Correlation of Hall and Shubnikov-de Haas Oscillations and Impurity States in \textit{Sn}- and \textit{I}- Doped Single Crystals \textit{p-Bi}_2\textit{Te}_3

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Abstract. Oscillations of the Hall coefficient and Shubnikov-de Haas (SdH) were observed in \textit{p-Bi}_2\textit{Te}_3 crystals doped with \textit{Sn} (acceptor) and with \textit{I} (donor) in magnetic fields up to 9 T parallel to the C\textsubscript{3} trigonal axis at low temperatures (2 K < T < 20K), which is an evidence of the spatial homogeneity of carriers in complex solid solutions. This supports the existence of a narrow band of \textit{Sn} states (partially filled) against the background of the valence band acting as a reservoir with high density of states partially filled with electrons. Previously, in these systems in which the Fermi level was in the light-hole valence band, both large Hall and SdH oscillations were observed, with \sim \pi phase shift between them, whereas when the Fermi level was in the heavy-hole valence band (larger acceptor content), no quantum oscillations were observed. It was concluded that the observed low amplitude quantum oscillations may be attributed to the shifting of the reservoir from the light-hole band to the heavy-hole, and the observed phase shift in the range 0 - \pi/2 between Hall and SdH oscillations may be attributed to filling factor of the reservoir with electrons, which varies with \textit{I} content. Experimental results along with theoretical explanation of these correlations are presented.

1. Introduction

Bismuth telluride (\textit{Bi}_2\textit{Te}_3) is a narrow gap semiconductor with \textit{E}_g \sim 0.1 \text{ 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. \textit{Bi}_2\textit{Te}_3 belongs to the class of layered \textit{R}_3\textit{snm} 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 (\times 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 statistics 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 ($A^3B^6$) and V-VI ($A^2B^6$) 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 \textit{et al} [2] in \textit{Bi}_2\textit{Te}_3-$\textit{Sb}_2\textit{Te}_3$ solid solutions, the most commonly used room temperature thermoelectric materials. 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 to full saturation. Further, the SdH oscillations started only at 10 Tesla.

Doping of \textit{Bi}_2\textit{Te}_3 - $\textit{Sb}_2\textit{Te}_3$ with \textit{Sn} leads to formation of a band of the quasi-local states on the background of the valence zone of \textit{Bi}_2\textit{Te}_3 - $\textit{Sb}_2\textit{Te}_3$. Also the impurity states of \textit{Sn} stabilize the hole concentration in the valence zone and pin down the Fermi level. This results in considerable improvement of the spatial homogeneity of electro-physical properties of \textit{Bi}_2\textit{Te}_3-$\textit{Sn}$ [3], which allows for the observation of high-amplitude SdH oscillations in lower magnetic field (3 Tesla), see Laiho \textit{et al}. [4]. This is an indication of the existence of the \textit{Sn} impurity states in the valence band of \textit{Bi}_2\textit{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 0.015-0.025 eV, due to its pinning effect by the \textit{Sn} impurities; this can be also considered as the average energy of the \textit{Sn} states.

In order to study the behavior of the \textit{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 Sn states. In view of this, the present work is on samples of Bi₂Te₃ doped with 0.5% Sn, which were additionally doped with iodine. The iodine was introduced in the above crystals in the form of Sbl₃ in concentrations of 0.05% (#97) and 0.1% (#98).

Sn is considered to be an acceptor impurity, while iodine is definitely a donor impurity, however, the picture is more complicated. This complication is due to the presence of many different point defects - vacancies (Schottky defects), pair defects (Frenkel) and anti-sites. Bi₂Te₃ has a layered structure in the form (Te(1)-Bi₂-Te(2)-Bi₂-Te(1)). So, based on the two Te different positions, an introduction of impurities shifts the equilibrium of defects, with hard to predict results since they depend on prevailing conditions (temperature, pressure, etc.) during doping. However, the effect of stabilization (pinning) of the Fermi level may be observed only if the impurity (Sn, here) band is partially filled with electrons. Then the band can donate and accept electrons, thus compensating for the influence of the various defects.

2. Experimental Details

The magnetoresistance (MR) and Hall Effect measurements were carried out in magnetic field (0 < H < 9 T) on thin samples (~ 80 μm), which were cleaved off of 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 source [5] and lock-in-detectors at relatively low frequency. Because we measured two samples at a time we chose 7.00 Hz and 13.0 Hz as two prime number frequencies which are neither multiples nor submultiples of the line frequency and cannot interfere with each other constructively.

To correlate the magnetoresistance and Hall Effect measurements we used six point contacts on a single sample and used two lock-in-detectors one for each signal. Additionally, to enhance the Hall Effect signal over the MR contribution, the ratio of the width of the sample to the distance between the longitudinal (MR) contacts was set at 5/6 – 6/7 and Hall contacts were aligned facing each other to better than 0.25 mm or ~1/20 the width of the sample. To avoid sample self-heating the excitation currents were inserted in a cryostat with a superconducting magnet capable of generating a 9 Tesla field. The field ramping up and down was at a maximum rate of 0.6 Tesla/minute, while the temperature was kept constant to better than 0.05K.

3. Results and Discussion

First, from the Hall Effect measurements in low magnetic field and resistivity measurements (magnetoresistance at zero field) the concentration of holes was deduced (see Fig.1 and Fig.2 for #97 and #98, respectively). This is quite different from Bi₂Te₃ samples with no impurity states (no Sn in our case). The observed constant concentration of holes for a certain range of temperatures (especially well seen for #98) is a characteristic of impurity states pinning the Fermi level, so that scattering of charge carriers on impurities becomes dominant up to higher temperatures. When more additional donor impurity (I in our case) is introduced in a sample, intrinsic conductivity becomes less significant and the Fermi level stabilizes up to higher temperatures, which can be seen by comparison of Fig. 1 and Fig. 2.

Second, we present the results of magnetoresistance measurements in an applied magnetic field 0 < H < 9T, for the two compositions at different temperatures (2 – 280K). The data is for field ramping up and down and as can be seen (Fig. 3 and Fig. 4), both curves show little or no hysteresis and a positive magnetoresistance with a quadratic field dependence, with a slight deviation at low fields. The non-oscillating part of magnetoresistance ρₓₓ(Hₓ) tends to saturate, and can be described by [4] the relation:

\[
\frac{R(H)}{R_0} = \frac{\rho(H)}{\rho_0} = 1 + \frac{H^2}{\frac{1}{1} + \frac{a}{1} \left(\frac{\rho(H)-\rho_0}{\rho_0}\right)^2}
\]

which leads to

\[
\frac{H^2}{\left(\frac{\rho(H)-\rho_0}{\rho_0}\right)^2} = a + bH^2,
\]
where $a = \frac{1}{(f_{||} - 1)(R_\sigma \sigma_0)^2}$ and $b = \left(\frac{1}{f_{||}} - 1\right)$. Thus, from the above equations, the coefficients $a$ and $b$ can be evaluated, then using their value the coefficients of the Hall carrier mobility, $R_\sigma \sigma_0$, and the Hall factor $f_{||}$ can be obtained.

Figure 1. Carrier concentration of $Be_2Te_3$ doped with 0.5% $Sn$ and 0.05% $SbI_3$ (#97) from 4.2K up to 280 K.

Figure 2. Carrier concentration of $Be_2Te_3$ doped with 0.5% $Sn$ and 0.1% $SbI_3$ (#98) from 4.2K up to 280 K.

Figure 3. Magnetoresistance, $\Delta p(H)/p_0$ vs. H of $Be_2Te_3$ doped with 0.5% $Sn$ and 0.05% $SbI_3$ (#97) at various temperatures.

Figure 4. Magnetoresistance $\Delta p(H)/p_0$ vs. H of $Be_2Te_3$ doped with 0.5% $Sn$ and 0.1% $SbI_3$ (#98) at various temperatures.

We found that the Hall factor has an average value of 0.35 (0.41 for #97 and 0.29 for #98), and is highly influenced by the anisotropy of effective mass and the orientation of the energy ellipsoids in the six-ellipsoid model of Drabble and Wolf [6] with respect to crystallographic axis. The difference in the Hall factor between the two compositions can also be explained by the deviation from classical square
root dependence of the density of states on energy. From the above equations the mobility, $R_0/g_{86}$, was evaluated and plotted together with the hole mobility obtained from the Hall effect in low magnetic field (see Fig.5 and Fig.6).

The higher values of mobility at low temperature, in comparison with undoped samples [7] are an indication of less variety of defects and smaller fluctuation of volumetric concentration. The difference in mobility obtained from the Hall Effect measurements and from magnetoresistance measurements at high fields may be attributed, first of all, to temperature dependence of the Hall factor, however, different non-linear effects should not be overlooked.

![Figure 5](image1.png)  
**Figure 5.** Hall mobility $\mu_{H}$ (diamonds) and magnetoresistance mobility $\mu_{MR}$ (squares) of Be$_2$Te$_3$ doped with 0.5% Sn and 0.05% SbI$_3$ (#97) from 4.2K up to 280 K.

![Figure 6](image2.png)  
**Figure 6.** Hall mobility $\mu_{H}$ (diamonds) and magnetoresistance mobility $\mu_{MR}$ (squares) of Be$_2$Te$_3$ doped with 0.5% Sn and 0.1% SbI$_3$ (#98) from 4.2K up to 280 K.

Third, we observed SdH and Hall oscillations in magnetic fields $0 < H < 9$ T for the two compositions below 4.2 K. The magnetoresistance for both samples starts exhibiting quantum oscillations for H ~ 2.5 T. The oscillating part of magnetoresistance for both samples (Fig.7) shows only one period of oscillations, which indicates that only one type of holes (light holes) contributes effectively to all transport properties in this system.

From the oscillation part of SdH and Hall Effect it was found that the period of oscillations in the inverse magnetic field $P(1/H)$ is $0.09$ T$^{-1}$ for the sample #97 and $0.1$ T$^{-1}$ for the sample #98. As known [8], the period of quantum oscillations $P(1/H)$ in SdH effect and Fermi surface cross section $S_F$ are related as $P(1/H) = \frac{2m_e}{eB_S F}$. Both materials (#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, for T< 10K.

Therefore, the hole effective masses stay close for the two donor doping concentrations, which shows that iodine doping does not change the zone structure of Bi$_2$Te$_3$ much, if at all. It has been shown in [9] that for 6-ellipsoid model of Drabble and Wolfe [6] $S_F = \frac{\pi^2}{3 \pi^2} \frac{\alpha_1 \alpha_2}{\sqrt{\alpha_1^2 \alpha_2^2}}$, where $K_6$ is the number of ellipsoids (6 in the Drabble-Wolfe model), $\alpha_{11}$, $\alpha_{22}$, $\alpha_{33}$, and $\alpha_{23}$ are the components of effective mass tensor, while $p$ is the full concentration of holes. From the above equation it is possible to find the full concentration of holes $p$, assuming that the Sn impurity does not change the shape of the ellipsoids. It was found that $p = 1.37 \times 10^{18}$ cm$^{-3}$ for the sample #97 and $p = 1.15 \times 10^{18}$ cm$^{-3}$.
for the sample #98. This is in good agreement with the concentration of holes at same low temperature obtained from the Hall Effect measurements (see Figs.1 and 2), where \( p = 1.34 \times 10^{18} \) cm\(^{-3}\) for sample #97 and \( p = 0.94 \times 10^{18} \) cm\(^{-3}\) for sample #98.

![Graph](image-url)

**Figure 7.** Oscillating part of magnetoresistance of \( \text{Be}_2\text{Te}_3 \) doped with 0.5\% Sn and 0.05\% \( \text{Sb}_1 \) (red) and 0.1\% \( \text{Sb}_1 \) (blue) at 4 K

In connection with quantum oscillations an interesting fact should be mentioned. Quantum oscillations for sample #97 were observed in the range of temperatures 2K – 7K. The amplitude of these oscillations exponentially decreased with an increase in temperature (40\% difference between 2K and 7K), whereas the oscillation frequency remained essentially the same (within 2\%), which is another evidence of the fact that the Fermi level is pinned by the Sn impurity states and does not change with temperature, making the system electrically well-stabilized.

Whereas in [4] the phase shift between SdH and Hall effect oscillations was about \( \pi \), in the present measurements the phase shifts of \( \pi/8 \) and \( \pi/6 \) were observed for sample #97 (see Fig.8) and #98, respectively, which is in correlation with the filling factor of Sn impurity states by electrons / holes.

Besides well-known conditions that should be met in order for quantum oscillations to be observed, i.e. the spacing between Landau levels should be higher that thermal broadening (\( h\omega_c \gg kT \)); the broadening due to scattering is less than the spacing between Landau levels (\( \omega_c \tau \gg 1 \)); and the Fermi level is higher than at least some of the Landau levels (\( \varepsilon_F > h\omega_c \)), for heavily doped systems the following condition must be met [7]: \( \sqrt{\langle \delta\varepsilon^2 \rangle} \ll h\omega_c \). This means that spatial fluctuations of chemical potential are much less than the spacing between Landau levels, i.e. the samples are electrically homogeneous.

4. Conclusion

The observation of quantum oscillations is a demonstration of excellent spatial homogeneity of electrical properties of quasi-local states of Sn, which act as a reservoir of charge carriers pinning the Fermi level and minimizing spatial fluctuations of chemical potential.

The results indicate that the most probable model for one-electron states in \( \text{Bi}_2\text{Te}_3 \) 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 - is the one that can be described by disproportionation reaction \( 2\text{Sn}(1e) \rightarrow \text{Sn}(0)^+ + \text{Sn}(2e) \) with respect to \( \text{Bi} \) sub-lattice.
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