Rearrangement of electronic structure of Pb$_{1-x-y}$Sn$_x$V$_y$Te under pressure

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Abstract. The galvanomagnetic properties in weak magnetic fields ($4.2 \leq T \leq 300$ K, $B \leq 0.07$ T) and the Shubnikov-de Haas effect ($T=4.2$ K, $B \leq 7$ T) in the single crystal Pb$_{1-x-y}$Sn$_x$V$_y$Te ($x=0.05$-0.20, $y \leq 0.01$) alloys at atmospheric pressure and under hydrostatic compression up to 15 kbar have been investigated. We found that the increase of the vanadium impurity content leads to the p-n-conversion, transition to the insulating phase and to the pinning of Fermi level by the deep impurity level, lying under the bottom of the conduction band. Under pressure a decrease of the activation energy of the vanadium level, the n-p-inversion of the conductivity type at low temperatures and an insulator-metal transition occur. The pressure and the temperature coefficients of vanadium deep level energy are determined and the diagram of the electronic structure rearrangement for Pb$_{1-x-y}$Sn$_x$V$_y$Te under pressure is proposed.

1. Introduction

Doping of lead telluride-based semiconductors with transition elements (Ti, V, Cr) creates donor-type deep impurity levels, stabilizing Fermi level in strongly doped samples near the bottom of conduction band [1]. In this case impurity level is partially filled with electrons and densities of occupied and empty states correspond to concentrations of impurity ions in 2+ and 3+ states, possessing different electrical and magnetic activities. Thus, these materials are diluted magnetic semiconductors whose electrical and magnetic properties should be dependent on their electronic structure (energy position of the impurity level relative to the band edges and occupancy of the level with electrons) [2,3].

It was known, that in PbTe vanadium induces appearance of a deep impurity level, situated under the bottom of conduction band ($E_v \approx E_c-20$ meV) [4,5]. In Pb$_{1-x}$Sn$_x$Te alloys activation energy of the level rises with the increase of the tin content and it approaches the middle of the gap [6]. To investigate the rearrangement of the electronic structure of vanadium doped alloys under pressure in the present work the galvanomagnetic properties ($T=4.2$-300 K, $B \leq 7$ T) of Pb$_{1-x-y}$Sn$_x$V$_y$Te ($x=0.05$-0.20, $y \leq 0.01$) at atmospheric pressure and under hydrostatic pressure $P \leq 15$ kbar have been studied.

2. Experimental details

Single crystal Pb$_{1-x-y}$Sn$_x$V$_y$Te ingot with nominal concentrations $x=0.08$ and $y=0.01$ was grown by the vertical Bridgman technique and cut into slices $\approx 1.5$ mm thick perpendicular to the growth direction.

The crystal structure was controlled at room temperature by powder high-resolution X-ray diffraction using Rigaku X-ray diffractometer. It is shown that all peaks in the diffraction patterns
correspond to those of the undoped PbTe, indicating that all samples are single-phase. The chemical composition was determined by the X-ray fluorescent microanalysis using scanning electron microscope LEO Supra 50 VP with Oxford Instruments INCA Energy+ system. It was found that, in accordance with the exponential distribution of substitution components, typical for A\textsuperscript{4}B\textsuperscript{6} solid solutions [7], the tin content grows monotonously from the origin to the end of ingot (x=0.05–0.20), where as the vanadium impurity concentration rises up to y≈0.010 and then remains almost constant.

At the atmospheric pressure temperature dependencies of the resistivity ρ and the Hall coefficient RH (T=4.2-300 K, B≤0.07 T) were measured by the four-probe technique. Then the sample with maximum tin content (x=0.20, y≈0.01) was studied under pressure. For this sample dependencies ρ(T) and RH(T), as well as Shubnikov-de Haas effect (T=4.2 K, B≤7 T) under pressure were measured. Pressures up to 15 kbar were obtained in the beryllium bronze chamber with kerosene-oil-pentane pressure transmitting media. The actual pressure in the chamber at helium temperatures was controlled by measuring the superconducting transition temperature in the pure tin as a function of pressure.

3. Galvanomagnetic properties under pressure

It is found that at atmospheric pressure lightly doped with vanadium samples from the origin of the ingot are p-type. Temperature dependencies of resistivity ρ and Hall coefficient RH exhibit metal-like behaviour due to the high density of free holes, typical for the undoped PbTe-based alloys. As the vanadium content in the samples grows, the hole concentration decreases, p-n-conversion and transition to the insulating phase at x≈0.08, y≈0.008 take place. In this phase dependencies ρ(1/T) and RH(1/T) have activation character due to the pinning of the Fermi level by the deep vanadium level EV, situated under the bottom of the conduction band. With the increase of the tin content, the slope of ρ(1/T) and RH(1/T) dependencies grows gradually, indicating an increase of activation energy ∆EV=E\textsubscript{c}-EV from 14 meV to 32 meV and slow shift of the level towards the middle of the gap [6].

Under pressure the resistivity ρ at helium temperature decreases monotonously by approximately seven orders of magnitude, while the slope of ρ(1/T), associated with the impurity ionization,
decreases up to the critical pressure $P^* \approx 7$ kbar (figure 1). Then the character of $\rho(1/T)$ dependencies changes to the metal-type one and an insulator-metal transition takes place. At the same time, on the temperature dependencies of the Hall coefficient $R_H(1/T)$ the n-p-inversion of the $R_H$ sign at pressures $P \geq 3.7$ kbar is observed (figure 2). With the increase of pressure the sign-reversal temperature $T_{inv}$ grows at a rate $dT_{inv}/dP = (7-16)$ K/kbar and the low-temperature Hall coefficient decreases gradually.

In the metallic phase ($P > 8.7$ kbar), the distinct Shubnikov-de Haas (SdH) oscillations are observed. The period of SdH oscillations in inverse magnetic field $\Delta(1/B)$ decreases, indicating an increase of the free hole concentration under pressure. Experimental observation of quantum SdH oscillations under pressure may be considered as a direct confirmation of the high crystal perfection of the sample and of the uniformity of vanadium distribution in the investigated $\text{Pb}_{1-x-y}\text{Sn}_x\text{V}_y\text{Te}$ alloy.

4. Energy level diagram under pressure

Obtained experimental results allow us to construct the following model of the electronic structure rearrangement for $\text{Pb}_{1-x-y}\text{Sn}_x\text{V}_y\text{Te}$ ($x=0.2$) under pressure (figure 3). At atmospheric pressure, the deep vanadium level stabilises the Fermi level in the upper half of the gap, slightly above its centre. Under pressure, the gap decreases linearly at a rate $dE_g/dP \approx -7.4$ meV/kbar [8], whereas the vanadium level intersects the middle of the gap $E_i$, moving almost parallel to the bottom of the conduction band. So, at pressures $P \geq 3.7$ kbar the p-n-inversion of the Hall coefficient on the $R_H(1/T)$ dependencies appears and the activation of electrons from the valence band to the level becomes the main thermal activation mechanism at low temperatures. Then the vanadium level approaches the top of the valence band and crosses it at the critical pressure $P^* \approx 7$ kbar, inducing an insulator-metal transition. In the metallic phase ($P > P^*$), the vanadium level moves down into the valence band and the concentration of free holes increases due to the flow of electrons from the band to empty states of the level.

Experimental values of the vanadium level energy $E_V$ (points in figure 3) were obtained from the analysis of the $\rho(1/T)$ dependencies and SdH data, supposing the pinning of the Fermi level by the impurity level in the whole pressure range. In the insulating phase $E_V$ values were estimated using the activation energy of the level $\Delta E_V$, while in the metallic phase – using the Fermi energy, calculated

![Figure 3. The model of electronic structure rearrangement for $\text{Pb}_{1-x-y}\text{Sn}_x\text{V}_y\text{Te}$ ($x=0.20$) under pressure. $T$, K: 1-4.2, 2-50, 3-100.](image)

![Figure 4. Pressure dependence of the $R_H$ sign-reversal temperature in $\text{Pb}_{1-x-y}\text{Sn}_x\text{V}_y\text{Te}$ ($x=0.20$). $\alpha$, meV/K: 1-0, 2-0.08, 3-0.12, 4-0.16.](image)
from the hole concentration in the framework of the two-band Kane dispersion law for $A^4B_6$ semiconductors [8] with parameters, determined for undoped Pb$_{1-x}$Sn$_x$Te ($x \approx 0.2$) [9]. One can see that over the entire investigated pressure range, the vanadium level $E_v$ moves almost parallel to the term $L_6^-$, slowly approaching the term $L_6^-$ at a rate about 0.5 meV/kbar.

To estimate the temperature coefficient of the motion of the vanadium level with respect to band edges, we plot the experimental pressure dependence of the sign-reversal temperature $T_{inv}$ (figure 4). A monotonous shift of the p-n-inversion point to higher temperatures under pressure indicates that the vanadium level moves with respect to the middle of the gap when the temperature is increased. Anticipating that the energy of the level, measured from the bottom of the conduction band, is only slightly dependent on temperature and that the vanadium level crosses the middle of the gap at $T = T_{inv}$, we have calculated theoretical dependence $T_{inv}(P)$, using well-known temperature dependence of the gap for Pb$_{1-x}$Sn$_x$Te alloys [8] (lines in figure 4). The best fit (full line in figure 4) is achieved assuming that as the temperature increases the vanadium impurity level moves with respect to the middle of the gap and slowly approaches the bottom of the conduction band at a rate $\alpha = d(E_v-E_c)/dT \approx 0.12$ meV/K.

5. Conclusion

Obtained experimental results allow us to conclude that doping of p-Pb$_{1-x}$Sn$_x$Te alloys with vanadium leads to the p-n-conversion and introduces a deep impurity level under the bottom of the conduction band ($\Delta E_v = E_c - E_v = 14-32$ meV for $x = 0.09-0.20$). Under pressure, the deep vanadium level in Pb$_{1-x}$Sn$_x$V$_y$Te ($x = 0.20$) alloy moves almost parallel to the conduction band bottom and subsequently intersects the middle of the gap and the top of the valence band, inducing the n-p-conversion and the insulator-metal transition at critical pressure $P^* \approx 7$ kbar at $T = 4.2$ K. In the metallic phase further increase of pressure leads to the increase of the hole concentration due to the redistribution of electrons between the valence band and the impurity level. With the increase of temperature at fixed pressure the opposite movement of the level, inducing the intersection of the level with the middle of the gap and the p-n-inversion of the conductivity type, takes place. In the framework of this model, the pressure and the temperature coefficients of the vanadium level energy, counted from the bottom of the conduction band, are estimated as $d(E_v - E_c)/dP \approx 0.5$ meV/kbar and $d(E_v - E_c)/dT \approx 0.12$ meV/K.

Acknowledgments

The authors would like to thank Dr. S.A. Ibragimov and Dr. A.V. Knotko (Faculty of Chemistry, Moscow State University) for performing the X-ray diffraction study and the X-ray fluorescent microanalysis. This research was supported by the Russian Foundation for Basic Research (Grant N 11-02-01298) and by the Ministry of Education and Science of the Russian Federation (State contract No 14.740.11.0051).

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