Electronic and Thermodynamic Properties of Sn and SbI3 Doped Single Crystals $p - Bi_2Te_3$

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Abstract. Bi$_2$Te$_3$ – Sb$_2$Te$_3$ solid solutions, the most commonly used thermoelectrics (~300K), are characterized by inhomogeneities and defects of various types, and doping contributes to spatial inhomogeneity. These impurity energy states fall into the band gap with small high-field SdH oscillations. However, it is known that Sn impurity pins the Fermi level and tremendously improves the spatial homogeneity, leading to observation of high amplitude SdH oscillations in lower magnetic field. The iodine (I) impurity was chosen to shift the Fermi level and affect the filling factor of impurity states. Numerous experimental results on magnetoresistivity, specific heat and magnetic susceptibility indicate that the most probable model for one-electron states in Bi$_2$Te$_3$ solid solutions doped with Sn is the presence of two impurity bands one filled and one empty- with the Fermi level pinned in-between. Earlier we reported on SdH oscillations at $T = 4.2$K and in magnetic Field up to 10T. Here, we report on investigations of the magnetoresistivity ($2 < T < 295$K) and its oscillations ($T < 12$K). We deduce the carriers mobility and concentration and their temperature dependence along with that of the dampening of SdH amplitude. We also report on specific heat measurements in the range ($2 < T < 295$K), with a low $T$ power law of exponent $p=3.5$ behavior.

1. Introduction

Bismuth telluride ($Bi_2Te_3$) is a narrow gap semiconductor with $E_g \sim 0.1$ eV and is of practical importance as a foundation material for developing high efficiency thermoelectric materials for use in cooling devices operating at $\sim 300$ K. $Bi_2Te_3$ belongs to the class of layered $R_{3mm}$ structures with anisotropic physical properties. Further, due to peculiarities in its phase diagram, material’s synthesis can result in the fact that even its most perfect crystals are plagued by a large quantity of various point defects and inhomogeneities ($\sim 10^{19}$cm$^{-3}$). These defects lead to considerable fluctuations of the electro-physical properties of crystals and their technical characteristics.

Usually, the doping of a semiconductor perturbs the material’s homogeneity and the introduced impurity states fall in the forbidden zone. However, in narrow gap semiconductors IV-VI ($A^4B^6$) and V-VI ($A^5B^6$), some species of impurities create quasi-local states located on the background of the allowed zone(s). Sn is such an unusual acceptor-like impurity in $Bi_2Te_3$. According to Zhitinskaya et. al.[1], and Kulbachinskii et. al.[2], doping of $Bi_2Te_3$ with Sn results in the formation of a band of the quasi-local states on the background of the valence band (VB) of bismuth telluride. Additionally, the impurity states of Sn stabilize the
concentration of holes in the VB by pinning down the Fermi level. This leads to considerable improvement of the spatial homogeneity of electro-physical properties of crystals Bi$_2$Te$_3$:Sn.

The Sn doped Bi$_2$Te$_3$ crystals studied by Zhitinskaya[1], Kulbachinskii[2], and Laiho[3] had different content of Sn and location of $E_F$. For meaningful crystal properties comparison, it is necessary to fix the content of Sn and to vary the Fermi level by doping with an additional impurity. In view of this, we pursue work on samples of Bi$_2$Te$_3$ doped with 0.5% Sn, which were additionally doped with iodine (I), as introduced in the form of SbI$_3$ (0.05% in sample #97 and 0.1% in #98). We investigate the nuances between the two compositions by obtaining magnetoresistance at various temperatures the range of 300 K down to 2 K.

The textbook [4] magnetoconductivity is given by

$$\sigma_{xx}(H) = \frac{\sigma_0}{1 + (\omega_c \tau)^2}$$

with $\omega_c = \frac{eH}{m}$. Rewriting this as the magnetoresistivity, $\rho_{xx}(H) = \rho_0(1 + (\omega_c \tau)^2)$ and further as:

$$\frac{\rho_{xx}(H) - \rho_0}{\rho_0} = \frac{R_{xx}(H) - R_0}{R_0} = (\omega_c \tau)^2 = \left(\frac{e^* H}{m}\right)^2.$$

Thus, for low to moderate field, the coefficient of the quadratic term in $H$ is $(\frac{e^*}{m})^2 = \mu^2$, just the squared mobility. The conductivity $\sigma_0 = \frac{1}{\rho_0} = pe\mu$, therefore resistivity measurements, in zero field along with scans to high fields, allow for the mobility to be obtained, and for concentration of carriers $p$ to be deduced, using the standard four-contact method instead of five or six contacts. This is especially convenient for highly magnetoresistive materials where Hall measurements may require more steps due to alignment difficulty of transverse contacts, as compared to longitudinal. This is also in the reverse order of the traditional method of measuring the resistivity and the Hall coefficient, which depend on the thickness of the sample, and then deducing the carriers mobility.

Previously, we reported on the resistivity temperature dependence, the low temperature SdH[5, 6], and specific heat[6]. Here, we expand on those results of the two compounds in light of the above and report on the carriers mobility and concentration and their temperature dependence, as well as the temperature dependence of SdH oscillations and estimate the carrier effective mass.

2. Experimental Details

The resistance measurements were carried out on thin samples using the standard four-point method, as has been described in previous reports [5, 6] and references therein. The applied magnetic field is perpendicular to the basal layers of the material and the probing current is parallel to them. All measurements were done in a Quantum Design PPMS cryostat with a superconducting magnet capable of ramping the field at 0.6 T/min. up to 9 T and sample’s temperature control for setting, holding and reproducibility < 1%.

The heat capacity measurements were carried out in the same PPMS cryostat using the pulsed method, whereby a heat pulse is applied while monitoring the sample’s temperature during the heating and drifting without heat. Then, standard routines were used in fitting temperature time response to obtain the heat capacity. This was done twice at the same temperature in the range 2 K - 295 K, first for determining the heat capacity of the addenda and then for the sample and addenda. The difference yields the sample’s heat capacity which can be converted into the molar specific heat.

3. Results and Discussion

First, we present the magnetoresistance in an applied magnetic field perpendicular to basal planes (0 < $H$ < 9T) for the two compounds at a multitude of temperatures (12 K- 280 K).
Figure 1. Magnetoresistivity, $\frac{\rho(H) - \rho_0}{\rho_0}$ vs. $H$ of $Be_2Te_3$ doped with 0.5% Sn and 0.05% SbI$_3$ (#97) at various temperatures.

Figure 2. Magnetoresistivity, $\frac{\rho(H) - \rho_0}{\rho_0}$ vs. $H$ of $Be_2Te_3$ doped with 0.5% Sn and 0.1% SbI$_3$ (#98) at various temperatures.

The data are shown in Fig. 1 for #97 and Fig. 2 for #98. Both sets of data show a positive magnetoresistance with a quadratic field dependence ($H < 2T$), which deviates at high fields and decreases with temperature. Note that the magnetoresistance for #97 is $2\times$ higher than for #98 and the spacings between the curves from one temperature to the next are different. Additionally, the magnetoresistance starts exhibiting quantum oscillations for $H > 2.5$ T and at temperature as high as 12 K.

For every temperature $\frac{\rho(H) - \rho_0}{\rho_0}$ vs. $H$, for $H < 1$ T, was least squares fit to a second order polynomial and the resulting coefficient of $H^2$ was used to obtain the mobility, $\mu$. Fig. 3 shows a log-log plot of $\mu$ as a function of $T$; as highlighted by the straight lines, $\mu$ decreases with temperature as $T^{-1}$ for #97 sample and slightly steeper then that for sample #98, indicative of additional scattering besides phonons, due to the added impurities. Below 10 K, both compounds have constant mobilities but of lower value for #97 sample and slightly steeper then that for sample #98, indicative of additional scattering besides phonons, due to the added impurities. Below 10 K, both compounds have constant mobilities but of lower value for #97 due to higher impurities and the other way around above 30 K due to phonons.

Further, using $\mu$ and $\rho(0)$ at that same temperature, one can deduce the carrier density, which is graphed in Fig. 4. Note the carrier density for #97 is constant ($\sim 2 \times 10^{18}$ cm$^{-3}$) up to 50 K then increases with temperature, and is higher than for #98, which is constant ($\sim 1.5 \times 10^{18}$ cm$^{-3}$) up to 10 K at most, and decreases to minimum between 150 and 200K and then increases with temperature. This behavior is consistent with the additional SbI$_3$ impurities, as they populate the valence band and create defects whose scattering effects become more prominent at intermediate temperatures.

The magnetoresistance for #97 for various low temperatures is shown in Fig. 5 and exhibits only one period of oscillations, which indicates that only one type of holes (light holes) effectively contribute to all transport properties in this system. The single period of oscillation is confirmed by extraction of the oscillations from the signal. This was accomplished by fitting the original data to a power law in $H^{-1}$, judged better than a polynomial, and subtracting it to obtain the
Figure 3. $\mu$ vs. $T$ for #97 (blue) and #98 (red), as obtained from the coefficient of $H^2$ in $\frac{\mu(H) - \mu_0}{\mu_0}$ vs. $H$ at the relevant temperature.

Figure 4. The Carrier density, $p(T)$, as deduced from the mobility and resistivity at the relevant temperature.

Figure 5. SdH Oscillations of #97 for field scans at several low temperatures (2 K to 12 K).

Figure 6. $\ln(A/T)$ vs. $\ln(T)$ (#97) for $2K < T < 7K$, showing the linear fit used to estimate $m^*$.

oscillating part. Then, using sine and cosine Fourier Transforms to assert the single frequency (11 T) and obtain the amplitude and its weak temperature dependence, as shown in Fig. 6. From the linear fit of $\ln(A/T)$ vs. $\ln(T)$ one can estimate [7] the carriers effective mass, $m^* \sim 0.2m_e$.

Second, we show the specific heat results in a log-log plot of the molar specific heat vs. temperature in Fig. 7. Note the linear behavior in low T and the saturation at high. The low
Figure 7. Molar specific heat, $C_P(T)$ for both compounds in the range 2K - 300K.

Figure 8. $\ln(C_P)$ vs. $\ln(T)$ in the range 2K - 10K, with least squares linear fits.

$T$ behavior is further shown to exhibit a power law with an exponent, $p=3.5$, as seen in Fig. 8. The high $T$ saturation has a value of $\sim 12R$ indicative of 24 degrees of freedom for atomic vibrations.

4. Conclusion

The introduction of donor impurity (iodine) with the same order of concentration as $Sn$ impurity, maintains the $Sn$ impurity zone but affects the filling factor of these states and shifts the Fermi level. The observation of quantum oscillations is a demonstration of excellent spatial homogeneity of electrical properties of quasi-local states of $Sn$. The observed frequency is 11 Tesla and the temperature variation of the amplitude of oscillations allows for an estimate of an effective mass of $0.2m_e$. Both results are an indication of a light effective mass and skinny cross-section ellipsoidal pocket. The specific heat temperature dependence is typical except for the low temperature $T^{3.5}$, which warrants even lower temperature heat capacity measurements.

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References

[1] M K Zhitinskaya, S A Nemov and T E Svechnikova 1997 Semiconductors 31, 375
[2] V A Kulbachinskii, A Y Kaminskii, N Miyajima, M Sasaki, H Negish, and H Kadomatsu 1999 JETP Letters 70 (11), 767.
[3] R Laiho, S A Nemov, A V Lashkul, E Lahderanta, T E Svechnikova and D S Dvornik 2007 Semiconductors 41 (5), 546.
[4] Kittel, 2005 Introduction to Solid State Physics J. Wiley
[5] M Z Tahar, S A Nemov, D I Popov and T E Svechnikova J. Phys.:Conf. Ser. 150 (2009) 022082
[6] M Z Tahar, D I Popov and S A Nemov J. Phys.:Conf. Ser. 400 (2012) 042056
[7] D Shoenberg, Magnetic Oscillations in Metals Cambridge University Press 1984