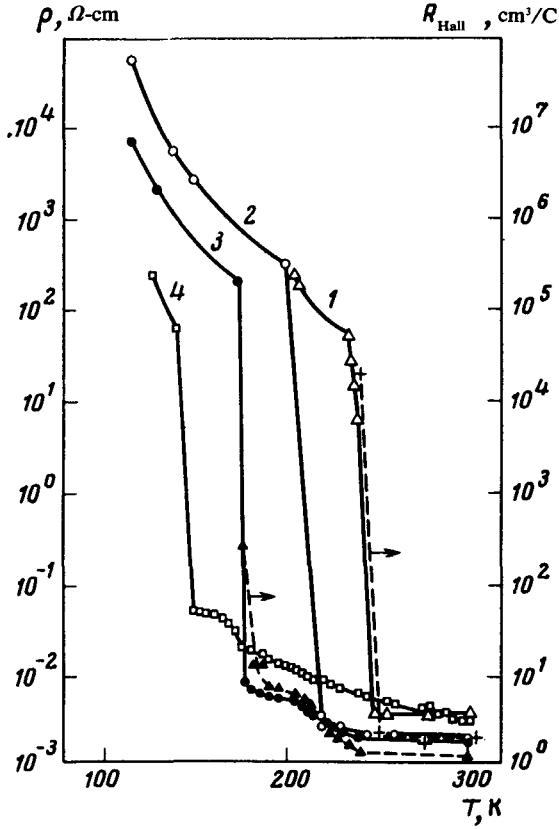

FIG. 1. Dependence of the resistivity (solid curves) and of the Hall constant (dashed curves) on the temperature in the following samples: $1-p=3\times10^{18}$ cm^{-3}, $2-n=4\times10^{18}$ cm^{-3}; $3-p=5.6\times10^{18}$ cm^{-3}, $4-p=7.2\times10^{18}$ cm^{-3}.

perature interval from 300 to 2 K, and the resistance decreases noticably only as a result of the change in the carrier scattering.[4]

In the present study we investigated the Hall constant and the resistivity as functions of the temperature and of the hydrostatic pressure of $Pb_{1-x}Sn_xSe$ crystals with tin content $x=0.41$. As established from the x-ray structure analysis data, the investigated crystals under normal conditions ($T=300$ K, $P=760$ Torr) have symmetry. The width of the forbidden band is $E_g\approx0.1$ eV and is determined by the energy distance between the bands $E_{L_6^1}-E_{L_6^2}$ at the L point of the Brillouin zone.

It is seen from Fig. 1 that the temperature dependences of the resistivity and of the Hall constant have an anomalous character. When a certain critical temperature is reached, both quantities increase sharply, and the temperature of the jump of ρ and of R_{Hall} depend on the carrier density, decreasing with increasing density. At $p>10^{19}$ cm^{-3} the plots of $\rho=f(T)$ and $R_{\text{Hall}}=f(T)$ had no singularities and exhibited the usual previously-observed behavior.[4]

We attribute the observed anomalies of ρ and R_{Hall} to the onset of a structural phase transition, which is induced by the electron-phonon interaction. The interband electron-phonon interaction exerts an influence on the electronic spectrum of the crystal and leads to a sharp increase of the width of the forbidden band when the critical

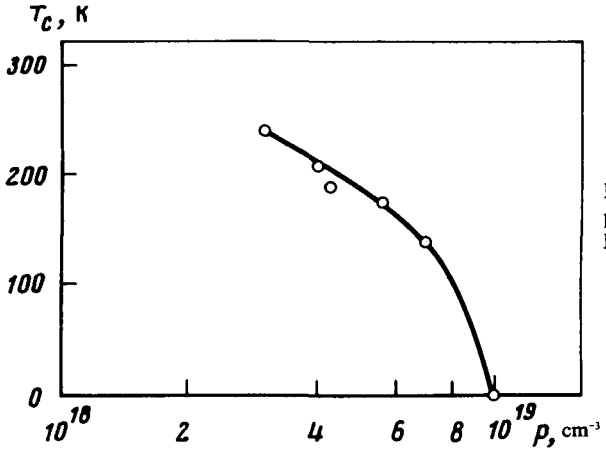

FIG. 2. Dependence of the critical temperature on the carrier density in $Pb_{0.59}Sn_{0.41}Se$.

temperature is reached in the crystal.[5] This causes a jumpwise decrease of the carrier density, as seen from measurements of the Hall effect and of the resistivity (Fig. 1).

It should be noted that the phase transition takes place both in p-type samples (Fig. 1, curves 1, 3, 4) and in n-type samples (Fig. 1, curve 2). The n-type conductivity is due to the Se vacancies, and the p-type conductivity to the metal vacancies (Pb and Sn). Account must be taken also of the intrinsic carrier density, which at $T=300$ K, $E_g=0.1$ eV and $m^*_d=0.5\ m_0$ can be of the order of 10^{18} cm^{-3}. An increase in the carrier density or in the Fermi energy affects the frequency of the soft mode,[6,7] and this leads to an effective weakening of the electron-phonon interaction and a lowering of

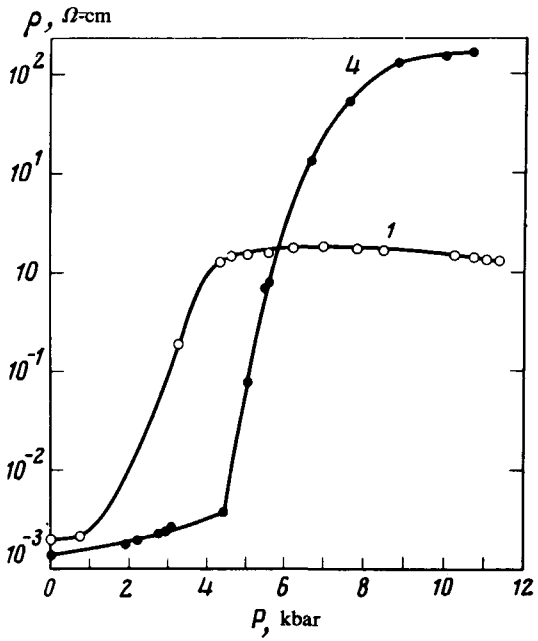

FIG. 3. Dependence of the resistivity on the pressure at $T=300$ K in the following samples: $1-p=3\times10^{18}$ cm^{-3}, $4-p=7.2\times10^{18}$ cm^{-3}.

the critical temperature T_c. The dependence of T_c on the carrier (electron or hole) density is shown in Fig. 2. A similar dependence was observed in SnTe crystals.[6]

In measurements of the resistivity under conditions of hydrostatic compression at $T=300$ K, it was observed that at a certain pressure the sample resistance increases sharply, after which saturation sets in. It follows from Fig. 3 that in a sample with hole density $p=3\times10^{18}$ cm^{-3} the resistance growth begins at a pressure $P=1$ kbar, and that at $p=7.2\times10^{18}$ cm^{-3} the abrupt growth of the resistance begins at $P=5$ kbar. The change of the Hall constant agrees with the change of the resistance.

It must be noted that the temperature and baric dependence of the resistance exhibited hysteresis, the residual resistivity decreasing with increasing carrier density. Thus, we have observed here, for the first time ever, a structural phase transition in the $Pb_{1-x}Sn_xSe$ system, which can be classified as a first-order transition in view of the jumplike character of the behavior of the galvanomagnetic coefficients and the hysteresis observed when the temperature and pressure were varied in the opposite direction.

The structure resulting from the phase transition is apparently orthorhombic (of the SnSe type). This structure can be obtained from the NaCl structure if the period in one of the (100) directions is quadrupled. What is unstable in this case is the transverse optical phonon with wave vector lying in the direction of the axis Δ with coordinates $(\frac{1}{2}, 0, 0)$ in the Brillouin zone of the fcc lattice. Since this point is not central on the Δ axis, such a phase transition goes first into a noncommensurate phase,[8] and then jumpwise into a commensurate one.

By assuming precisely this evolution of the phase transition, we can understand the resistance growth that preceeds the jump.

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