ELECTRONIC AND OPTICAL PROPERTIES OF SEMICONDUCTORS

Pressure-induced insulator–metal transition in electron-irradiated $Pb_{1-x}Sn_xSe$ ($x\leqslant 0.03$) alloys

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Galvanomagnetic effects ($B\leqslant 7$ T) in electron-irradiated n- and p-type $Pb_{1-x}Sn_xSe$ ($x\leqslant 0.03$) alloys ($T\approx 300$ K, $E=6$ MeV, $\Phi\leqslant 5.7\times 10^{17}$ cm^{-2}) in the neighborhood of a pressure-induced insulator–metal transition ($P\leqslant 18$ kbar) are discussed. The field dependences of the Hall coefficient calculated in terms of the two-band model are in satisfactory agreement with the experimental data, and the main parameters of the charge carriers in irradiated alloys are determined. It is shown that there is an increase in the hole concentration in the metallic phase under the action of pressure, associated with the motion of the energy bands at point L of the Brillouin zone, and that electrons overflow from the valence band into the band E_{t1} of resonance states induced by electron irradiation; the parameters of this band are estimated.
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1. INTRODUCTION

It is well known that electron irradiation of $Pb_{1-x}Sn_xSe$ alloys causes two radiative levels (radiative-defect bands) E_t and E_{t1}, apparently associated with two types of radiative defects, to appear in the energy spectrum of the alloys.[1,2] The main parameters of the E_t band (the defect-generation rate, the energy position, and the band structure) are well known for virtually the entire existence domain of the cubic phase of the alloys ($0.07\leqslant x\leqslant 0.34$). At the same time, there is much less information on the E_{t1} level.

In particular, it has been established[3,4] that the position of the E_{t1} radiative level on an energy scale depends on the alloy composition and the pressure (Fig. 1). In PbSe, the E_{t1} level lies in the band gap close to the top of the valence band, L_6^+. As the Sn concentration in the alloy increases, the level almost does not change its position relative to the middle of the band gap, moving relative to the L_6^+ term approximately according to the linear law

$$E_{t1}[\text{meV}]=E(L_6^+)+35-600x.$$

Thus, in alloys with a tin concentration of $x<0.06$, the middle of the E_{t1} band is in the band gap, whereas, for $x>0.06$, it falls within the valence band.

The E_{t1} band possesses donor–acceptor properties. Therefore, electron irradiation of crystals with $x<0.06$ reduces the charge-carrier concentration both in n-type and in p-type samples. For sufficiently large irradiation fluxes, a transition occurs to the insulating state, in which the Fermi level is ''softly'' stabilized by a band of radiative defects partly filled with electrons. Hydrostatic compression of irradiated crystals causes the E_{t1} band to approach the top of the valence band and causes an insulator–metal transition associated with the overflow of electrons from the valence band into the radiative-defect band (Fig. 1).

The character of the dependences of the conductivity and the Hall coefficient of irradiated samples on pressure[3,4] is evidence that there are at least two conductivity mechanisms in the neighborhood of the insulator–metal transition. It should also be pointed out that, in the neighborhood of the transition, significant variations of the charge-carrier parameters occur in a rather wide range of pressures. This circumstance indicates that the E_{t1} band has a finite width. However, the width and structure of the radiative-defect band, as well as the radiative-defect generation rate during irradiation, is not yet known.

To obtain information on the conductivity mechanisms in electron-irradiated alloys and to determine the main parameters of the radiative-defect band E_{t1}, we analyzed the field dependences of the Hall coefficient of electron-irradiated $Pb_{1-x}Sn_xSe$ ($x\leqslant 0.03$) alloys in the neighborhood of the pressure-induced insulator–metal transition.

2. SAMPLES. MEASUREMENT TECHNIQUE

Single-crystal samples of $Pb_{1-x}Sn_xSe$ ($x=0$, 0.03) with an initial electron or hole concentration of n, $p=(0.4–1.6)\times 10^{17}$ cm^{-3} were irradiated at room temperature on an ÉLU-6 linear electron accelerator ($E=6$ MeV, $\Phi\leqslant 5.7\times 10^{17}$ cm^{-2}). The conductivity and the field dependences of the Hall coefficient ($B\leqslant 7$ T) at $T=4.2$ K in the irradiated crystals were studied at atmospheric pressure and under conditions of hydrostatic compression. The parameters of the samples, studied under pressure before and after irradiation by the maximum electron fluxes, are shown in Table I. Hydrostatic pressures of up to 18 kbar were obtained in a cham-

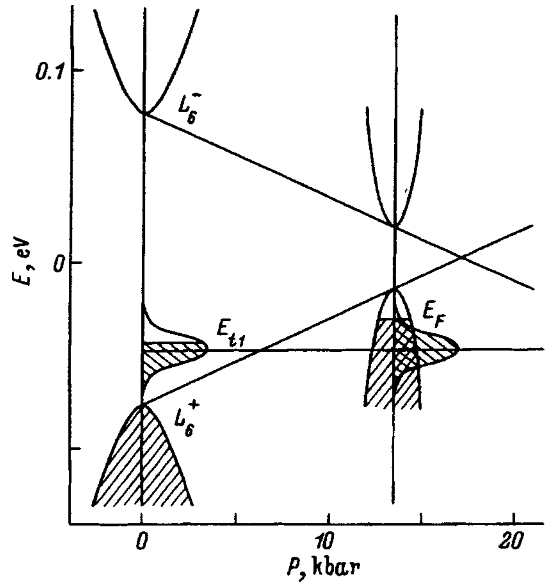

FIG. 1. Model of the reconstruction under pressure of the energy spectrum of electron-irradiated *n*-PbTe.

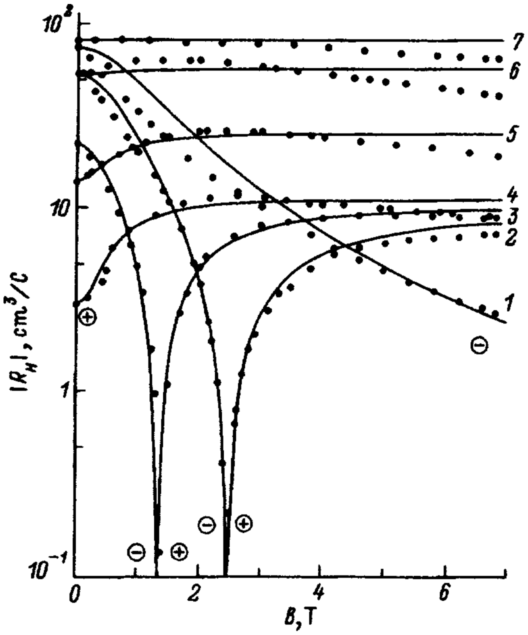

FIG. 2. Field dependences of Hall coefficient R_H at $T=4.2$ K for sample K-22 ($\Phi=2.8\times10^{17}$ cm^{-2}) in the neighborhood of the insulator–metal transition under the action of pressure: P, kbar: *1*—0.9, *2*—1.4, *3*—2.6, *4*—3.2, *5*—4.2, *6*—6.2, *7*—18.2. The solid curves show calculated results in accordance with Eqs. (1)–(3).

ber made from heat-treated beryllium bronze. A kerosine–oil–pentane mixture was used as the pressure-transmitting medium.

3. FIELD DEPENDENCES OF THE HALL COEFFICIENT IN THE NEIGHBORHOOD OF THE INSULATOR–METAL TRANSITION

It has been established that the Hall coefficient R_H of electron-irradiated samples strongly depends on the magnetic field even at atmospheric pressure, and that the absolute value of R_H decreases by more than an order of magnitude in the range of magnetic field studied here (Fig. 2). Hydrostatic compression reduces R_H more sharply and inverts the sign of the Hall coefficient as the magnetic field increases. As the pressure increases, the sign-inversion point of R_H shifts toward weaker magnetic fields, and, after the transition to the metallic phase ($P>P^*$), the Hall coefficient has a positive sign, increasing as the magnetic field increases. Finally, in the region of maximum pressures, the Hall coefficient is virtually independent of magnetic field.

The character of the field dependences of the Hall coefficient in the test samples confirms the assumption that at least two types of charge carriers of opposite sign coexist in electron-irradiated $Pb_{1-x}Sn_xSe$ ($x=0$; 0.03) alloys. The appearance of a sign-inversion point for R_H and the change in the form of the $R_H(B)$ dependences accompanying hydrostatic compression of irradiated crystals evidently indicates that the parameters of the charge carriers vary and that the main conduction mechanism changes when the insulator–metal transition occurs. To determine the main parameters of the charge carriers in the irradiated samples in terms of a two-band model, we calculated the field dependences of the Hall coefficient in the test samples:[5,6]

$$R_H=\frac{\sum \sigma_k\mu_k/(1+\mu_k^2B^2)}{\left[\sum \sigma_k/(1+\mu_k^2B^2)\right]^2+\left[\sum \sigma_k\mu_kB/(1+\mu_k^2B^2)\right]^2}, \tag{1}$$

$$1/\rho=\sum \sigma_k=\sum e_kn_k\mu_k, \tag{2}$$

where e_k, n_k, σ_k, and μ_k are the charge, concentration, conductivity, and mobility for each type of charge carrier, denoted by subscript *k*. In the limits of a weak magnetic field ($\mu_kB\ll1$), the expression for the Hall coefficient takes the form

TABLE I. Parameters of $Pb_{1-x}Sn_xSe$ samples studied under pressure at $T=4.2$ K.

Sample	x	Conductivity type	Irradiation flux Φ, 10^{17} cm^{-2}	Electron concentration n, 10^{17} cm^{-3}	Resistivity ρ, 10^{-4} $\Omega\cdot$cm	Mobility μ_H 10^5 cm^2/(V·s)
N8	0	*n*	0	1.06	7.3	0.81
		n	5.7	0.27	220.0	0.105
K-22	0.33	*p*	0	0.40	47.7	0.31
		n	2.8	0.82	269.0	0.028

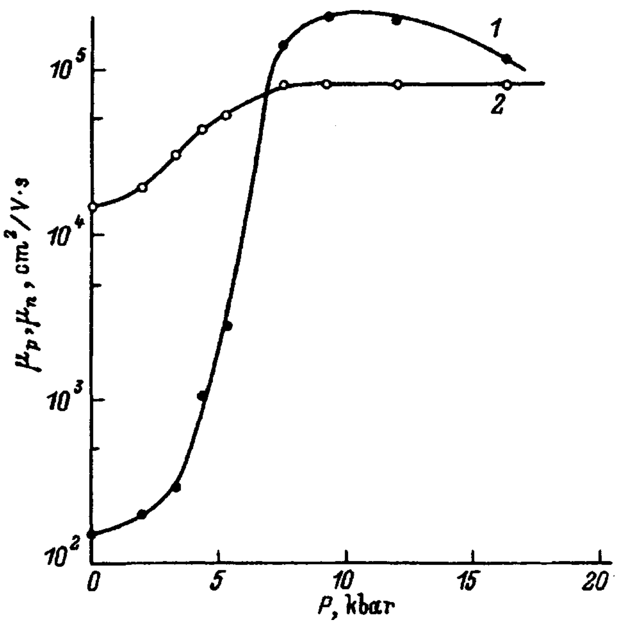

FIG. 3. Hole mobility μ_p (*1*) and electron mobility μ_n (*2*) in electron-irradiated sample N8 ($\Phi=5.7\times10^{17}$ cm^{-2}) vs pressure.

$$R_H=\frac{\sum e_k n_k \mu_k^2}{\left(\sum e_k n_k \mu_k\right)^2}. \quad (3)$$

The parameters of the charge carriers were determined by adjusting the dependences given by Eq. (1) to the experimental data (Fig. 2). The program for doing the calculations involved the variation of only two parameters of the model (usually the charge-carrier mobilities). Two other parameters of the model (usually the conductivities σ_k) were determined by direct calculation from the Hall coefficients in a weak magnetic field, using Eq. (3), and from the conductivity at $T=4.2$ K, using Eq. (2). The $R_H(B)$ dependences thus calculated are in satisfactory agreement with the experimental data in the entire range of pressures and magnetic fields studied here (see Fig. 2).

The results of calculating the charge-carrier parameters for one of the test samples are shown in Figs. 3 and 4. An analysis of these dependences shows that, as the pressure increases, the electron mobility in the irradiated samples increases appreciably and reaches values of $\mu_n=(1.5\text{–}8)\times10^4$ cm^2/(V·s). These mobilities are about an order of magnitude lower than values characteristic of band conductivity; nevertheless they are too large for conductivity via local states and most likely correspond to electron-type surface conductivity. The behavior of the electron conductivity σ_n under pressure apparently shows an appreciable reduction of the electron concentration in the surface layer of the irradiated crystals under the action of pressure. The variations of the electron parameters occur mainly in the insulator phase, whereas the $\mu_n(P)$ and $\sigma_n(P)$ dependences go to saturation after the transition to the metallic phase. This circumstance makes it possible to assume that the variations of the electron

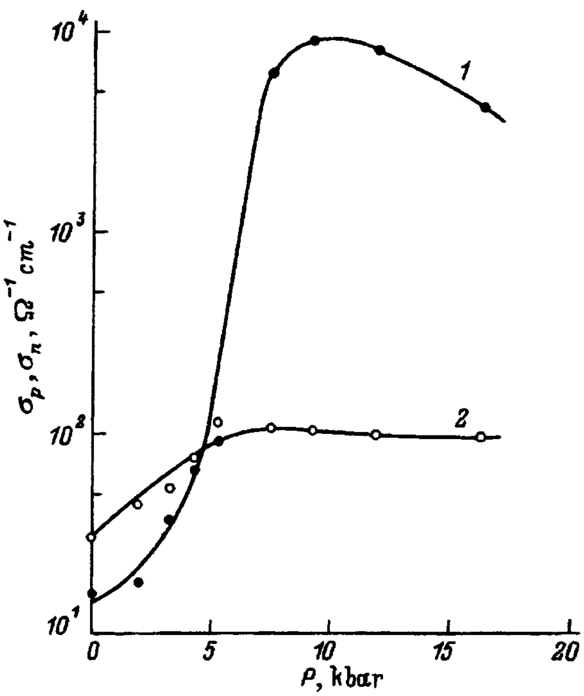

FIG. 4. Hole conductivity σ_p (*1*) and electron conductivity σ_n (*2*) in electron-irradiated sample N8 ($\Phi=5.7\times10^{17}$ cm^{-2}) vs pressure.

parameters in the surface layer are caused by a change in the position of the Fermi level relative to the top of the valence band.

The hole conductivity and mobility vary under the action of pressure in a consistent way, rapidly increasing by several orders of magnitude in the neighborhood of the insulator–metal transition. In the region of maximum pressures, the hole mobility reaches values typical of band conductivity in $Pb_{1-x}Sn_xSe$ alloys, $\mu_p=(1\text{–}2.5)\times10^5$ cm^2/(V·s). At the same time, the hole mobility is only $\mu_p\simeq2\times10^2$ cm^2/(V·s) at atmospheric pressure. Such low values of the hole mobility were observed earlier in the insulator phase of electron-irradiated $Pb_{1-x}Sn_xSe$ ($x=0.125$, 0.25) alloys[6] with conductivity along radiative-defect band E_t lying within the band gap. The μ_p and σ_p values calculated from Eqs. (1) and (2) are therefore evidently effective values and take into account both the contribution of the hole conductivity along the band E_{t1} of localized states and the contribution of conductivity along the valence band.

Thus, in electron-irradiated $Pb_{1-x}Sn_xSe$ ($x=0$; 0.03) alloys, it is apparently necessary to take into account the existence of three conductivity mechanisms when the energy spectrum is reconstructed under the action of pressure. In low-pressure regions (in the insulator phase), the dominant mechanisms are electron-type surface conductivity and hole conductivity via the radiative-defect band, whereas, in the neighborhood of the insulator–metal transition, they are hole band conductivity and electron conductivity over the surface.

4. DEPENDENCES OF THE HOLE CONCENTRATION ON PRESSURE IN THE NEIGHBORHOOD OF THE INSULATOR–METAL TRANSITION AND THE PARAMETERS OF THE E_{t1} BAND

The results presented above make it possible to construct the dependence of the hole concentration on pressure after

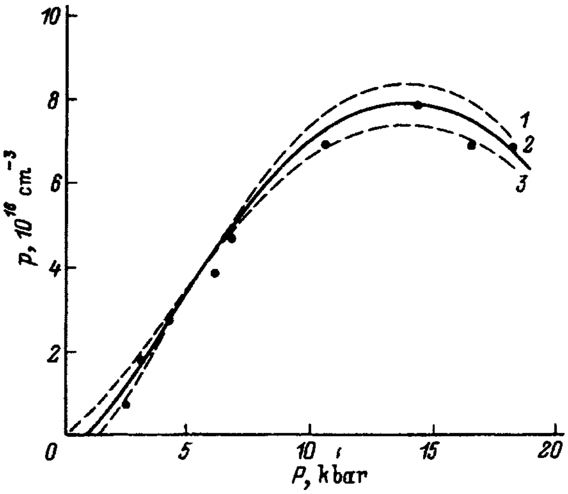

FIG. 5. Hole concentration at $T=4.2$ K in electron-irradiated sample K-22 ($\Phi=2.8\times10^{17}$ cm^{-2}) vs pressure. Curves *1–3* show calculated results from the model given by Eqs. (4)–(6), with $\Delta E_{t1}=17$ meV, $\sigma=15$ meV, and variation of the concentration of radiative defects: *1*—$N_{t1}=1.45\times10^{17}$ cm^{-3}, *2*—$N_{t1}=1.25\times10^{17}$ cm^{-3}, *3*—$N_{t1}=1.05\times10^{17}$ cm^{-3}.

the transition of irradiated alloys to the metallic phase, using the two-band model. Such a dependence can be obtained in several ways. First, the hole concentration can be calculated in terms of the two-band model, using the $\rho(P)$ and $R_H(P)$ dependences in a weak magnetic field given by Eqs. (2) and (3). For simplicity, fixed values (for example, the limiting mobilities and conductivities for each sample at atmospheric pressure) or the $\mu_n(P)$ and $\sigma_n(P)$ dependences calculated above (Figs. 3 and 4) can be chosen in this case as the electron conductivity and mobility in the surface layer. Second, it is possible to directly calculate the hole concentration from

$$p(P)=\sigma_p(P)/e\mu_p(P),$$

using data concerning the variation of the conductivity $\sigma_p(P)$ and hole mobility $\mu_p(P)$ under pressure obtained from the field dependences of the Hall coefficients (Figs. 3 and 4).

Analysis showed that, regardless of the method of calculation, after the transition to the metallic phase, the hole concentration rapidly increases, passes through a maximum, and monotonically decreases with increasing pressure (Fig. 5). Such behavior qualitatively agrees with theoretical concepts concerning the reconstruction of the energy spectrum under pressure (Fig. 1) and makes it possible to estimate the parameters of radiative-defect band E_{t1} by comparing the experimental and theoretical dependences of the hole concentration on pressure.

It was assumed in constructing the theoretical dependences that the generation of radiative defects during irradiation results in the appearance of half-filled states in the radiative-defect band; the position of the middle of the E_{t1} band relative to the middle of the band gap does not change under the action of pressure:[3,4]

$$E_{t1}-E_v=\Delta E_{t1}[\text{meV}]=35-600x-4.25P[\text{kbar}];$$

the density-of-states function $g_{t1}(E)$ in the radiative-defect zone is described by a Gaussian curve, while the defect-generation rate $dN_{t1}/d\Phi$ is independent of the radiation flux. Since it follows from the experimental data that, with hydrostatic compression, the hole concentration increases because electrons overflow from the valence band into the radiative-defect band, it was also assumed that, at any pressures P, the sum of the hole concentrations in the valence band, $p(P)$, and in the radiative-defect band, $p_{t1}(P)$, equals the starting concentration $p_{t1}(0)$ of unfilled states in the E_{t1} band at atmospheric pressure:

$$p_{t1}(0)=p(P)+p_{t1}(P), \tag{4}$$

$$p_{t1}(P)=\int_{E_F}^{\infty}g_{t1}(E)dE, \tag{5}$$

$$g_{t1}(E)=(N_{t1}/\sigma\sqrt{2\pi})\exp[-(E-E_{t1})^2/2\sigma^2], \tag{6}$$

where $N_{t1}=(dN_{t1}/d\Phi)\Phi$ is the total capacity of the radiative-defect band with hole concentrations of

$$p_{t1}(0)=(N_{t1}/2)-n_0$$

or

$$p_{t1}(0)=(N_{t1}/2)+p_0$$

for *n*-type and *p*-type samples, respectively; E_F is the Fermi level, calculated in terms of Dimmock's six-band model,[7] with parameters given in Ref. 8; and σ is the width of the E_{t1} band.

The parameters $dN_{t1}/d\Phi$ and σ of the resonance band were optimized by computer. To estimate the accuracy with which the generation rate $dN_{t1}/d\Phi$ of radiative defects and the width σ of the resonance band are determined, the values of N_{t1} and σ were varied for each sample (dashed curves in Fig. 5). The best agreement of the experimental and theoretical results was achieved for the following values of the parameters of the model:

$$dN_{t1}/d\Phi=(0.45\pm0.1)\times10^{17}\ \text{cm}^{-1},\quad \sigma=(15\pm5)\text{meV}.$$

Thus, the parameters of radiative-defect band E_{t1} turned out to be quite comparable with the analogous parameters of the E_t band, obtained in Ref. 2. However, the accuracy of determining the parameters of the model is extremely low. This circumstance, in particular, makes it impossible to estimate how the generation rate $dN_{t1}/d\Phi$ of radiative defects changes as the radiation flux increases and to determine the degree of deviation of the density-of-states function in the E_{t1} band from a Gaussian form.

5. CONCLUSIONS

The experimental results obtained in this paper indicate that, in electron-irradiated $Pb_{1-x}Sn_xSe$ ($x\leqslant0.03$) alloys in the neighborhood of the pressure-induced insulator–metal transition, it is necessary to take into account the existence of three conduction mechanisms: electron-type surface conduction, band hole conduction, and hole conduction along the radiative-defect band E_{t1}. The field dependences of the Hall coefficient, calculated in terms of the two-band model, satisfactorily agree with the experimental data in the entire range of pressures and magnetic fields considered here and make it possible to determine the charge-carrier parameters in the irradiated samples. In such alloys, the insulator–metal transition under the action of pressure is accompanied by an overflow of electrons from the valence band to the E_{t1} band and by an increase of the free-hole concentration. The experimental dependences of the hole concentration on pressure are in satisfactory agreement with the theoretical values obtained in terms of the model proposed earlier for the reconstruction of the energy spectrum by the electrons of alloys under pressure. An analysis of these dependences is evidence that the radiative-defect band E_{t1} has a significant width ($\simeq 10$ meV) and makes it possible to estimate its main parameters.

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