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Energy spectrum and the nature of irradiation-induced defects in $Pb_{1-x}Sn_xSe$ alloys with inverse band structure

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Abstract. This paper is devoted to the investigation of the effect of electron irradiation (T = 300 K, E = 6 MeV, $\Phi \leq 7.1 \times 10^{17}$ cm^{-2}) on the galvanomagnetic properties of $Pb_{1-x}Sn_xSe$ (x = 0.20, 0.25) alloys. Experimental results were explained in the frame of the earlier proposed model of the energy spectrum for electron-irradiated $Pb_{1-x}Sn_xSe$ alloys, assuming that electron irradiation leads to appearance of a wide radiation defect band of the acceptor type in the forbidden band of the alloys and to redistribution of electrons between the conduction band and the radiation defect band. By comparing theoretical and experimental dependences of the electron concentration on the radiation flux the main model parameters of the defect formation process (the defect generation rate $dN_t/d\Phi$, the width σ and the energy position of the band E_t) were determined in the alloys under investigation. It was shown that agreement between experimental and theoretical data took place only under the assumption that the introduction rate of radiation defects decreases with an increase in the radiation flux. In the present work we put forward the model according to which the major mechanism of the defect formation process in the alloys is the generation of complexes including the primary radiation defects and the intrinsic structure defects typical of initial crystals.

1. Introduction

It is known that electron irradiation of $Pb_{1-x}Sn_xSe$ ($0.19 < x < 0.35$) alloys with the inverse band structure results in the emergence of an empty deep level (band) of the radiation defects E_t, located within the forbidden band [1–3]. Upon an increase in the tin concentration x in the alloy, the position of the middle of the radiation defect band E_t passes through the gap. It moves almost linearly relative to the top of the valence band (the term L_6^-): $E_t \approx L_6^- + (87 - 250x)$ meV. So the middle of the E_t band intersects the bottom of the conduction band at the tin concentration $x \approx 0.19$ and the top of the valence band at $x \approx 0.35$. Therefore one would expect that in the alloys of p-type conductivity the electron irradiation would not affect the free charge carrier concentration and galvanomagnetic properties of the samples. At the same time in the n-type alloys the introduction of radiation defects leads to the flow of electrons from the conduction band into the radiation defect band E_t (figure 1(a)). Thus, the free electron concentration decreases upon an increase in the radiation flux and a metal–insulator transition takes place [1]. Under a sufficiently high radiation flux the electron-irradiated alloys are in the insulating state in which the Fermi level is 'softly' stabilized by the wide E_t band that is partially filled with electrons. The occupancy of the E_t band in the insulating state depends on both the charge carrier concentration in the initial crystals and the radiation flux.

At low radiation fluxes (in the metal phase) the rate of electron concentration decrease would be determined only by the introduction rate of radiation defects that in the first approximation is independent of the radiation flux [3]. However, at high radiation fluxes, upon approaching the metal–insulator transition point the dependence of the electron concentration on the radiation flux can be distorted as a result of both varying the radiation defect introduction rate and the radiation defect band overlapping the conduction band (figure 1(b)). Thus, investigation of the galvanomagnetic properties of electron-irradiated alloys in the vicinity of the metal–insulator transition makes it possible to determine the radiation defect introduction rate and its dependence on the radiation flux as well as to obtain some information about the radiation defect

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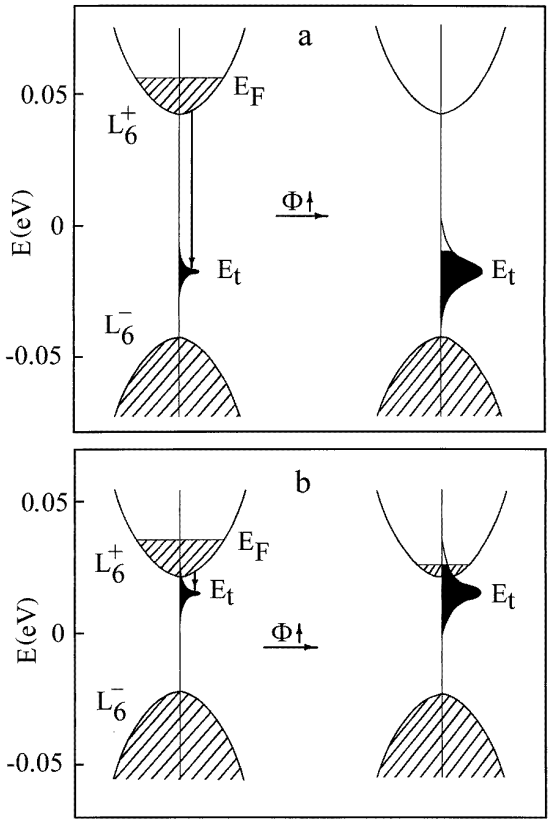

Figure 1. Energy spectrum of electron-irradiated $Pb_{1-x}Sn_xSe$ with inverse band structure. (a) $x = 0.25$, (b) $x = 0.20$.

band parameters [4] and the microscopic structure of the defects.

For this purpose in the present work the effect of deep electron irradiation on the galvanomagnetic properties of n- and p-type alloys with the inverse energy spectrum ($x = 0.20$, $x = 0.25$) was investigated and the comparison of the experimental dependences of the electron concentration in electron-irradiated alloys on the radiation flux with theoretical ones calculated in the frame of the energy spectrum model of electron-irradiated $Pb_{1-x}Sn_xSe$ [3] was made.

2. Experimental details

$Pb_{1-x}Sn_xSe$ ($x = 0.2, 0.25$) single crystals used in this study were irradiated at room temperature by 6 MeV electrons from a linear electron accelerator ($d\Phi/dt \approx 10^{12}$ cm^{-2} s^{-1}, $\Phi \leq 7.1 \times 10^{17}$ cm^{-2}).

In each sample the temperature dependences of the resistivity ρ and the Hall constant R_H ($4.2 \leq T \leq 300$ K, $B \leq 0.04$ T) were measured before and after irradiation with several radiation fluxes. Also the dependences of the Hall constant R_H at $T = 4.2$ K on the magnetic field and Shubnikov–de Haas effect ($\boldsymbol{B} \parallel \langle 100 \rangle$, $B \leq 7$ T) were investigated. The main parameters of the samples studied are presented in table 1.

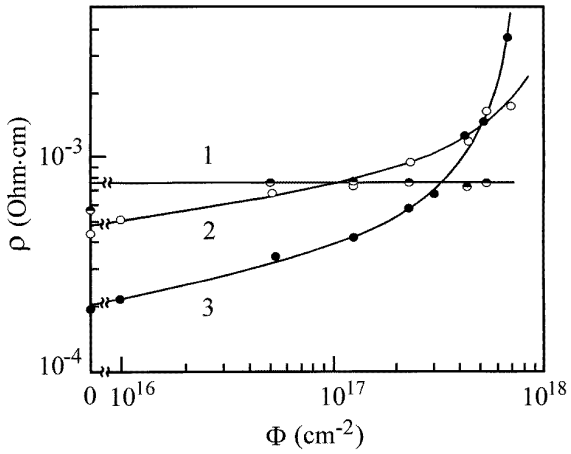

Figure 2. Dependence of resistivity in samples $Pb_{1-x}Sn_xSe$ ($x = 0.20$) at $T = 4.2$ K on the radiation flux. Samples: 1—W-7, 2—W-4, 3—W-14.

3. Galvanomagnetic effects in electron-irradiated $Pb_{1-x}Sn_xSe$ alloys

It was found that, as expected, the parameters of the sample p-$Pb_{1-x}Sn_xSe$ ($x = 0.20$) remained practically unchanged under irradiation (figure 2). At the same time in all investigated n-$Pb_{1-x}Sn_xSe$ samples the resistivity ρ and the absolute value of the Hall constant $|R_H|$ increase monotonically under irradiation that indicates the decrease in the electron concentration in the conduction band of the alloys. Under all irradiation fluxes distinct oscillations of the transverse magnetoresistance were observed in quantizing magnetic fields in the investigated samples (figure 3), which is obviously indicative of high uniformity of the radiation defect introduction under irradiation. Upon an increase in the radiation flux the period of Shubnikov oscillations $\Delta_{100}(1/B)$ increases monotonically, which points to a decrease of the electron concentration in the conduction band. The free electron concentration calculated from the oscillation periods $\Delta_{100}(1/B)$ at $T = 4.2$ K coincided to within 5% with the values calculated from the Hall constant R_H.

In n-$Pb_{1-x}Sn_xSe$ ($x = 0.25$) alloys the radiation defect band E_t is situated within the forbidden band near the top of the valence band L_6^- (see figure 1(a)). Consequently, electron irradiation leads to a decrease in the electron concentration and metal–insulator transition at a certain radiation flux Φ^*. At the same time in alloys with the tin concentration $x = 0.20$ the rate of electron concentration change decreases noticeably with increasing radiation flux and the metal–insulator transition was not observed at all over the investigated range of the radiation flux variation in this case. One can suppose that the radiation defect band E_t in n-$Pb_{1-x}Sn_xSe$ alloy lying within the gap near the bottom of the conduction band L_6^+ has an appreciable width and overlaps strongly with the conduction band, forming a single band of allowed states (see figure 1(b)). Apparently this circumstance, as well as a high initial concentration of electrons in the samples, did not allow us to attain the metal–insulator transition over the investigated range of radiation fluxes.

Table 1. Parameters of $Pb_{1-x}Sn_xSe$ samples investigated at T = 4.2 K.

Sample	x	Type	$\rho \times 10^4$ (Ω cm)	$\lvert R_H \rvert$ ($cm^3\ C^{-1}$)	$N \times 10^{-17}$ (cm^{-3})	$\mu_H \times 10^{-5}$ ($cm^2\ V^{-1}\ s^{-1}$)
W-7	0.20	p	4.8	1.2	51.0	0.026
W-4	0.20	n	4.4	2.3	26.7	0.053
W-14	0.20	n	4.9	2.7	22.9	0.056
W-3	0.25	n	17.6	13.4	4.7	0.076
W-6	0.25	n	13.9	15.4	4.1	0.111

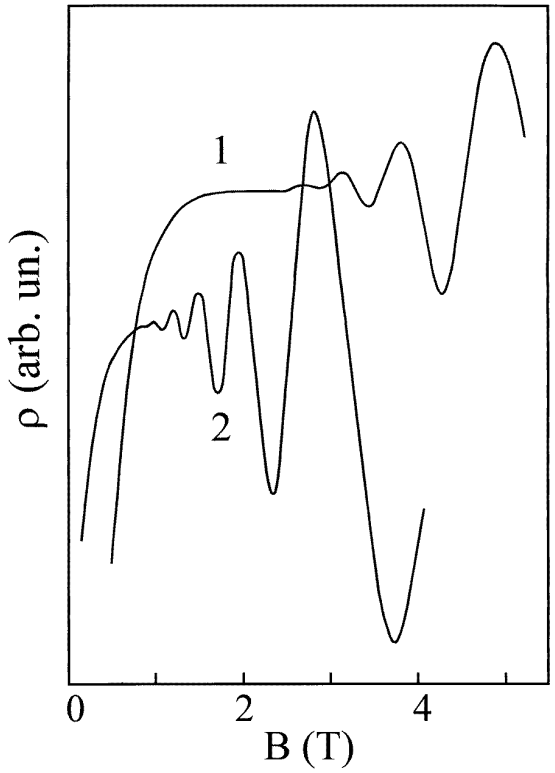

Figure 3. Shubnikov–de Haas oscillations of the sample W-4 at T = 4.2 K. Curve 1—Φ = 0; curve 2—$\Phi = 4.4 \times 10^{-17}$ cm^{-2}.

4. Energy spectrum model in electron-irradiated alloys $Pb_{1-x}Sn_xSe$

In order to obtain the introduction rate of radiation defects as well as the parameters of the radiation defect band E_t in the alloys under study in the present work the dependences of the electron concentration on the radiation flux at $T = 4.2$ K were calculated in the frame of the earlier proposed model of the energy spectrum [3]. The calculation was made under the assumption that the sum of electron concentrations in the conduction band $n(\Phi)$ and in the radiation defect band $n_t(\Phi)$ is equal to the initial electron concentration n_0 in the sample:

$$n_0 = n(\Phi) + n_t(\Phi) \tag{1}$$

$$n_t(\Phi) = \int_{-\infty}^{E_F} g_t(E)\,\mathrm{d}E \tag{2}$$

where $g_t(E)$ is the density of states function in the radiation defect band, E_F is the Fermi energy calculated according to Dimmock's energy–momentum relation [5] with the values of the parameters presented in [6].

Besides, we tentatively suppose that the introduction rate of radiation defects $\mathrm{d}N_t/\mathrm{d}\Phi$ is independent of the radiation flux, the total capacity of the radiation defect band depends linearly on the radiation flux ($N_t = \Phi\,\mathrm{d}N_t/\mathrm{d}\Phi$) and the density of states function in the radiation defect band $g_t(E)$ does not undergo any changes in its form upon an increase in the radiation flux and may be described by the Gaussian-type curve:

$$g_t(E) = \left(\frac{N_t}{\sigma\sqrt{2\pi}}\right)\exp\left[-\frac{(E-E_t)^2}{2\sigma^2}\right] \tag{3}$$

where N_t and σ are the total capacity and the width of the radiation defect band E_t, respectively.

Preliminary calculations showed that the variation of the model parameters (n_0, $\mathrm{d}N_t/\mathrm{d}\Phi$, E_t, σ) do not permit us to achieve a satisfactory agreement between theoretical and experimental dependences $n(\Phi)$ for the samples with $x = 0.20$. Moreover, independent determination of the numerical values of all the radiation defect band parameters in the alloys $Pb_{1-x}Sn_xSe$ ($x = 0.20$, 0.25) turned out to be considerably hampered due to a low sensitivity of the electron concentration dependence on radiation flux to the variation of the parameters E_t and σ. Therefore, a comparison of the theoretical results with the experimental data was carried out assuming that for the radiation defect band width σ we can take the values 18 meV characteristic of electron-irradiated alloys $Pb_{1-x}Sn_xSe$ ($0.07 < x < 0.34$) and the position of the middle of the E_t band relative to the bottom of the conduction band may be calculated in accordance with [2]: $E_t \approx L_6^- + (87 - 250x)$ meV. Thus, making calculations we have varied only the defect introduction rate $\mathrm{d}N_t/\mathrm{d}\Phi$ and the initial electron concentration n_0.

Theoretical dependences $n(\Phi)$ obtained in such a way are shown by solid curves in figure 4 and the model parameters for each investigated sample are presented in table 2. For all samples the introduction rate of radiation defects turned out to be identical. The agreement between experimental data and results of theoretical calculations for the sample with $x = 0.25$ can be considered as satisfactory. At the same time for samples with $x = 0.20$ theoretical dependences $n(\Phi)$ deviate significantly from experimental points in the range of high radiation fluxes, which indicates the existence of the transition to the insulating state over

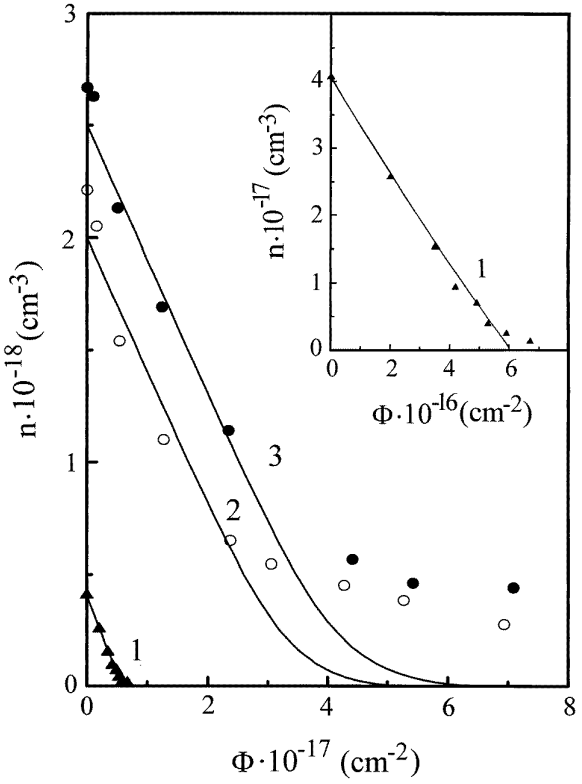

Figure 4. Dependence of the electron concentration at T = 4.2 K in n-$Pb_{1-x}Sn_xSe$ (x = 0.25, 0.20) on radiation flux. The solid curves are the results of calculation based on the model (1)—(3) with the parameters presented in table 2. Samples: 1—W-6, 2—W-14, 3—W-4.

the range of radiation fluxes studied in the present work. One can suppose that the discrepancy between theoretical and experimental data may be due to the violation of some assumptions made during calculations based on the proposed model. It is quite possible that the assumption concerning the fact that the value of the defect generation rate is independent of radiation flux is not indisputable.

5. Mechanism of the defect formation process in electron-irradiated alloys $Pb_{1-x}Sn_xSe$

As a matter of fact, an analysis of theoretical dependences $n(\Phi)$ under the variation of the model parameters showed that the possibility of a good agreement between theoretical and experimental data comes into being only under the assumption that the defect generation rate decreases with increase of the radiation flux.

The phenomenon of a decrease of the defect generation rate is well known for classical semiconductors Ge, Si under electron- and γ-irradiation and has been associated with the formation of complexes including primary radiation defects (vacancies) with impurity atoms [7–9]. For example, the radiation defect formation process in germanium doped with group V elements can be presented as the succession-parallel reaction of the vacancies V with both donor impurity atoms D and complexes of donor plus vacancy DV:

$$\mathrm{D} + \mathrm{V} \xrightarrow{K_1} \mathrm{DV} \qquad \mathrm{DV} + \mathrm{V} \xrightarrow{K_2} \mathrm{DVV} \tag{4}$$

where K_1 and K_2 are the constants of the reaction rates of the donor–vacancy complex formation and the donor–two vacancy complex formation, respectively.

In this case K_1 is much greater than K_2 and at first there is mainly an accumulation of the electrically neutral complexes DV. Upon subsequently increasing the radiation flux the concentration of the complexes DV decreases as the intermediate product and concentration of the complexes DVV increases and tends to its limiting value which is equal to the donor impurity concentration. The dominant mechanism of the defect formation process at the initial stage is the formation of DV complexes. So the rate of the defect generation decreases with increasing radiation flux as a result of decrease in the concentration of electrically active donors and the electron concentration decreases exponentially (see inset in figure 5):

$$n(\Phi) = n_0 \exp\left(-K\frac{\Phi}{n_0}\right) \tag{5}$$

$$\frac{\mathrm{d}n}{\mathrm{d}\Phi} = -K \exp\left(-K\frac{\Phi}{n_0}\right) \tag{6}$$

$$N_{DV}(\Phi) = N_D\left[1 - \exp\left(-K\frac{\Phi}{N_D}\right)\right] \tag{7}$$

$$\frac{\mathrm{d}N_{DV}}{\mathrm{d}\Phi} = K \exp\left(-K\frac{\Phi}{N_D}\right) \tag{8}$$

where K is the initial rate of the electron concentration decrease (to put it in another way, it is the initial rate of defect generation), N_D is the donor concentration and N_{DV} is the DV complex concentration.

By using the logarithmic scale for experimental data on the electron concentration in the irradiated samples $Pb_{1-x}Sn_xSe$ ($x = 0.20, 0.25$) we obtained the dependences which are, at least in the initial range, well described by a straight lines (figure 5). Just as in the case of germanium doped with group V donors [7] (see inset in figure 5), the slope of the straight lines increase with decreasing initial electron concentration in the samples which is in keeping with the fact that the initial rates of electron concentration decrease are approximately the same for all the investigated samples upon irradiation. The obvious likeness between the dependences $n(\Phi)$ presented in figure 5 makes it possible to assume that the major mechanism of the defect formation process in electron-irradiated $Pb_{1-x}Sn_xSe$ alloys is the generation of complexes from primary radiation defects with intrinsic structure defects typical of the initial crystals. This circumstance allows us to use the dependences of the radiation defect concentration and the rates of the defect generation on radiation flux which are identical with those from (7) and (8). So during calculation the dependence $n(\Phi)$ was determined by the following equations:

$$N_t(\Phi) = N_d\left[1 - \exp\left(-K\frac{\Phi}{N_d}\right)\right] \tag{9}$$

$$\frac{\mathrm{d}N_t}{\mathrm{d}\Phi} = K \exp\left(-K\frac{\Phi}{N_d}\right) \tag{10}$$

Table 2. Parameters of the model of defect formation process for alloys $Pb_{1-x}Sn_xSe$ irradiated with electrons at $N_t = \Phi\, dN_t/d\Phi$.

N	Sample	*x*	$E_c - E_t$ (meV)	σ (meV)	$n_0 \times 10^{-17}$ (cm^{-3})	$dN_t/d\Phi$ (cm^{-1})
1	W-6	0.25	60	18	4.0	6.0
2	W-14	0.20	6	18	20.0	6.0
3	W-4	0.20	6	18	20.0	6.0

Table 3. Parameters of the model of defect formation process for alloys $Pb_{1-x}Sn_xSe$ irradiated with electrons at $N_t = N_d[1 - \exp(-K\Phi/N_d)]$.

N	Sample	*x*	$E_c - E_t$ (meV)	σ (meV)	$n_0 \times 10^{-17}$ (cm^{-3})	*K* (cm^{-1})	$N_d \times 10^{-17}$ (cm^{-3})
1	W-6	0.25	60	18	4.2	10.1	6.5
2	W-14	0.20	6	18	21.9	12.0	21.0
3	W-4	0.20	6	18	27.5	12.0	25.0

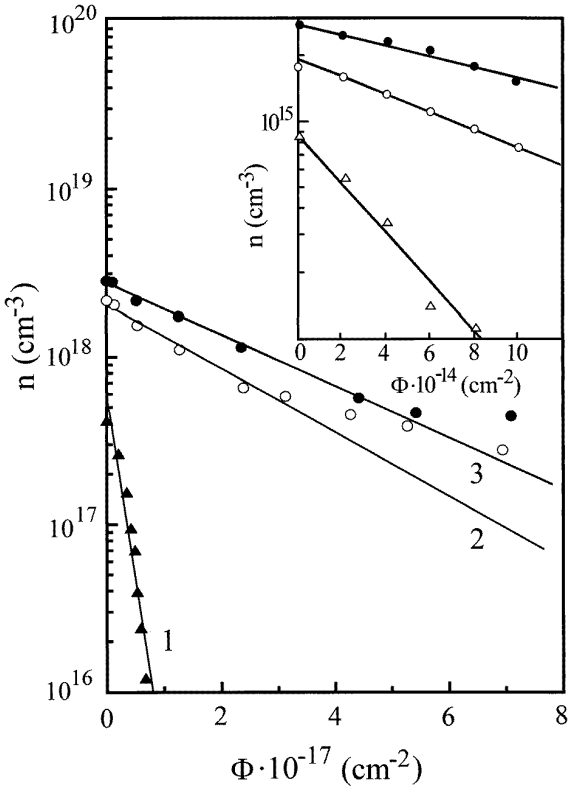

Figure 5. Dependences of the electron concentration at $T = 4.2$ K in n-$Pb_{1-x}Sn_xSe$ ($x = 0.25, 0.20$) and in germanium doped with Sb [7] (in the inset) on radiation flux. Samples: 1—W-6, 2—W-14, 3—W-4.

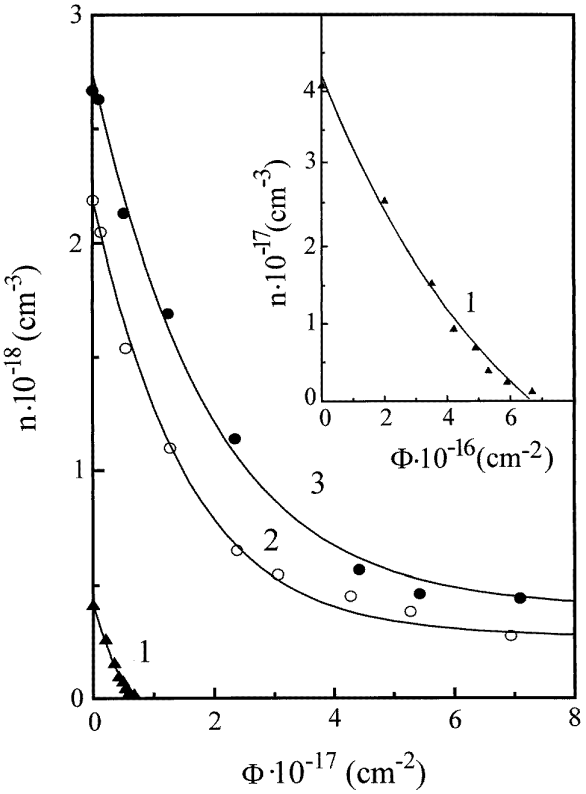

Figure 6. Dependence of the electron concentration at $T = 4.2$ K in n-$Pb_{1-x}Sn_xSe$ ($x = 0.25, 0.20$) on radiation flux. The solid curves were calculated assuming the decrease of the defect formation rate under irradiation (the model parameters are presented in table 3). Samples: 1—W-6, 2—W-14, 3—W-4.

where N_d is the concentration of the native structure defects typical of the initial crystals, K is the initial rate of the defect formation process.

The variation of the parameters K and N_d permits us to obtain a satisfactory agreement between theory and experiment for all the investigated samples (figure 6) in the frame of the energy spectrum model of $Pb_{1-x}Sn_xSe$ alloys presented in figure 1. The model parameters for each sample are presented in table 3.

Finally, it should be noted that a detailed microscopic structure of the complexes arising under electron irradiation of $Pb_{1-x}Sn_xSe$ alloys investigated remains not clear so far. However, taking into account the fact that irradiation

with fast electrons results in an emergence of the radiation defect band E_t unfilled with electrons and a decrease of the free electron concentration at high initial rate $dn/d\Phi \approx 10\ cm^{-1}$, one can suppose that complexes are of the acceptor nature and include selenium vacancies (in the free state a selenium vacancy is a source of two electrons). In the case of undoped alloys $Pb_{1-x}Sn_xSe$ any structure defects, such as atoms of residual impurities (for instance, oxygen), dislocations and even vacancies existing before irradiation in the initial crystals, can be analogous to the donor impurity atoms in germanium.

6. Conclusion

Thus, in the present work the galvanomagnetic properties and kinetics of the electron concentration variation in $Pb_{1-x}Sn_xSe$ ($x = 0.20,\ 0.25$) alloys irradiated with electrons were investigated. A decrease of the variation rate of free electron concentration in the vicinity of the metal–insulator transition induced by electron irradiation was observed. That is connected both with a decrease in the rate of defect formation process and with the overlap of the radiation defect band and the conduction band under a high radiation flux.

In the frame of the energy spectrum model of electron-irradiated alloys $Pb_{1-x}Sn_xSe$ the dependence of electron concentration on the radiation flux in the investigated alloys was constructed and the main parameters of this model were determined. The results of theoretical calculations are in good agreement with available experimental data over the entire range of the radiation flux variation.

To explain the effect of the decrease of radiation defect generation rate with increasing radiation flux, the model of the defect formation process was put forward. This model was constructed assuming that under irradiation complexes are formed including the primary radiation defects and intrinsic point structure defects typical of the initial crystals.

Acknowledgments

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