Electronic properties of $Sn$ and $SbI_3$ doped single crystal $p$-$Bi_2Te_3$

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Abstract. Traditionally impurity energy states fall in the band gap, which leads to statistical distribution of free carriers, contributing to spatial inhomogeneity, and small high-field Shubnikov-de Haas (SdH) oscillations in solid solutions of $Bi_2Te_3 - Sb_2Te_3$, the most common room temperature thermoelectrics. However, in these solid solutions with $Sn$ impurity, the $Sn$ states pin the Fermi level and tremendously improve the spatial homogeneity of carriers. This results in observation of high-amplitude SdH oscillations in lower magnetic field. The Fermi level was estimated to be at the top of the second valence band (heavy holes). However, the additional doping has not been studied. We chose $Bi_2Te_3$ doped with $Sn$ and $I$ impurities to shift the Fermi level and investigate the model that best fits the $Sn$ impurity states. The introduction of similar levels of concentration for the two dopants preserves the $Sn$ impurity states but affects the filling factor. Our results of SdH effect show different frequencies around 4.2 K for samples with 0.05 % and 0.1 % of $I$ and no feature in specific heat at low temperature. This indicates that the model for one-electron states in $Bi_2Te_3$ doped with $Sn$ is that of two impurity bands with the Fermi level pinned in-between.

1. Introduction

Bismuth telluride ($Bi_2Te_3$) is the narrow gap semiconductor with $E_g \sim 0.1$ eV. It is of practical importance since it is a foundation compound for developing high efficiency thermoelectric materials used for manufacturing cooling devices operating at room temperatures. $Bi_2Te_3$ belongs to the class of layered $R_{30mm}$ structures. The anisotropy of physical properties and peculiarities in its phase diagram result in the fact that even the most perfect crystals are characterized by a large quantity of various point defects and inhomogeneities ($\sim 10^{19} \text{cm}^{-3}$). This leads to considerable fluctuations of the electro-physical properties of crystals and their technical characteristics.

Usually impurities in semiconductors do not create impurity states in the allowed zone, but in the forbidden zone, which leads to statistical distribution of free carriers, contributing to spatial inhomogeneity and low-amplitude Shubnikov-de Haas (SdH) oscillations at high-field. However, a number of impurities in narrow gap semiconductors IV-VI ($A^4B^6$) and V-VI ($A^4B^6$) create quasi-local states on the background of the allowed zone of the conduction electrons or holes [1]. The same phenomenon has been observed by Kulbachinskii et al [2] in $Bi_2Te_3 - Sb_2Te_3$ solid solutions, the most commonly used room temperature thermoelectrics. For the first time
quantum oscillations of SdH effect in a bulk sample (for these systems) were observed, with the tendency of magnetoresistance saturation but not the full saturation. Further, the SdH oscillations started only at \( \sim 10 \) Tesla.

Doping of \( \text{Bi}_2\text{Te}_3 - \text{Sb}_2\text{Te}_3 \) with \( \text{Sn} \) leads to formation of a band of the quasi-local states on the background of the valence zone (VZ) of \( \text{Bi}_2\text{Te}_3 - \text{Sb}_2\text{Te}_3 \). Also the impurity states of \( \text{Sn} \) stabilize the hole concentration in the VZ and pin down the Fermi level. This results in considerable improvement of a spatial homogeneity of electro-physical properties of \( \text{Bi}_2\text{Te}_3 : \text{Sn} \) [3], which allowed for the observation of high-amplitude SdH oscillations in lower magnetic field ( 3 Tesla), see Laiho et al [4]. This is and indication of the existence of the \( \text{Sn} \) impurity states in the valence band of \( \text{Bi}_2\text{Te}_3 \). The position of the Fermi level was estimated to be at the top of the second valence band (heavy holes). From the Hall effect measurements the Fermi level was estimated at 15-25 meV, due to its pinning effect by the \( \text{Sn} \) impurities; this can be also regarded as the average energy of the \( \text{Sn} \) states.

In order to study the behavior of the \( \text{Sn} \) impurity states, an additional iodine donor-like impurity was introduced to shift the Fermi level in order to understand what model can be used for the \( \text{Sn} \) states. In view of this, the present work is on single crystals of \( \text{Bi}_2\text{Te}_3 \) doped with 0.5\% \( \text{Sn} \), which were additionally doped with iodine. The iodine was introduced in the above crystals in the form of \( \text{SbI}_3 \) in concentrations of 0.05\% (\#97) and 0.1\% (\#98).

\( \text{Sn} \) is considered to be an acceptor impurity, while iodine is definitely a donor impurity. However, the picture is more than complicated. This is due to presence of many different point defects - vacancies (Shottky defects), pair defects (Frenkel) and antisites. \( \text{Bi}_2\text{Te}_3 \) has a layered structure in the form \( (\text{Te}(1) - \text{Bi} - \text{Te}(2) - \text{Bi} - \text{Te}(1)) \). So, based on the 2 \( \text{Te} \) different positions, an introduction of impurities shifts the equilibrium of defects, with hard to predict result as they depend prevailing conditions (temperature, pressure, etc...) during doping. However, the effect of stabilization (pinning) of the Fermi level may be observed only if the impurity (\( \text{Sn} \), here) band is partially filled with electrons. Then the band can donate and accept electrons, thus compensating the influence of the various defects, above.

2. Experimental Details

The transport measurements were carried out on thin samples (\( \sim 80\mu\text{m} \)), which were cleaved off a thicker slab using adhesive tape, which was subsequently removed using acetone. Four electrical contacts were made using a two component silver loaded epoxy which was cured at ambient temperature for 24 hrs. Special attention was made for the current contacts across the edge of the sample and the voltage contacts were made in the middle third of the sample to minimize the anisotropy effects and maximize the sensed voltage. Since the materials have thermoelectric properties that may depend on the kind of leads, and the temperature and its gradient across the leads we chose AC excitation current and used a floating current sources [5] and lock-in-detectors at relatively low frequency. Because we measured two samples at a time we chose 7 Hz and 13 Hz as two prime number frequencies which are neither multiples nor submultiples of the line frequency and cannot interfere with each other constructively. To avoid sample self heating the excitation currents were so that the total power dissipation was under 5\( \mu \text{W} \). As for the quantum oscillations, the samples were inserted in a cryostat with a superconducting magnet capable of generating a 10 Tesla field. The field ramping up and down was at a maximum rate of 0.5 Tesla/minute. The specific heat measurement were also carried out using AC method[6], whereby a low frequency (2 - 10 Hz) AC current supplied to heater glued with diluted GE varnish on one end of the sample (in vacuum), while monitoring the temperature of small ruthenium oxide resistor a distance (\( \sim 0.5 \) cm) on the other end of the sample, which was also glued to a \( \text{Cu} \) link to the He bath.
3. Results and Discussion

First, we present the magneto-resistance in an applied magnetic field, $0 < H < 10T$, for the two compositions at 4.2 K. The data is for field ramping up and down and as can be seen (Fig.11), both curves show little or no hysteresis and a positive magneto-resistance with a quadratic field dependence, with a slight deviation at low fields. The magneto-resistance for both samples starts exhibiting quantum oscillations for $H \sim 2.5$ T. The oscillating part of magneto-resistance for both samples (Fig.2) shows only one period of oscillations, which shows that only one type of holes (light holes) effectively contribute to all transport properties in this system. Both samples (#97 and #98) exhibit relatively similar values of the Fermi surface cross sections (11.1 and 10.2 Tesla, respectively), differing by 10%, which is similar to the difference in Hall concentrations for these samples. Therefore, the holes effective mass stays close for the two donor doping concentrations, which shows that iodine doping does not change the zone structure of $Bi_2Te_3$ much, if at all. The non-oscillating part of magneto-resistance $\rho_{xx}(H)$ tends to saturate, and can be described by the relation\cite{4}, $\frac{R(H)}{R_0} = \frac{\rho(H)}{\rho_0} = \frac{1+(R_{0\sigma_0}H)^2/f_\parallel}{1+(R_{0\sigma_0}H)^2}$, which leads to the linearized relation $\frac{H^2}{(\rho(H)−\rho(0))/(\rho(H))} = a + bH^2$, where $a = \frac{1}{(f_\parallel−1)(R_{0\sigma_0})^2}$ and $b = \frac{1}{(f_\parallel−1)}$.

Figure 3. Non-oscillating part of magnetoresistance of samples #97 and #98) at 4 K, showing a linear fit in the high field region.

Figure 4. Molar specific heat vs. $T^2$ of sample #98 below 4.2 K, with different behavior at lower and higher temperatures.

Thus, from the magnetoresistance data and the Hall mobility of carriers, $(R\sigma)$, the Hall factor $f_\parallel$ in $H$ direction can be evaluated and Fig. 3 as graph of the linearized relation, using
the experimental data of Fig. 1 is given for that purpose. Note that at low fields the law $a + bH^2$ does not hold. There is no saturation observed, though non-dimensional field $\mu H/c (\mu$-mobility) for these samples is of the order of 6. The above equations allow for determination of the mobility in the crystallites of polycrystalline samples. The Hall factor has an average value of $\sim 0.35$ (0.41 for #97 and 0.29 for #98), and is highly influenced by the effective mass anisotropy and the orientation of the energy ellipsoids in the six-ellipsoid model of Drabble-Wolfe [7] with respect to crystallographic axis. Thus, the deviation from the classical law at low fields, no saturation and the significant difference in the Hall factor between the two samples, which cannot be attributed to the change in the hole concentration, require further investigation. From the above equations one can estimate the Hall mobility, $R_\sigma$, to be $0.7 \times 10^4$ for #97 and $0.58 \times 10^4$ for #98. These values are higher than the values for $Be_2Te_3$ with no $Sn$ impurity [2], indicating that there is no resonance scattering, as in $PbTe$ doped with $Tl$ [8], which makes the presence of two-level electron systems, one level filled and one is empty is more viable.

Second, we report specific heat measurements results, as shown in Fig. 4, as $c(T)/T$ vs. $T^2$, to exhibit the electronic and lattice contributions, with a $\Theta_D \sim 60$ K which is comparable to that of major elements in this material. There is a peak at $\sim 2.3$ K that may be attributed to a Schottky anomaly, which indicative of the presence of two-level system. However, zone structure in these compounds can be even more complicated if one-zone model of Drabble-Wolfe [7] does not hold. The valence band in $Bi_2Te_3$ is realized via p-orbitals, where $Sn$ substitutes $Bi$ with 3 p valence electrons and has one extra electron in the outer shell. The valence equal to 1 is non-observable, therefore it is quite possible that 2 $Sn$ atoms, 1 electron each in the outer shell, exchange electrons, so that if a two-level electron system for $Sn$ electrons is viable for $Bi_2Te_3$ solid solutions doped with $Sn$, the disproportionation reaction occurs: $2Sn(1e) \rightarrow Sn(0) + Sn(2e)$

4. Conclusion

The introduction of iodine impurity with the same order of concentration as $Sn$ impurity, maintains the $Sn$ impurity zone but affects the filling factor of these states by holes. The observation of quantum oscillations is a demonstration of excellent spatial homogeneity of electrical properties of quasi-local states of $Sn$. The results indicate that the most probable model for one-electron states in $Bi_2Te_3$ solid solutions doped with $Sn$ is the presence of two impurity bands - one filled and one empty of carriers with the Fermi level pinned in-between, which can be described by disproportionate reaction $2Sn(1e) \rightarrow Sn(0) + Sn(2e)$ with respect to $Bi$ sub-lattice. However, zone structure of $Bi_2Te_3$ solid solutions doped with $Sn$ seems to be more complicated than one-zone model proposed by Drabble and Wolfe. This requires further investigation.

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