Electronic structure and structural phase transition in Pb$_{1-x}$Ge$_x$Te:Cr under pressure

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Abstract. We investigate galvanomagnetic effects near the insulator-metal transition induced by pressure in Pb$_{1-x}$Ge$_x$Te ($x=0.10$, 0.13) alloys doped with chromium ($4.2\leq T\leq300$ K, $B\leq8$ T). We observe nonlinearity in the magnetic field dependencies of Hall voltage and peaks of anomalous scattering in the temperature dependencies of resistivity. These are due to the conductivity via chromium impurity band and to the structural phase transition from the cubic NaCl phase to the rhombohedral GeTe phase. Magnetic field dependencies of the Hall coefficient $R_H(B)$ are calculated in the framework of two-band conduction model. The main parameters of charge carriers are determined. Pressure dependencies of the critical phase transition temperature are obtained.

1. Introduction
Doping of Pb$_{1-x}$Ge$_x$Te ($x\geq0.10$) alloys with chromium introduces a deep impurity level in the gap near the bottom of conduction band and stabilizes the Fermi level [1]. Under pressure, the gap decreases, whereas the position of the chromium level with respect to the middle of the gap $E_i$ is only slightly modified (figure 1). At a sufficiently high pressure, the level enters the conduction band and an insulator-metal transition takes place [2]. This transition is induced by pressure and it is due to the flow of electrons from the chromium impurity level to the conduction band. However, it was found that just after the transition to the metallic phase, pressure dependencies of the free electron concentration and Fermi energy, calculated in the framework of the electronic structure diagram of figure 1, significantly deviate from experimental data. These deviations may be explained by assuming that the chromium impurity level is significantly widened and partially overlaps with the conduction band already in the insulating phase, and by the structural phase transition from the cubic to the rhombohedral phase at low temperatures, typical for the undoped Pb$_{1-x}$Ge$_x$Te alloys [3, 4].

To investigate the influence of the chromium impurity band and the effect of the structural phase transition on the pressure dependence of the free electron concentration near the insulator-metal transition and to reveal the structural phase transition under pressure, in the present work we study galvanomagnetic properties of Pb$_{1-x}$Ge$_x$Te:Cr ($x=0.10$, 0.13) under hydrostatic pressure up to 17 kbar.

2. Experimental details
Single crystals Pb$_{1-x}$Ge$_x$Te:Cr ($x=0.10$, 013) were grown by the Bridgman method. The chemical composition was determined using the X-ray fluorescence analysis. The crystal structure of the samples was controlled by powder X-ray diffraction, carried out at room temperature. It was shown
that there are no secondary phases in the samples.

At the atmospheric pressure and under pressure up to 17 kbar, temperature dependencies of resistivity $\rho$ and Hall coefficient $R_H$ (T=4.2-300 K, B\leq 0.08 T) as well as magnetic field dependencies of the Hall coefficient $R_H$ (T=4.2 K, B\leq 8 T) were measured by the four-probe technique. Hydrostatic pressures were obtained in the beryllium bronze chamber with kerosene-oil-pentane pressure transmitting medium. We controlled the actual pressure in the chamber at helium temperatures by measuring the superconducting transition temperature in pure tin as a function of pressure [5].

3. Magnetic field dependencies of the Hall coefficient

In the insulating phase (P<2 kbar), the magnetic field dependencies of the Hall voltage are nonlinear and the absolute value of the Hall coefficient $R_H$ decreases with magnetic field (points 1 in figure 2). This indicates the existence of at least two types of conductivity mechanisms: conduction band conductivity and conductivity via the chromium impurity band. In the metallic phase (P>2 kbar), the free electron concentration increases and the conduction band conductivity gives the main contribution to galvanomagnetic properties. The value of $R_H$ becomes independent of magnetic field (see figure 2).

To determine the parameters of each type of charge carriers near the insulator-metal transition, we calculated magnetic field dependencies of the Hall coefficient $R_H(B)$ using the two-band conduction model [6]. We then used the equation for $R_H(B)$ to fit our experimental data with mobility of free electrons $\mu_n$ and mobility for the conductivity via the impurity band $\mu_i$ as two free fit parameters. The two other parameters of the model (conductivities $\sigma_n$ and $\sigma_i$) were determined independently from the values of the Hall coefficient and the resistivity under weak magnetic field ($\mu B<<1$) at T=4.2 K. The best fit to measured dependencies $R_H(B)$ (lines in figure 2) was achieved by assuming an electron-type conductivity via the impurity band with mobility $\mu_i\approx 400$ cm$^2$/V$\cdot$s independent of pressure. This value of mobility is typical for conductivity via localized states in IV-VI semiconductors [6].

The pressure dependence of the free electron concentration was determined as $n(P)=\sigma_n(P)/e\mu_n(P)$
using the values of the electron conductivity and mobility (figure 3). It was shown that even at the atmospheric pressure, a non-vanishing free electron concentration \( n \approx 10^{16} \text{ cm}^{-3} \) exists. Under pressure, the concentration increases sharply by almost three orders of magnitude, in a narrow range of pressures \( (P \leq 6 \text{ kbar}) \). On the one hand, this result confirms our hypothesis about the partial overlap of the impurity band with the conduction band in the alloy with \( x=0.10 \) even at the atmospheric pressure. On the other hand, there is still no satisfactory agreement between the experimental data (points 2 in figure 3) and theoretical predictions (solid line in figure 3). This discrepancy may arise from the splitting of four equivalent conduction band minima in L points of the Brillouin zone due to the structural phase transition from the cubic to the rhombohedral phase of the alloy at low temperatures.

4. Structural phase transition under pressure

Both at the atmospheric pressure and under hydrostatic compression up to 17 kbar, pronounced peculiarities were revealed in the temperature dependencies of resistivity \( \rho(T) \) (figure 4). The temperature at which these anomalies occur strongly depends on the matrix composition and on the pressure, shifting upwards with the increase of germanium content in the alloy and downwards under pressure. Similar anomalies (peaks of anomalous scattering) were observed earlier in undoped \( \text{Pb}_{1-x}\text{Ge}_{x}\text{Te} \) alloys at atmospheric pressure. They were associated with the structural phase transition from the cubic \( \text{NaCl} \) phase to the rhombohedral \( \text{GeTe} \) phase, taking place at a sufficiently low temperature [3, 4].

In order to elucidate the temperature at which anomalies of resistivity take place, we calculated the derivatives of resistivity under pressure with respect to temperature. The critical temperature of the structural phase transition \( T_c(P) \), determined using these dependencies, is shown in figure 5. At the atmospheric pressure, the critical transition temperatures \( T_c \) are approximately 175 K and 185 K in the alloys with \( x=0.10 \) and \( x=0.13 \), respectively, whereas in the undoped alloys of the same compositions these values were approximately 230 K and 270 K. Thus, one can conclude that at the atmospheric pressure, doping with chromium reduces the critical transition temperature \( T_c \) by 60-80 K. Under pressure \( T_c \) decreases linearly at a rate \( dT_c/dP \approx -8.3 \text{ K/kbar} \). Taking into account the reduction of the transition temperature under doping, our experimental data satisfactorily agree with the well-known data for the undoped \( \text{Pb}_{1-x}\text{Ge}_{x}\text{Te} \) (\( x=0.01-0.05 \)) alloys for which the pressure coefficient of the critical temperature varies in a wide range: \( dT_c/dP=-(5–12) \text{ K/kbar} \) [3, 4].
Figure 4. Temperature dependencies of resistivity in Pb$_{1-x}$Ge$_x$Te:Cr ($1 - x=0.13$, 2-11 – $x=0.10$). P, kbar: 1,2-0, 3-0.5, 4-1.2, 5-2.2, 6-4.4, 7-6.3, 8-9.1, 9-11.7, 10-14.4, 11-16.4.

Figure 5. Critical phase transition temperature versus pressure in Pb$_{1-x}$Ge$_x$Te:Cr ($x=0.10$). Points 1 and 2 were obtained under increase and under decrease of pressure, respectively.

4. Conclusion

In this work, we characterized conductivity via the chromium impurity band and studied pressure dependence of the free electron concentration near the insulator-metal transition in Pb$_{1-x}$Ge$_x$Te ($x=0.10, 0.13$) alloys doped with chromium. We measured magnetic field dependencies of the Hall coefficient $R_H(B)$ and interpreted them in the framework of the two-band conduction model. We proved that at the atmospheric pressure, the overlap of the chromium impurity band with the conduction band exists. Splitting of the conduction band minima in L points of the Brillouin zone due to the structural phase transition from the cubic to the rhombohedral phase at low temperatures was proposed as a mechanism that might explain remaining discrepancies between theory and experiment. Dependencies of the critical phase transition temperature $T_c$ on the composition and on pressure were studied. It was shown that at the atmospheric pressure, doping with chromium reduces $T_c$ by 60-80 K. The pressure coefficient of $T_c$ was found to be $dT_c/dP \approx -8.3$ K/kbar.

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