Hall effect and photoconductivity of $Pb_{1-x}Sn_xTe$ with indium

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It was established from measurements of the Hall coefficient of $Pb_{1-x}Sn_xTe$ with $C_{In} > 0.5$ at.% at $4.2 < T < 300$ K that In greatly increases the number of states near the bottom of the conduction band, increases the width of the forbidden band and has no significant effect on the location of the band of heavy holes. A two-minimum model, which accounts for the long-term photoconductivity relaxation and the electrical properties of the material, is proposed.

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The introduction of indium into $Pb_{1-x}Sn_xTe$ solid solutions drastically alters the properties of the original semiconductor. A number of new phenomena have been observed in the indium-doped material at low temperatures: a strong influence of light on the conductivity, accompanied by its long-term relaxation,[1] N-shaped I-V characteristics recorded as a result of illuminating the samples,[2] the appearance of nonequilibrium states in strong magnetic fields,[3] etc.

In this paper we present the results of a study of the Hall effect in a wide temperature range $4.2 < T < 300$ K in darkness and with illumination. We propose a two-minimum model of the impurity states, which accounts for the galvanomagnetic and photoelectric effects in $Pb_{1-x}Sn_xTe$(In).

The studies were performed using n-$Pb_{1-x}Sn_xTe$ samples with $x = 0.18$, $x = 0.22$, $x = 0.25$, and $x = 0.30$, doped with indium with a concentration of $0.5 < C_{In} \lesssim 2.7$ at.%. The investigated temperature region can be divided into three parts according to the temperature dependence of the Hall coefficient R_x.

I. The region $T < 20$ K is characterized by an instability of the R_x values and of the resistivity ρ measured in darkness (the sample was completely shielded from outside radiation): these values reach a steady state over a long period of time. In this region the samples are very sensitive to illumination and have a residual photoconductivity. As a result of optical excitation by an IR injection laser, we established that the red limit of photoconductivity is at $\lambda > 20$ μm. Figure 1 shows the dependence of R_x on $1/T$ measured in the dark-R_x^{dark} (curve 1) and under illumination (thermal radiation of room-temperature background)-R_x^{ill} (curve 1'). We can see that R_x^{dark} increases monotonically with decreasing T, whereas R_x^{ill} passes through a maximum and decreases at $T < 20$ K. The resistivity of this sample ρ^{dark} (curve 2) and ρ^{ill} (curve 2') is also shown in Fig. 1. It can be seen that the corresponding curves are similar. The influence of illumination on the $Pb_{1-x}Se_xTe$ crystals at low temperatures is evident not only with In doping but also with other impurities. Figure 1 shows ρ^{ill} of one of the zinc-doped

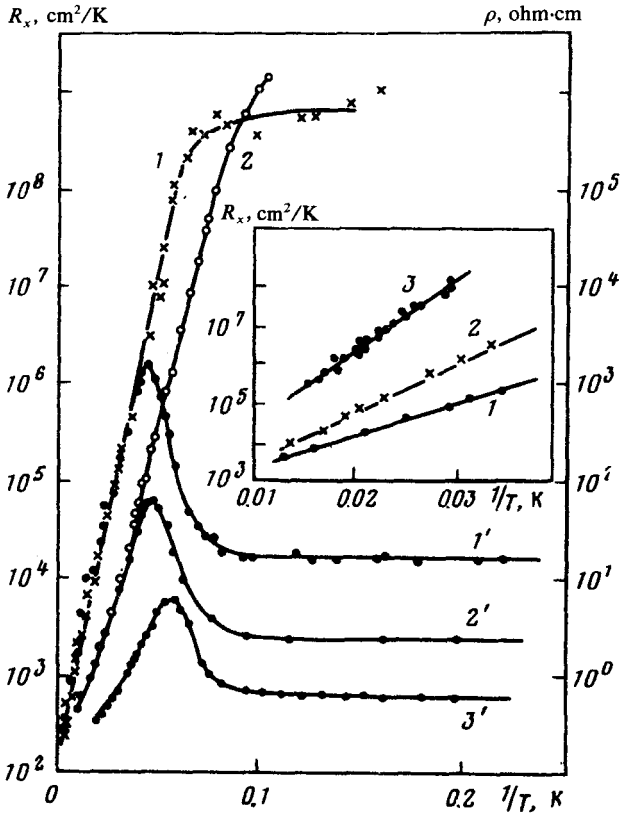

FIG. 1. Dependence of the Hall coefficient R_x and resistivity ρ on $1/T$: curves 1 and 2—R_x^{dark} and ρ^{dark}, curves 1′ and 2′—R_x^{ill} and ρ^{ill}—dark and light values for the sample with $x = 0.22$ and $C_{\text{In}} \approx 0.7$ at.%; curve 3—ρ^{ill} for the zinc-doped sample with $x = 0.20$. Inset: curves 1, 2, and 3—R_x for the samples with $x = 0.22$ and $C_{\text{In}} \approx 0.7$ at.%; $C_{\text{In}} = 2.7$ at.%, respectively.

samples (curve 3). It should be noted that such R_x curves observed in Refs. 4 and 5, with a maximum at $T \approx 20$–40 K are apparently due to an incomplete shielding of the samples from external radiation during the measurement.

II. In the region $20 < T < 100$ K the dark values of R_x and ρ coincide with the light values. The slope of $\log R_x = f(1/T)$ (inset in Fig. 1), which depends on C_{In}, is 15, 23, and 37 meV for the samples with $x = 0.22$ and $C_{\text{In}} \approx 0.7$, $C_{\text{In}} = 1.0$, and $C_{\text{In}} = 2.7$ at.%, respectively.

III. In the region $100 < T < 300$ K the dependence of R_x on $1/T$ is shown in Fig. 2. The slope of the linear parts of the $\log R_x = f(1/T)$ curves is independent of x and C_{In}. However, the smaller are the absolute R_x values, the larger is C_{In}.

A calculation of the concentration from the R_x values with allowance for the three types of carriers (electrons and light and heavy holes) shows that the contribution of the holes can be disregarded because of their low mobility.[6] The density of thermally excited electrons in this temperature region can be assumed to be intrinsic

$$n = \sqrt{N_e N_v} \exp(-\Delta E/2kT) . \quad (1)$$

The densities of states for the conduction band and the valence band of the light holes at 300 K are $N_e \approx N_v \approx 10^{18}$ cm^{-3} and for the band of heavy holes, $N_{vT} \approx 5 \times 10^{19}$

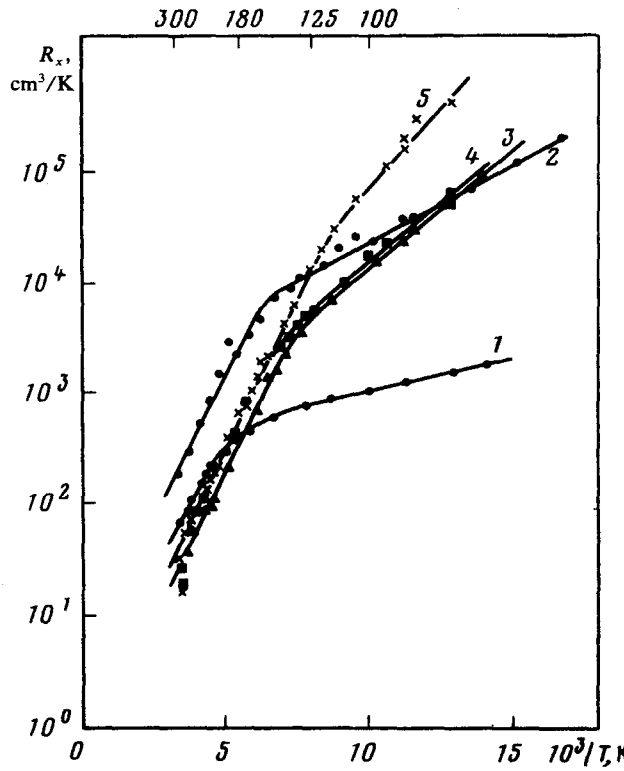

FIG. 2. Dependence of R_x on $1/T$ in the temperature region $77 < T < 300$ K for the samples: curve 1—$x = 0.18$, $C_{In} \approx 1$ at.%; curve 2—$x = 0.22$, $C_{In} \approx 1$ at.%; curve 3—$x = 0.22$, $C_{In} \approx 1.6$ at.%; curve 4—$x = 0.25$, $C_{In} \approx 1$ at.%; curve 5—$x = 0.30$, $C_{In} \approx 1$ at.%.

cm^{-3}. The values of N_e and N_v can also be large if they include the impurity states that have merged with the bands. ΔE is the energy gap between the filled and empty states.

A comparison of the experimental data with Eq. (1) shows that $\Delta E \approx 200$ meV and $\sqrt{N_e N_v} \approx 10^{20}$ cm^{-3} at 300 K. Such a large value can be obtained only as a result of transitions of the heavy holes from the valence band to the impurity level with $N_{lev} \approx 10^{20}$ cm^{-3} at the edge of the conduction band. This value is consistent with the case when the top of the valence band and the edge of the conduction band have impurity levels with $N_{lev} \approx 10^{20}$ cm^{-3}. The calculated density of impurity states increases with increasing C_{In} for identical x's (curve 2 and 3) in Fig. 2.

It should be noted that a slope corresponding to transitions from the band of light holes has not been observed in the curves of R_x vs $1/T$. We can conclude from this that indium doping with $C_{In} > 0.5$ at.% increases the width of the forbidden band. This is confirmed by the results of measurements of the optical absorption edge. The very steep temperature dependence of the electron mobility in the region $T > 100$ K is unusual: $\mu \sim T^{-3}$–T^{-4}.

To explain the observed systematic features, we shall assume that the charge image of the bottom of the conduction band has the shape depicted in Fig. 3a. Digressing for a moment from the origin of this image, we shall assume that state 1 is noncon-

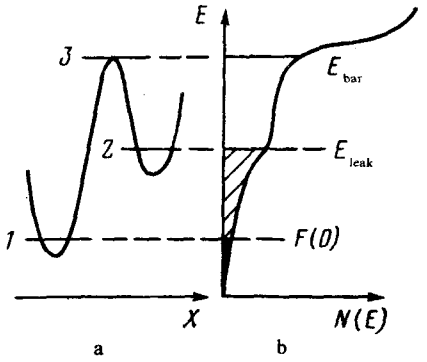

FIG. 3. Charge image (a) and density of states (b) in the impurity band. $F(0)$ is the Fermi level at $T = 0$ K, E_{leak} is the leakage level, and E_{bar} is the peak of the potential barrier.

ducting and states 2 and 3 are conducting. States 1 and 2 are separated by a potential barrier. As a result of analyzing the experimental data according to this scheme for a sample with $x = 0.22$ and $C_{In} \approx 0.7$ at.%, we obtained the following effective densities of states: $N_1 = 6\times10^{15}$ cm^{-3}, $N_2 = 3\times10^{16}$ cm^{-3}, $N_3 = 2\times10^{19}$ cm^{-3} and the energy gaps $\Delta_{12} \approx 30$ meV, $\Delta_{23} \approx 17.6$ meV. The barrier width of 3×10^{-6} cm was estimated from the experimental data, assuming that there is electron tunneling. This value is ten times greater than the distance $N_3^{-1/3}$, which is close to the interimpurity distance and almost coincides with one-half the distance between type 1 wells, i.e., $0.5\,N_1^{-1/3}$. We can assume from these numbers that the charge image in Fig. 3a is produced primarily because of large-scale fluctuations of the impurity distribution. Thus, we can assume that as a result of introduction of indium into $Pb_{1-x}Sn_xTe$, an empty impurity band with a total number of states (N_3) comparable to C_{In} is formed near the bottom of the conduction band. This can occur when In is a deep acceptor or a multiply charged center with an empty upper state and a filled lower state at the edge of the heavy holes. However, the donor influence of indium in p-$Pb_{1-x}Sn_xTe$ can be explained by the fact that it "plugs up" the metal vacancies which are the hole suppliers. The density of states near the edge of the conduction band is illustrated in Fig. 3b. At $T = 0$ a small part of the nonconducting states (1) with $E > F(0)$, where $F(0)$ is the Fermi level, is filled because of defects other than In (possibly Te vacancies). In the region $T < 100$ K the activation energy of ρ and R_x is determined by the energy spacing between the (1) states and the leakage level E_{leak}. The barrier between the states (1) and (2) accounts for the maximum in the $1/T$ dependence of ρ^{ill} and R_x and for the long-term relaxation. The states with an energy $E > E_{bar}$ have the highest density. These states, which appear at $T > 100$ K (Fig. 2), account for the large pre-exponential coefficient in Eq. (1). The anomalous properties of $Pb_{1-x}Sn_xTe$(In) were recently accounted for[7,8] by using the potential barrier produced as a result of localization of an electron in an impurity. Such a model[9] was also used to explain the properties of residual photoconductivity in $Al_xGa_{1-x}As$. Although we prefer the fluctuation potential model for the explanation of the properties of $Pb_{1-x}Sn_xTe$(In), we cannot completely ignore the model used in Refs. 7–9.

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