Influence of Thallium on the Shubnikov – de Haas effect and Thermoelectric Properties of Sb$_2$Te$_3$ and Bi$_2$Se$_3$

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Abstract. Influence of Tl-doping on the Shubnikov de Haas effect (SdH) at $T=4.2$ K in magnetic field up to 38 T of $p$-Sb$_{2-x}$Tl$_x$Te$_3$ ($x=0; 0.005; 0.015; 0.05$) and $n$-Bi$_{2-x}$Tl$_x$Se$_3$ ($x=0, 0.01; 0.02; 0.04; 0.06$) single crystals has been investigated. By increasing the Tl content, the frequency of the SdH effect and hence the extremal cross-sections of the Fermi-surface decreases in both materials. The hole concentration decreases in Sb$_{2-x}$Tl$_x$Te$_3$ due to a donor effect of Tl and the electron concentration decreases in $n$-Bi$_{2-x}$Tl$_x$Se$_3$ due to an acceptor effect of Tl. Temperature dependence of the Seebeck coefficient $S$, electrical conductivity $\sigma$, thermal conductivity $k$ and the figure of merit $ZT$ single crystals were measured in the temperature range $77$ K – $300$ K. The values of $k$ and $\sigma$ decrease due to Tl doping in Sb$_{2-x}$Tl$_x$Te$_3$ and $n$-Bi$_{2-x}$Tl$_x$Se$_3$ and the Seebeck coefficient $S$ for all compositions increases in the whole temperature range. The figure of merit $ZT$ increases in both materials. The preferential scattering mechanism in Tl-doped samples changes from the acoustic phonon scattering to the ionized impurity scattering.

1. Introduction

The efficiency of thermoelectric generators is limited to a fraction of their Carnot efficiency, determined by the dimensionless thermoelectric material figure of merit $\text{ZT}=S^2\sigma T/k$, where $S$ is the thermoelectric power or the Seebeck coefficient of the thermoelectric material, $\sigma$ and $k$ are the electrical and thermal conductivities, respectively, and $T$ is the absolute temperature [1]. Because $\text{ZT}$ also depends on the carrier’s group velocity via the electrical conductivity, the value of $E_F$ that maximizes $\text{ZT}$ is somewhat different from the value that maximizes the Seebeck coefficient $S$. Crystals of Sb$_2$Te$_3$ always exhibit $p$-type conductivity due to the high concentration of charged point defects of predominantly antistructural type (i.e., Sb atoms occupy the positions of Te atoms). The formation of such defects is due to weak polarity of Sb–Te bonds. A change in the bond polarity upon doping changes the concentration of point defects and, hence, the hole concentration. The single crystals of Bi$_2$Se$_3$ prepared from stoichiometric melt show an excess of bismuth over the stoichiometric composition. This is the reason why the crystal matrix contains negatively charged defects of bismuth atoms on selenium sites $\text{Bi}^{-1}_{\text{Se}}$ and positively charged vacancies in the selenium sublattice $V_{\text{Se}}^{+2}$ [2]. The concentration of vacancies exceeds the concentration of $\text{Bi}^{-1}_{\text{Se}}$ defects and the Bi$_{2+\delta}$Se$_3$ crystals exhibit $n$-type conductivity. Despite a considerable research on this material, there are

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few papers concerning the doping with Tl of Bi$_2$Se$_3$ [3], Sb$_2$Te$_3$ [4] and Sb$_{1.5}$Bi$_{0.5}$Te$_3$[5]. Here we investigated Shubnikov-de Haas effect of Tl-doped single crystals Sb$_2$Te$_3$ and n-Bi$_2$Se$_3$ in a magnetic field up to 30-38 T. We report also the influence of Tl doping on the thermoelectric properties of $p$-Sb$_{2-x}$Tl$_x$Te$_3$ and $n$-Bi$_{2-x}$Tl$_x$Se$_3$ single crystals in the temperature range 77K–300 K.

2. Experimental

In this work, we investigated pristine and Tl-doped $p$-Sb$_{2-x}$Tl$_x$Te$_3$ ($x=0; 0.005; 0.015; 0.05$) and $n$-Bi$_{2-x}$Tl$_x$Se$_3$ ($x=0; 0.01; 0.02; 0.04; 0.06$) single crystals grown by the Bridgman method. In the measurements of the SdH effect, the current flowed along the $C_3$ axis and the magnetic field was directed along the $C_3$ axis of the crystals. In the measurements of the thermopower $S$ and heat conductivity $κ$, the temperature gradient and a heat flux were directed along the $C_3$ axis. The concentration of Tl in the studied samples is shown as loaded for the growth.

In order to determine the concentration of light holes (or electrons) and the Fermi energy $E_F$, we used the SdH effect at $T = 4.2$ K in high pulsed magnetic fields [6]. Some parameters of samples are listed in table 1 for $p$-Sb$_{2-x}$Tl$_x$Te$_3$ and table 2 for $n$-Bi$_{2-x}$Tl$_x$Se$_3$.

Table 1. SdH oscillation frequency $F$, Fermi-energy $E_F$ and concentration of light holes $p$ in $p$-Sb$_{2-x}$Tl$_x$Te$_3$

| $N_0$ | composition          | $F$, T | $E_F$, meV | $p$, cm$^{-3}$ |
|------|----------------------|--------|------------|---------------|
| 1    | Sb$_2$Te$_3$         | 54     | 97,1       | 2,8*10$^{19}$ |
| 2    | Sb$_{1.95}$Tl$_{0.05}$Te$_3$ | 52,1   | 93,7       | 2,7*10$^{19}$ |
| 3    | Sb$_{1.98}$Tl$_{0.02}$Te$_3$ | 51,3   | 92,2       | 2,6*10$^{19}$ |
| 4    | Sb$_{0.96}$Tl$_{0.05}$Te$_3$ | 34     | 61,1       | 1,4*10$^{19}$ |

Table 2. SdH oscillation frequency $F$, Fermi-energy $E_F$ and concentration of electrons in $n$-Bi$_{2-x}$Tl$_x$Se$_3$

| $N_0$ | composition          | $F$, T | $E_F$, meV | $n$, cm$^{-3}$ |
|------|----------------------|--------|------------|---------------|
| 1    | Bi$_2$Se$_3$         | 167,6  | 161,7      | 2,2*10$^{19}$ |
| 2    | Bi$_{1.99}$Tl$_{0.01}$Se$_3$ | 166   | 160,1      | 2,1*10$^{19}$ |
| 3    | Bi$_{1.98}$Tl$_{0.02}$Se$_3$ | 159   | 153,4      | 1,9*10$^{19}$ |
| 4    | Bi$_{1.96}$Tl$_{0.04}$Se$_3$ | 145,4  | 140,3      | 1,6*10$^{19}$ |
| 5    | Bi$_{1.94}$Tl$_{0.06}$Se$_3$ | 134,8  | 130        | 1,4*10$^{19}$ |

As can be seen from tables 1 and 2, the carrier concentration decreases with Tl doping in the both $p$-Sb$_{2-x}$Te$_3$ (holes) and $n$-Bi$_2$Se$_3$ (electrons) single crystals. The simultaneous measurements of the temperature dependence of the Seebeck coefficient, a heat conductivity, and the electrical conductivity were performed using an original setup including a low temperature cryostat [7].

3. The Shubnikov-de Haas effect data

In high magnetic field there are SdH oscillations in $p$-Sb$_{2-x}$Tl$_x$Te$_3$ and $n$-Bi$_{2-x}$Tl$_x$Se$_3$. In figure 1a oscillations of the transverse magnetoresistance are shown for different samples $p$-Sb$_{2-x}$Tl$_x$Te$_3$ in magnetic field parallel to the $C_3$ axis of the crystal. In this orientation the extremal cross-sections of all six ellipsoids of the Fermi surface of the upper valence band in $p$-Sb$_{2-x}$Tl$_x$Te$_3$ coincide. We observed a single frequency $F$ in Sb$_{2-x}$Tl$_x$Te$_3$ single crystals as it is seen in the Fourier transform in figure 1b. Tl-doping decreases the value of $F$ in $p$-Sb$_{2-x}$Tl$_x$Te$_3$. The six-ellipsoidal non parabolic model satisfactory describe the energy spectrum of the light holes in the highest valence band of Sb$_2$Te$_3$ [6,8]. Using this model and the SdH effect data we calculated the carriers concentrations and Fermi energies, listed in Table 1. The method of calculation is described elsewhere [6,8].

In $n$-Bi$_{2-x}$Tl$_x$Se$_3$ we observed a clear SdH oscillations with a single frequency as it is shown in figure 2 for different samples in magnetic field parallel to the $C_3$ axis of the crystals. As it is seen in
figure 2 Tl-doping decreases the value of $F$ in $n$-Bi$_{2-x}$Tl$_x$Se$_3$. From the frequency $F$ of the SdH oscillation the extremal cross section $S_c$ of the Fermi surface in the momentum space perpendicular to the direction of $B$ may be evaluated by a relation $S_c = 2\pi e h F$. According to experimental and theoretical investigations, [9,10] there are two conduction bands in Bi$_2$Se$_3$. However, almost nothing is known about the upper conduction band. The lower conduction band is located at the $\Gamma$ point of the Brillouin zone and is represented by an ellipsoid elongated in the $C_3$ direction with cross-sections, $S_a = S_b = \eta S_c$ with a volume $V$. From the known dependence of the anisotropy $\eta$ of the ellipsoidal Fermi surface on the electron concentration or the frequency $F$, we can calculate the volume $V$ of the ellipsoid and the value of the electron concentration $n$ [10]. Evaluated electron concentrations are listed in Table 2 for various samples. For the last sample the frequency of oscillations was extrapolated using experimental data for all other samples. As the effective mass does not depend on the carrier concentration [10] it is possible to use simple parabolic dispersion relation to calculate the Fermi energy from the SdH effect data $S_c = \pi p_{LF}^2 = 2\pi m^* E_F$, where $p_{LF}$ is the Fermi momentum in the direction perpendicular to the magnetic field. From the known value of $m^*$ [10] and experimentally determined the extremal cross section $S_c$ of the Fermi surface, $E_F$ was calculated for the lower conduction band, and listed in Table 2.
4. Thermoelectric properties

The value of the Seebeck coefficient $S$ is positive in $\text{Sb}_{2-x}\text{Tl}_x\text{Te}_3$. Tl-doping increases the thermoelectric power of $\text{Sb}_2\text{Te}_3$ single crystal in the whole temperature interval. The heat conductivity $k$ and the conductivity $\sigma$ of $\text{Sb}_{2-x}\text{Tl}_x\text{Te}_3$ crystals decreases due to Tl doping as compared with pristine $\text{Sb}_2\text{Te}_3$. A decrease in the heat conductivity and an increase of the Seebeck coefficient lead to the increase of the value of the dimensionless thermoelectric figure of merit (figure 3a) from $ZT=0.20$ in $\text{Sb}_2\text{Te}_3$ up to 0.37 at $T=292$ K in the Tl-doped sample $\text{Sb}_{0.95}\text{Tl}_{0.05}\text{Te}_3$.

The Seebeck coefficient $S$ increases under Tl-doping while the heat conductivity $k$ decreases in $\text{Bi}_{2-x}\text{Tl}_x\text{Se}_3$. When temperature decreases the conductivity always increases in $\text{Bi}_{2}\text{Tl}_{0.02}\text{Se}_3$ The conductivity has a tendency to decrease under Tl-doping. An increase of the Seebeck coefficient and a decrease of the heat conductivity increase the value $ZT$ in the whole temperature range: $ZT=0.02$ in pristine $\text{Bi}_{2}\text{Se}_3$ and $ZT=0.14$ in $\text{Bi}_{1.94}\text{Tl}_{0.06}\text{Se}_3$ at $T=290$ K (Figure 3b). Note that it is very important to subtract the thermoelectric voltage during the measurements of the conductivity $\sigma$ in order to get a proper value of $\sigma$. Otherwise it can lead to a higher value of the conductivity in doped samples as compared with undoped.

The simple model with square dispersion law and isotropic relaxation time $\tau$ given by

$$\tau = \tau_0 E F^r,$$

yields in the following expression for the Seebeck coefficient:

$$S(T) = \frac{k_B}{e} \left( \frac{(2r+5)F_{r+1/2}(\eta)}{(2r+3)F_{r+1/2}(\eta)} - \eta \right),$$

where $k_B$ being the Boltzmann constant, $e$ being electron charge, $E_F$ being the Fermi energy, $\eta = E_F / k_B T$ is the reduced Fermi energy, and $r$ is a parameter characterizing the scattering mechanism ($r = -1/2$ for acoustic phonon scattering, $r = 1/2$ for polar optical scattering and $r = 3/2$ for ionized impurity scattering); $F_r(\eta)$ is the Fermi integral. Using simple model with a square dispersion law and isotropic relaxation time $\tau$ given by (1) we evaluate the temperature dependence of the scattering parameter $r$ using formula (2). In Tl-free crystals parameter $r$ is close to -1/2 at high temperatures indicating the major role of the acoustical phonon scattering. Tl doping leads to a pronounced increase of $r$. This points to the change of the scattering mechanism from the phonon scattering to the ionized impurity scattering in doped samples. Thus in all samples the reason in a increase of $ZT$ is a decrease of the carrier concentration (holes in $\text{Sb}_{2-x}\text{Tl}_x\text{Te}_3$) (electrons in $n$-$\text{Bi}_{2-x}\text{Tl}_x\text{Se}_3$) and the Fermi energy and change of the scattering mechanism due to the Tl-doping.
Incorporating of the Tl atoms into the Sb$_2$Te$_3$ lattice decreases the free hole concentration. The bonds between Sb and Te atoms are very weakly polarized, Sb atoms may enter a Te sublattice forming antistructural (AS) defects $Sb'_{Te}$ (Sb in the Te site). The substitution of Sb atoms by Tl atoms leads to the formation of uncharged defects $TI'_{Sb}$. Tl atoms have a lower value of the electronegativity with respect to Sb atoms. Hence, the bonds between the defects $TI'_{Sb}$ and surrounding Te atoms are more polar than the Sb-Te bonds. Positive charges arise at the points defects whose increase the bond ionicity. The higher ionicity of the $TI'_{Sb}$ defects results in the suppression of the formation of the antistructural defects $Sb'_{Te}$, responsible for the hole concentration.

As mentioned above, doping with Tl decreases the free electron concentration in $n$-Bi$_2$Se$_3$ single crystals. The crystal matrix contains negatively charged AS defects of Bi atoms on Se sites $Bi^{-1}_{Se}$ and positively charged vacancies in the selenium sublattice $V^{+2}_{Se}$ [2,3]. The concentration of vacancies exceeds the concentration of AS defects and the Bi$_{2-x}$Se$_3$ crystals exhibit $n$-type conductivity; the concentration of free electrons $n$ is given by the difference of the concentration of both native defects. Tl atoms enter the sublattice of Bi forming $TI'_{Bi}$ substitutional defects. Let us assume that Tl forms uncharged defects $TI'_{Bi}$ with the valence state +3. In this way Tl produces no free carriers. From the chemical point of view the more stable form of Tl is the valence +1, i.e. it can capture two electrons from conduction band and reduce the free electron concentration. However the nonlinear concentration dependence of the lattice parameter on the Tl content indicates that this is not the only process running upon a Tl doping. The actual concentration of Tl is smaller than the nominal one [3]. A single crystal with Tl grew from the melt containing an overstoichiometric amount of Se leads to a crystal with suppressed concentration of selenium vacancies. This fact can account for the observed decrease in free electron concentration. Thus both the formation of $TI^{+2}_{Bi}$ and the descending vacancies concentration $V^{-2}_{Se}$ can account for the decrease in the free electron concentration. The experimental results do not allow us to specify the dominant mechanism.

5. Conclusions

We investigated SdH effect and thermoelectric properties of Tl-doped $p$-Sb$_{2-x}$Tl$_x$Te$_3$ ($x$=0; 0.005; 0.015; 0.05) and $n$-Bi$_{2-x}$Tl$_x$Se$_3$ ($x$=0, 0.01; 0.02; 0.04; 0.06) single crystals. We found that Tl has a donor behavior in the solid solutions $p$-Sb$_{2-x}$Tl$_x$Te$_3$ while in $n$-Bi$_{2-x}$Tl$_x$Se$_3$ Tl has an acceptor behavior. The figure of merit ZT increases up to 0.37 at T=292 K in $p$-Sb$_{2-x}$Tl$_x$Te$_3$ with x=0.05 and increases up to ZT=0.14 in $Bi_{3-x}Tl_xSe_3$ with x=0.6 at T=290 K.

6. References

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