Pressure-induced inversion of the Hall coefficient and the thermal emf in narrow-gap lead-tin-selenium semiconductors

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(Submitted 6 February 1986)
Pis'ma Zh. Eksp. Teor. Fiz. **43**, No. 6, 303–306 (25 March 1986)

The behavior of the Hall coefficient R_H, the conductivity σ, the Shubnikov-de Haas effect, and the thermal emf α of the system of solid solutions $Pb_{1-x}Sn_xSe$ has been studied at $T = 4.2$ K at pressures up to 30 kbar. The sign of R_H and α changes at $P \geqslant 18$ kbar. It is concluded that there is a resonant band with a p-type conductivity and that fluctuations of the bottom of the band have a strong effect on the electron mobility in these semiconductors.

Energy levels of intrinsic defects and of impurities in IV–VI narrow-gap semiconductors may lie in the spectrum of allowed states. Some of these levels lie near extrema of bands and have a significant effect on the transport of charge carriers.

In the present study of the system of undoped solid solutions $Pb_{1-x}Sn_xSe$ we have detected a band of resonant states with a p-type conductivity, superimposed on the continuum of the conduction band and lying near its bottom. In addition, we have found a sharp decrease in the mobility of band electrons with a decrease in the Fermi energy $\mathscr{E}_F$ (within the conduction band), caused by fluctuations of the bottom of the band. These two effects lead to a sharp decrease in the thermal emf α and in the Hall coefficient R_H with decreasing $\mathscr{E}_F$ and, in some of the samples, a change in the sign of these properties.

 0021-3640/86/060391-05$01.00 © 1986 American Institute of Physics

The customary way to study the impurity band in Ge, Si, and GaAs has been to vary the degree of compensation of the sample, making it possible to scan $\mathscr{E}_F$ over this band. We have used a different method. The application of hydrostatic pressure to IV–VI narrow-gap semiconductors can, as we know, change the gap width $\mathscr{E}_g$ by an amount comparable to $\mathscr{E}_g$. This change is accompanied by a significant change in the state density in the main band and thus $\mathscr{E}_F$. We have shown previously that there is a band of resonance states in $Pb_{1-2}Sn_xSe$ near the bottom of the conduction band.[1,2] In order to study the contribution of this band to transport phenomena, it was accordingly necessary to arrange experimental conditions such that $\mathscr{E}_F$ would smoothly approach the bottom of the band. These conditions were arranged in $Pb_{1-x}Sn_xSe$ with an inverse arrangement of bands ($x \geqslant 0.15$), since an increase in the pressure increases $\mathscr{E}_g$ in these crystals, leading to an increase in the state density and a decrease in $\mathscr{E}_F$. Over the pressure range 0–30 kbar, $\mathscr{E}_F$ changes from 37 to 2 meV.

We studied $Pb_{1-x}Sn_xSe$ single crystals with $x = 0.06$–0.33 and with electron densities 5×10^{17}–3×10^{18} cm^{-3} at liquid-helium temperature. We studied the behavior of the Hall coefficient R_H, the conductivity σ, and the thermal emf α as a function of the hydrostatic compression over the range 0–30 kbar. We also studied the Shubnikov-de Haas effect.

Figure 1 illustrates the results of the study for a sample containing 15 at.% tin, with an electron density $n = 7\times10^{17}$ cm^{-3} and a mobility $\mu = 3\times10^5$ cm^2/(V · s) at atmospheric pressure.

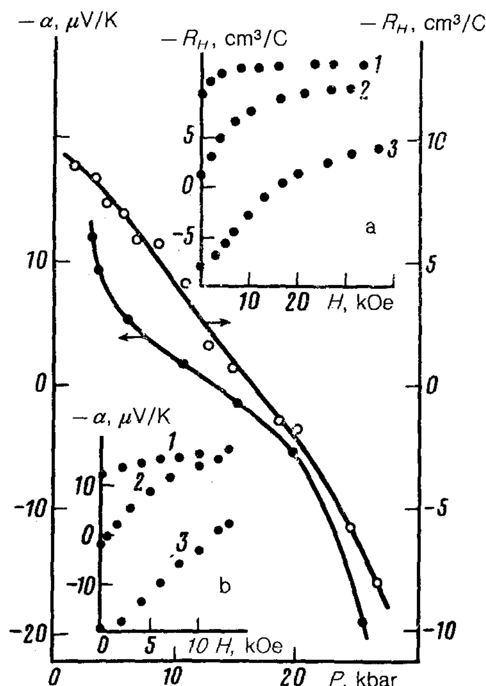

FIG. 1. R_H ($H = 600$ Oe) and α versus the hydrostatic pressure at $T = 4.2$ K in a $Pb_{0.85}Sn_{0.15}Se$ sample. Insets a and b: R_H and α versus H. 1—$P = 0$; 2—$P = 15$ kbar; 3—$P = 27$ kbar.

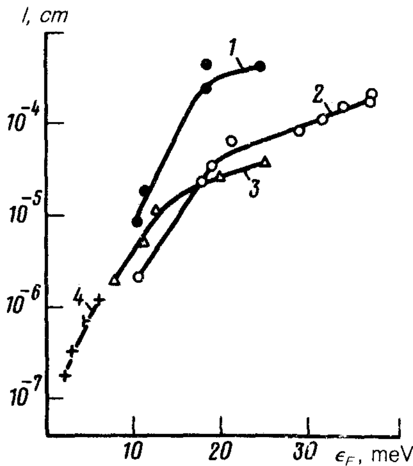

FIG. 2. The mean free path l versus the Fermi energy $\mathscr{E}_F$ at $T = 4.2$ K for samples with the following compositions: 1—$x = 0.06$; 2—$x = 0.15$; 3—$x = 0.20$; 4—$x = 0.31$.

We see from Fig. 1 that at pressures $P \geqslant 18$ kbar in a weak magnetic field ($\mathscr{H} \leqslant 1$ kOe) there is an inversion of the sign of R_H and α. We also observe a strong dependence of R_H and α on the magnetic field; at fields $\mathscr{H} > 10$ kOe, the "electron" sign of R_H and α is restored (Fig. 1). This behavior of R_H and α is found when two types of carriers, with charges of different signs, participate in the conductivity. In these semiconductors, however, we do not have a semimetallic situation, since a study of the Shubnikov-de Haas effect shows that the extrema of the valence and conduction bands lie at the $\mathscr{L}$ point in k space. These results can be explained in terms of a contribution of a resonant band to the transport. Numerical calculations of $R_H(H,P), \sigma(P)$, and $\alpha_0(P)$ on the basis of a two-band model yield the partial contributions of the carriers of the main and resonant bands. It turns out that the mobility of the band electrons decreases by a factor of nearly 100 as the pressure P is raised to 30 kbar. As a result, the resonant band becomes dominant. Figure 2 shows the electron mean free path versus the Fermi energy for samples with various tin concentrations. The mean free path was calculated from

$$l = v_F \tau = \frac{(3\pi^2)^{1/3}}{l^2} \; \frac{\sigma}{n^{2/3}} .$$

The electron density n was determined from the Shubnikov-de Haas effect.

All the curves have a change in slope at $\mathscr{E}_F \simeq 14$–16 meV. The initial and relatively weak decrease in l can be explained well on the basis of the scattering peculiar to this alloy, caused by the disorder of the atoms of the solid solution.

In the Born approximation, and for this scattering mechanism, l is given by

$$l = \frac{\hbar p_F}{2\pi x(1-x)\Delta^2 \rho(\mathscr{E}_F) a^3 m^*} \tag{1}$$

where P_F is the Fermi momentum, $\Delta - 1$ eV is the energy difference between the p shells of Pb and Sn (Ref. 3), and a is the lattice constant.

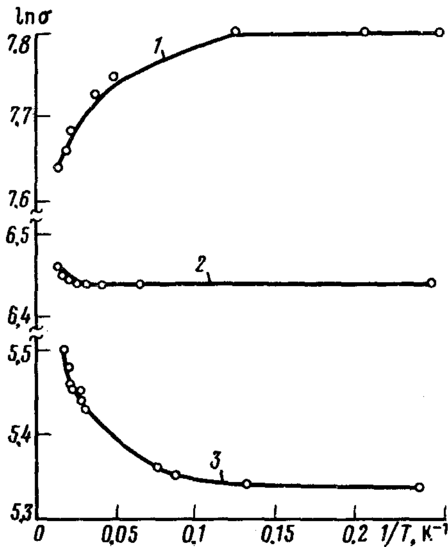

FIG. 3. Temperature dependence of σ in a $Pb_{0.67}Sn_{0.33}Se$ sample. 1—$P=0$; 2—$P=5$ kbar; 3—$P=12.5$ kbar.

This expression gives a correct description of the behavior of l as a function of the composition (x) and $\mathscr{E}_F$ in the energy interval 35–16 meV. At $\mathscr{E}_F < 14$–16 meV, there is a sharp decrease in l, and in the limit $\mathscr{E}_F \to 0$ we have $l \sim a$.

We believe that the most likely reason for this tendency toward localization is a local redistribution of the electron density of valence electrons, caused by the replacement of Pb by Sn. Preliminary calculations show that an excess negative charge $\approx 0.2e$ forms near a Sn atom (a positive charge of the same magnitude of course arises at the periphery). An estimate of the corresponding fluctuation potential (with allowance for the spatial dispersion of the dielectric constant) yields ≈ 10 meV. The tendency toward localization is supported by the temperature dependence $\sigma(T)$ (Fig. 3). It can be seen from Fig. 3 that at $P=0$ the conductivity decreases with increasing T as a result of scattering by phonons. At $P > 10$ kbar, corresponging to $\mathscr{E}_F \leqslant 5$ meV, the curves of $\sigma(T)$ are of the opposite nature. An increase in σ with the temperature indicates a sharp increase in τ with the energy. As the temperature is raised, the energy of the electrons near $\mathscr{E}_F$ increases, so that these electrons move away from the percolation level. The fact that the behavior of σ as a function of T at low temperatures does not reflect an activation energy, which would be typical of a hopping conductivity, is evidence that $\mathscr{E}_F$ lies above the mobility threshold.

In summary, this study shows that there are fluctuations in the energy of the bottom of the conduction band and that there is a resonant band with a p-type conductivity in the conduction band. A possible reason for the positive sign of R_H in the resonant band is that the state generating it has split off from valence bands.[4] Estimates of the carrier mobility in the impurity band on the basis of the two-band model yield $\sim 10^4$ cm^2/V $\cdot$ s) at 7 K. This value may be far too high, however, since the calculation ignored the effect of the magnetic field on R_H and μ the impurity band. It also follows from the two-band model that the thermal emf in the impurity band is

high, $\sim 100\ \mu V/K$. The sign of the thermal emf in the impurity band depends on the extent to which this band is filled. In a crystal with $x = 0.15$ we have $\alpha > 0$, implying that the impurity band is more than half full.

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Translated by Dave Parsons