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Insulator–metal-type transitions induced by electron irradiation in gallium-doped PbTe-based alloys

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Abstract

We report the results of our study of the electron irradiation effect ($E = 6$ MeV, $\Phi \leqslant 8 \times 10^{17}$ cm^{-2}) on the galvanomagnetic (4.2 K $\leqslant T \leqslant 300$ K, $B \leqslant 0.1$ T) properties of gallium-doped PbTe, n-$\mathrm{Pb}_{1-x}\mathrm{Ge}_x\mathrm{Te}$ ($0.04 \leqslant x \leqslant 0.06$) and $\mathrm{Pb}_{1-y}\mathrm{Sn}_y\mathrm{Te}$ ($y = 0.19, 0.23$) narrow-gap semiconductors. Depending on the features of the initial electronic structure of the alloys, a p–n-inversion, a transition from metal to insulating or from insulating to metal-type conductivity and an increase in the free electron density under electron irradiation were revealed. The rate of defect generation under irradiation was found to be abnormally high for $\mathrm{A}^4\mathrm{B}^6$ materials. The activation character of the temperature dependences of the galvanomagnetic parameters, caused by the presence of deep gallium-induced defect levels in the gap, was observed for the alloys in the insulating state. The results were explained assuming that electron irradiation of gallium-doped PbTe-based alloys creates primarily donor-like defects, which leads to an increase of the electron concentration and a change in the occupancy of the allowed and localized bands. Additionally, electron irradiation seems to cause a change in the charge activity of gallium centres within the bulk, providing a high rate of defect generation.

1. Introduction

The characteristics of the doping action of gallium in the lead-telluride-based alloys are usually ascribed to the mixed valence impurities, which drastically change the energy spectrum of charge carriers due to the formation of deep impurity levels in these materials [1, 2]. The presence of these defect levels results in the appearance of unusual features in the alloys, such as Fermi level pinning and the persistent photoconductivity effect. At the same time the materials doped with gallium have some special features which still have not been explained unambiguously.

In particular, the dependence of the free carrier concentration in PbTe:Ga on the gallium content has an unusual behaviour; at least two saturation regions have been observed in experiments [3–5]. Gallium acts as a donor when its concentration is low. As the doping level of gallium increases, a transition from p- to n-type conductivity occurs. The first saturation region lies slightly above this point: the Fermi level turns out to be pinned by a deep impurity-induced level E_{Ga1} within the gap and the electron concentration approaches almost intrinsic values [1]. A further rising of the gallium content leads to an increase in free electron concentration and to a second saturation, which was recently explained by the formation of a second gallium-induced deep defect level E_{Ga} situated on the background of the conduction band in PbTe:Ga [6, 7]. It should be noted that the ranges of the Fermi level stabilization are fairly narrow and the values of N_{Ga}, which correspond to these ranges, vary appreciably, depending on the sample growth method and therefore on the homogeneity of the gallium distribution in the bulk of the sample.

On the other hand, it is known that electron irradiation results in a gradual and uniform change of the concentration of the electrically active defects in the bulk of the sample and the formation of radiation defect levels in the energy spectrum of lead-telluride-based alloys [8]. Redistribution of the charge carriers between impurity-induced and radiation defect states and allowed bands makes it possible to vary the concentration of the free charge carriers and to realize metal–insulator-type transitions induced by electron irradiation. For example, it was shown that electron irradiation of the undoped p-$\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Te}$ alloys causes a decrease in the free hole concentration and a transition to the insulating state due to the generation of electrically active n- and p-type defects and the flow of electrons from the radiation donor level to the valence band [9].

Thus, irradiation with fast electrons may prove to be an extremely effective method to modify the properties of the lead-telluride-based alloys and to determine the nature of the gallium doping action in these materials. In this paper we present the results of an experimental study of the electron irradiation effect on the electrical properties of gallium-doped PbTe:Ga, $\mathrm{Pb}_{1-y}\mathrm{Sn}_y\mathrm{Te}$:Ga and $\mathrm{Pb}_{1-x}\mathrm{Ge}_x\mathrm{Te}$:Ga alloys in order to determine whether the properties of the alloys can be controlled by means of irradiation and to determine how irradiation affects the energy spectrum of the alloys under consideration. It was anticipated that varying the alloy parameter x or y would make it possible to vary smoothly the gap value of the alloys and hence the mutual arrangement of gallium-induced deep levels and allowed bands, while changing the irradiation dose was expected to alter the defect structure of crystals and hence the free carrier concentration.

2. Experimental details and samples

Single crystals of n- and p-type PbTe:Ga ($C_{\mathrm{Ga}} \approx$ 0.1–0.5 mol%) and $\mathrm{Pb}_{1-y}\mathrm{Sn}_y\mathrm{Te}$:Ga ($y = 0.19, 0.23$, $C_{\mathrm{Ga}} \approx$ 0.2–0.3 mol%) were grown by the Czochralski method and n-type $\mathrm{Pb}_{1-x}\mathrm{Ge}_x\mathrm{Te}$:Ga ($0.04 \leqslant x \leqslant 0.06$, $C_{\mathrm{Ga}} \approx$ 1.5–2 mol%) single crystals were synthesized from the vapour phase by sublimation. The alloy parameter x or y was estimated by x-ray diffractometry. The impurity content was determined from the initial amount of substance in the furnace charge, taking into account the distribution of impurities along the ingot during the growth process.

The test samples, approximately 3 mm × 0.7 mm × 0.7 mm in size were cut out from the original crystal bulk by using an arc cutting machine so that sample sides would coincide with the $\langle 100\rangle$-type axis. The Hall, the potential and the current contacts to the samples were made via indium-tinned copper wire 0.05 mm in diameter. The current contacts were soldered to each end of the sample, using the alloy of indium with 4% Ag and 1% Au. Potential and Hall contacts were attached by spark-discharge welding them to the samples.

Table 1. Parameters of PbTe:Ga, $Pb_{1-x}Ge_xTe$:Ga and $Pb_{1-y}Sn_yTe$:Ga samples at $T = 4.2$ K before irradiation and after irradiation with the maximal radiation fluxes.

Sample	x, y	C_{Ga} (mol%)	Type	ρ (Ω cm)	N (cm^{-3})	μ_H (cm^2 V^{-1} s^{-1})	Φ_{max} ($\times 10^{17}$ cm^{-2})
Ga-01	—	0.1	p	1.6×10^0	5.2×10^{14}	7.6×10^3	3.0
Ga-02	—	0.2	p	3.5×10^{-1}	7.9×10^{15}	2.3×10^3	2.9
Ga-02M	—	0.3	p	4.5×10^0	5.8×10^{15}	2.5×10^2	0.6
Ga-04	—	0.4	n	3.7×10^5	$<7.6 \times 10^9$	$<2.2 \times 10^3$	2.3
Ge-4-7	0.04	1.5	n	9.1×10^2	$<3.0 \times 10^{14}$	$<1.0 \times 10^0$	0.24
Ge-4-9	0.04	2	n	9.9×10^{-1}	1.6×10^{16}	4.0×10^2	0.12
Ge-4-3	0.04	3	n	2.1×10^{-2}	6.8×10^{17}	4.4×10^2	0.12
Ge-6-4	0.06	1.5	n	3.4×10^1	$<4.0 \times 10^{11}$	$<3.0 \times 10^3$	0.24
Sn-1	0.19	0.2	n	8.4×10^{-5}	2.1×10^{17}	2.9×10^5	8.1
Sn-2	0.19	0.2	n	7.9×10^{-5}	1.3×10^{17}	4.9×10^5	2.0
Sn-3	0.19	0.3	n	2.1×10^{-3}	1.5×10^{16}	1.7×10^5	0.6
Sn-4	0.23	0.3	p	5.9×10^{-3}	5.2×10^{17}	1.7×10^3	2.1

The original samples were irradiated at room temperature by fast electrons from a linear electron accelerator ELU-6 ($E = 6$ MeV, $d\Phi/dt \approx 10^{12}$ cm^{-2} s^{-1}). For each sample the temperature dependences of the resistivity ρ and Hall coefficient R_H ($B \leqslant 0.1$ T, 4.2 K $\leqslant T \leqslant$ 300 K) were measured before and after the irradiation with fast electrons from a linear electron accelerator ($T = 300$ K, $E = 6$ MeV, $\Phi \leqslant 8.1 \times 10^{17}$ cm^{-2}). Table 1 summarizes the main parameters characterizing the samples at $T = 4.2$ K.

3. Results and discussion

It was established that for all investigated alloys the galvanomagnetic parameters depend strongly on the irradiation dose, but the character of changes is essentially different for various systems. The temperature dependences of resistivity $\rho(1/T)$ and Hall coefficient $R_H(1/T)$ measured for the p-PbTe:Ga before irradiation show the metallic character of alloy conductivity (figures 1(a), (b)). Electron irradiation causes a monotonic increase of the resistivity ρ and the Hall coefficient R_H at low temperatures and the appearance of the activation region on the $\rho(1/T)$ and $R_H(1/T)$ dependences. The activation energy determined from the slope of the ρ versus $1/T$ curve gives ΔE_{Ga1} = 55–65 meV ($\rho = \rho_0 \exp(\Delta E_{Ga1}/kT)$). This is usually associated with a thermal activation of electrons from the deep gallium-induced defect level E_{Ga1} to the conduction band [1, 2]. At a certain electron flux $\Phi = \Phi^*$ a p–n-inversion takes place and further irradiation only slightly affects the parameters of the test samples over the experimental temperature range. The critical flux Φ^* is governed by the content of gallium in the samples: it decreases with increasing impurity concentration.

It should also be noted that the temperature dependences of the Hall coefficient exhibit several anomalies near the point of the p–n-inversion: the Hall coefficient decreases sharply; the signal from the Hall contacts vanishes or several points of inversion of the Hall coefficient appear at low temperatures. These anomalies, in our view, may be connected with a strong compensation and perhaps with an appreciable inhomogeneity of the gallium distribution in the crystals. Similar features have previously been observed when inversion of the conductivity type is attained by increasing the doping level in p-PbTe:Ga.

A highly resistive n-type PbTe:Ga sample has an initial electron concentration approximately equal to the intrinsic value at low temperatures (see table 1), which means therefore that it is in an insulating state. The temperature dependences of resistivity and Hall

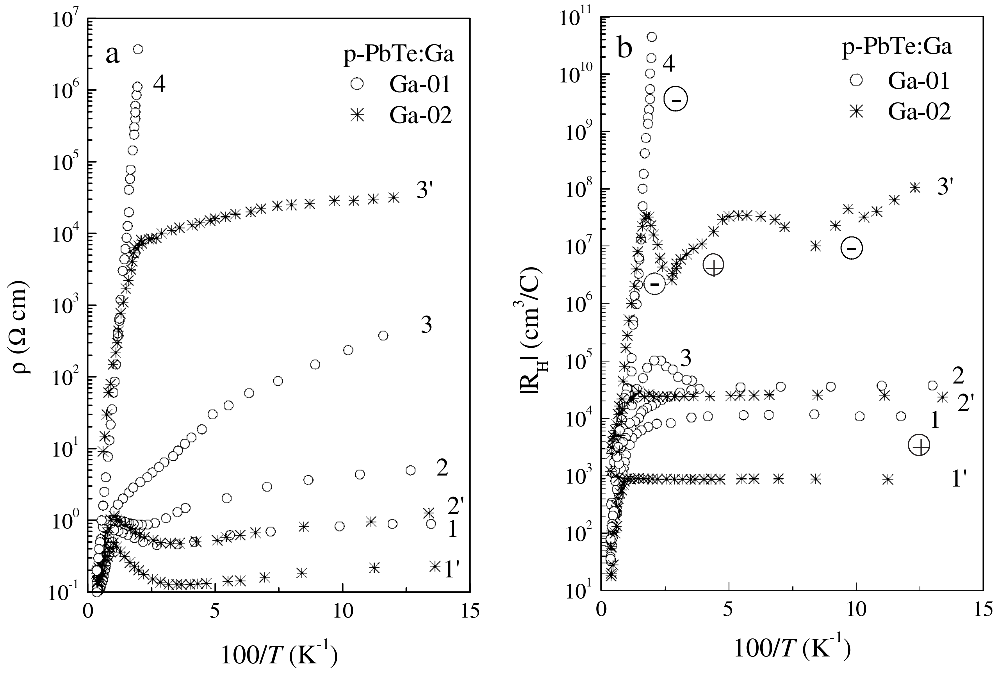

Figure 1. Temperature dependences of the resistivity (a) and the Hall coefficient (b) in p-PbTe:Ga before and after exposure to the electron irradiation with various fluxes. Φ (cm^{-2}): curves 1, 1′-0, curves 2—1×10^{16}, curves 3—6.2×10^{16}, curves 4—1.4×10^{17}, curves 2′—4.9×10^{16}, 3′—2.3×10^{17}.

coefficient exhibit two activation regions in this case: the first low-temperature one is associated with the presence of a deep gallium level in the forbidden band while the second one observed at $T > 250$ K is attributable to the intrinsic ionization of the charge carriers. Electron irradiation has virtually no effect on the electrical characteristics of the Ga-04 sample over the whole experimental range of temperature variation, which is consistent with the behaviour of the p-PbTe:Ga samples irradiated after the transition to the insulating state.

The dependences $\rho(1/T)$ and $R_{\mathrm{H}}(1/T)$ measured for non-irradiated n-Pb$_{1-x}$Ge$_x$Te:Ga crystals (curves 1 in figures 2(a), (b)) have an activation character corresponding to the stabilization of the Fermi level by the Ga-induced defect level E_{Ga} within the forbidden band [6, 7]. In addition, an anomalous minimum in the curves $\rho(1/T)$ and $R_{\mathrm{H}}(1/T)$ is seen, which can be attributed to the transition of the samples to the rhombohedral phase of Pb$_{1-x}$Ge$_x$Te at low temperatures [10]. At the lowest temperatures ($T < 20$ K) the resistivity saturates, and the Hall effect signal vanishes, accompanied by a rapid decrease in the Hall mobility of charge carriers. This behaviour is thought to be associated with a change in the dominant conductivity mechanism. Conduction at low temperatures may occur via impurity states in the bulk or through surface pathways.

Under electron irradiation the resistivity and absolute value of the Hall coefficient decrease by more than three orders of magnitude, the activation character of their temperature dependences gradually changes for the metallic one and the signal from the Hall contacts becomes measurable. Typical results obtained for samples exposed to various radiation fluxes are shown in figures 2(a), (b). The free electron concentration, calculated using the value of the Hall coefficient, increases with increasing irradiation dose and attains $n \approx 1 \times 10^{18}$ cm^{-3} for

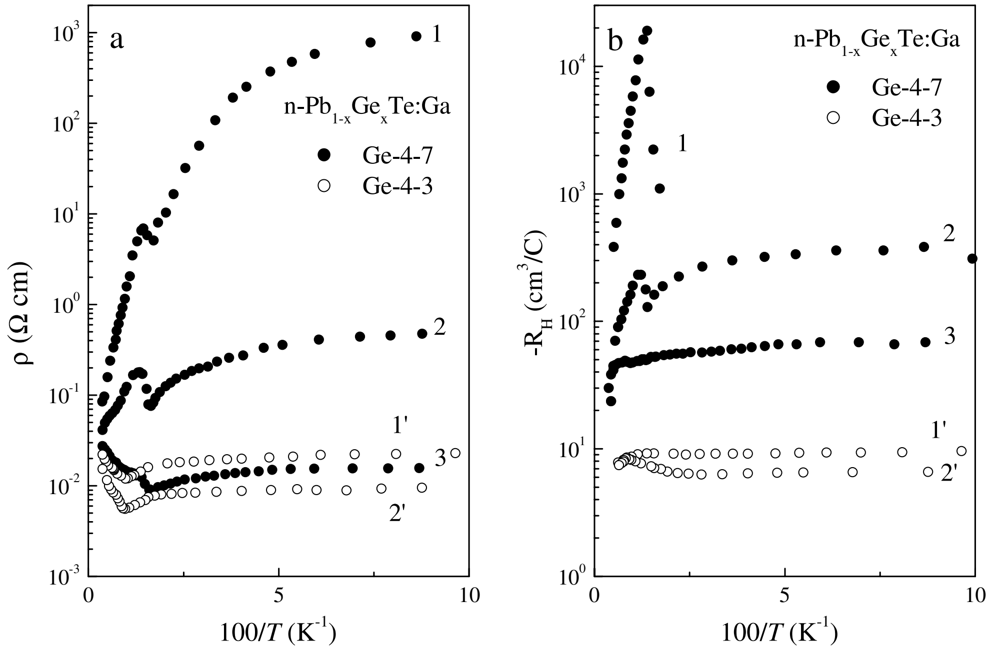

Figure 2. Temperature dependences of the resistivity (a) and the Hall coefficient (b) in n-Pb$_{1-x}$Ge$_x$Te:Ga before and after exposure to the electron irradiation with various fluxes. Φ (cm^{-2})—curves 1, 1′: $\Phi = 0$; curves 2, 2′: $\Phi = 1.2 \times 10^{16}$; curves 3: $\Phi = 2.4 \times 10^{16}$.

the maximal radiation flux. Obviously such a character of the electrical parameters changing under irradiation is indicative of a transition of the test samples from the insulating to the metallic state with the electron-type band conductivity as the main conductivity mechanism in the entire temperature range considered.

At last it was found that the parameters of n-Pb$_{1-x}$Sn$_x$Te:Ga crystals irradiated follow a metallic-type behaviour before irradiation and up to the highest radiation dose attained ($\Phi_{\max} = 8 \times 10^{17}$ cm^{-2}). The temperature dependences of the galvanomagnetic parameters measured are presented in figures 3(a), (b). Measurements show a monotonic decrease of the resistivity and Hall coefficient at low temperature with increasing radiation dose (figure 4). In this case we observed almost linear growth of the free electron concentration under irradiation. The Hall mobility of electrons gradually decreases but its absolute value remains quite large ($\mu_H > 4 \times 10^4$ cm^2 V^{-1} s^{-1}) up to the maximal radiation flux.

The experimental results obtained can be unambiguously explained assuming that the electron irradiation of Ga-doped PbTe-based crystals generates primarily n-type defects. This causes the test crystals to undergo two successive electronic transitions under irradiation. The first one is a transition from the metallic state (the p-type region) to the insulating state followed by p–n-conversion of the conductivity type and the second is a transition from the insulating state to the metallic state, accompanied by the destruction of the Fermi level pinning effect. Estimations show that the rate of defect generation under irradiation in gallium-doped PbTe-based crystals attains the value $\mathrm{d}n/\mathrm{d}\Phi = 5$–6 cm^{-1}, which is significantly higher than typical figures observed for undoped A^{4}B^6 semiconductors $\mathrm{d}n/\mathrm{d}\Phi = 0.1$–1 cm^{-1} [8]. Apparently, in addition to the characteristics of the gallium doping, electron irradiation also provides a useful means to modify the electrical properties of PbTe-based alloys doped with gallium.

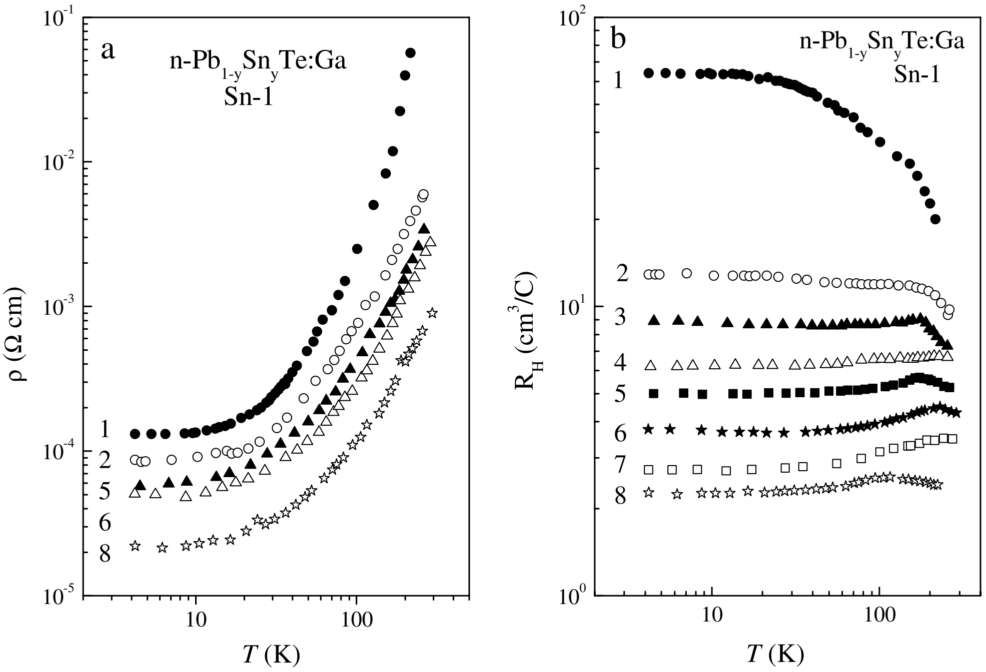

Figure 3. Temperature dependences of the resistivity (a) and the Hall coefficient (b) in n-Pb$_{1-y}$Sn$_y$Te:Ga before and after exposure to the electron irradiation with various fluxes. Φ (cm^{-2})—curves 1: $\Phi = 0$; curves 2: $\Phi = 3.8 \times 10^{16}$; curve 3: $\Phi = 8 \times 10^{16}$; curve 4: $\Phi = 1.5 \times 10^{17}$; curves 5: $\Phi = 2 \times 10^{17}$; curves 6: $\Phi = 3.2 \times 10^{17}$; curve 7: $\Phi = 4.4 \times 10^{17}$; curves 8: $\Phi = 5.6 \times 10^{17}$.

In order to explain the experimental results obtained, we propose a model of the energy spectrum reconstruction under irradiation assuming that the electron irradiation causes the formation of a donor-type radiation defect band located high on the background of the conduction band of the tested crystals. The electrons from this band can occupy the free states in the allowed bands and gallium-induced levels, causing a decrease of hole concentration and p–n-conversion in p-type alloys and an increase of the electron concentration in n-type alloys. Also, it is quite possible that electron irradiation increases the uniformity of the gallium distribution in the lattice, causing transitions of the Ga atoms from the neutral state to an electrically active state. This circumstance may also explain the abnormally high rate of defect generation under irradiation.

4. Conclusion

Thus, in this experimental study we have established that electron irradiation of gallium-doped lead-telluride-based alloys gives rise to a generation of primarily n-type defects. This circumstance makes it possible, depending on the parameters of the initial electronic structure of the alloys, to realize a p–n-inversion, and a transition from metal to insulating or from insulating to metal-type conductivity accompanied by an increase of the free electron density under electron irradiation. Also, the electron irradiation increases the uniformity of the gallium distribution in the lattice, causing transitions of the Ga atoms from the neutral state to an electrically active state. That is, the electron bombardment of gallium-doped alloys makes it

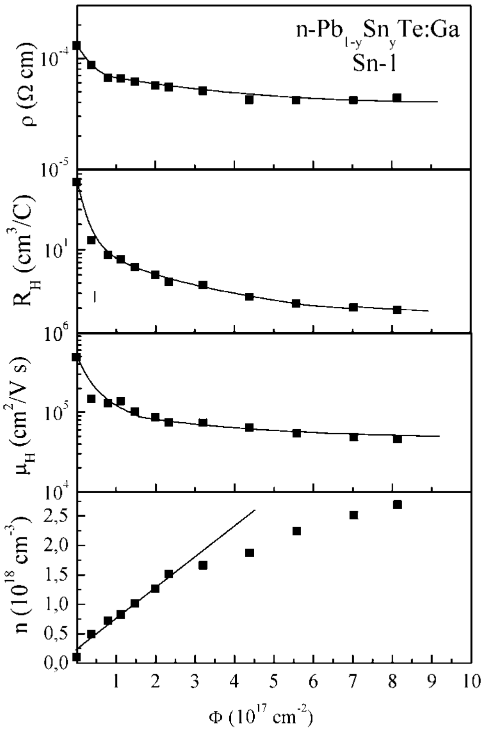

Figure 4. The dependences of galvanomagnetic parameters in n-Pb$_{1-y}$Sn$_y$Te:Ga on the radiation flux at $T = 4.2$ K.

possible to realize any desired occupancy of band and localized states with charge carriers, therefore it may serve as an effective tool to modify the properties of doped crystals under investigation.

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