Physics of Semiconductors. Semiconductors

UDC 538.9 + 535.3

EDN RVKOKJ
https://www.doi.org/10.33910/2687-153X-2022-3-3-144-148

Nernst mobility of holes in Bi_2Te_3

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For citation: Nemov, S. A., Demyanov, G. V., Povolotskiy, A. V. (2022) Nernst mobility of holes in Bi_2Te_3. *Physics of Complex Systems*, 3 (3), 144–148. https://www.doi.org/10.33910/2687-153X-2022-3-3-144-148 EDN RVKOKJ
Received 1 June 2022; reviewed 6 June 2022; accepted 6 June 2022.
Funding: The study did not receive any external funding.

Abstract. This paper presents the results of a study of the electrical conductivity coefficient, the Hall coefficient, the Seebeck coefficient, the transverse Nernst-Ettingshausen coefficient and their anisotropy in a Bi_2Te_3 single crystal with a hole concentration $p = 1 \times 10^{10–19}$ cm^{-3} at temperatures 77–350 K. It is established that hole scattering occurs mainly on long-wave acoustic phonons. Despite the fact that the chemical potential level is located near the top of the additional extreme of the valence band, no interband scattering was detected. The complex structure of the valence band is confirmed.

Keywords: Bismuth telluride, hole conductivity, temperature dependence, specific electrical conductivity, thermopower coefficient, Hall coefficient, Nernst-Ettingshausen coefficient, hole scattering mechanism, Nernst mobility, acoustic phonons

Introduction

Currently, there is an unusual situation with the interpretation of experimental data on the transport phenomena in hole chalcogenides of elements V of group V of the Mendeleev table $Bi_{1-x}Sb_xTe_{1-y}Se_y$, including in Bi_2Te_3. Single-band and double-band models are used to describe experimental data on transport phenomena in the temperature range of 100–600 degrees Celsius. For example, at temperatures above room temperature, minor carriers are also taken into account.

On the one hand, temperature dependences of the coefficients of specific electrical conductivity (σ) and thermopower (α) do not have any features and have the form typical for strongly doped semiconductors. The electrical conductivity decreases according to the law $\sigma \sim T^{-n}$, $n \approx 1.7$, and the thermopower is proportional to the temperature $\alpha \sim T$.

Such dependences σ (T) and α (T) are well described by a single-band model at temperatures of 77–300 K with the participation of one class of current carriers in the transport phenomena. This model is convenient for estimating the fundamental parameters of the band structure, determining the dominant scattering mechanisms, and calculating the thermoelectric properties of material (Goltsman et al. 1972; Lukyanova et al. 2005).

On the other hand, there is a significant increase in the Hall coefficient R(T) with temperature, which is traditionally associated in semiconductor physics with the redistribution of holes between two non-equivalent extremes of the valence band. Thus, such a dependence of R(T) indicates a complex structure

of the valence band and the participation of several types of current carriers in the transport phenomena. In this case, the calculations usually use a two-band model with two types of holes with different effective masses m^*_1 and m^*_2, respectively.

It should also be noted that most of the previous studies of transport phenomena were not comprehensive. They were carried out on poly-crystal samples and had a practical orientation.

Considering the practical significance of solid solutions $Bi_{1-x}Sb_xTe_{1-y}Se_y$, which are the main components of materials used in thermoelectric energy converters, operating in the temperature range of 200–600 K it is is advisable to continue studying the electrophysical properties of crystals of these materials and, first of all, the main component Bi_2Te_3.

Experiment

In the present work, studies of the kinetic coefficients were carried out on a single crystal grown by the Czochralski method with a Hall hole concentration $p = 1 \times 10^{10-19}$ cm^{-3}. The choice of the crystal is due to the fact, that, according to quantum oscillation data, the chemical potential level μ at 4.2 K at such a hole concentration is located near the additional extreme of the valence band, in this case $\mu \approx \Delta E_v \approx 0.03$ эВ, where ΔE_v is the energy gap between the peaks of the nonequivalent bands (Sologub et al. 1975). In this case, if the two-band model of the valence band is valid, we can expect the manifestation of features in the kinetic coefficients and, first of all, in the transverse Nernst–Ettingshausen effect, related to the interband scattering of "light holes" during their transition to additional extrema at low temperatures ($T \geq 77$ K).

In this paper, the temperature dependences of the main kinetic Hall (R), electrical conductivity (σ), thermopower (α), and the transverse Nernst–Ettingsgazuen (Q) coefficients and their anisotropy in the temperature range 77–350 K were measured. The obtained values of the coefficients R, σ, and α and their temperature dependences almost coincided with the literature data for samples with close Hall hole concentrations. Their values used in calculations are shown in Table 1.

Table 1. Basic kinetic coefficients of the p-Bi_2Te_3 crystal

	T, K	σ_{11}, Om^{-1}cm^{-1}	R_{123}, cm^3/C	α_{11}, mcV/K	$\frac{Q_{123}}{k_0/e}, \frac{\text{cm}^{-2}}{V \times s}$	x < 0	r
1	100	4800	0.38	50	–450	–0.427	0.051
2	150	2600	0.45	90	–451	–0.370	0.094
3	200	1600	0.52	140	–400	–0.297	0.157
4	250	1100	0.56	180	–280	–0.218	0.230
5	300	800	0.54	205	–140	–0.137	0.319
6	350	500	0.38	202	–10	–0.225	0.323

Temperature dependences of two components of the Nernst–Ettingsgazuen tensor Q_{123} and Q_{132} are shown in Figure 1.

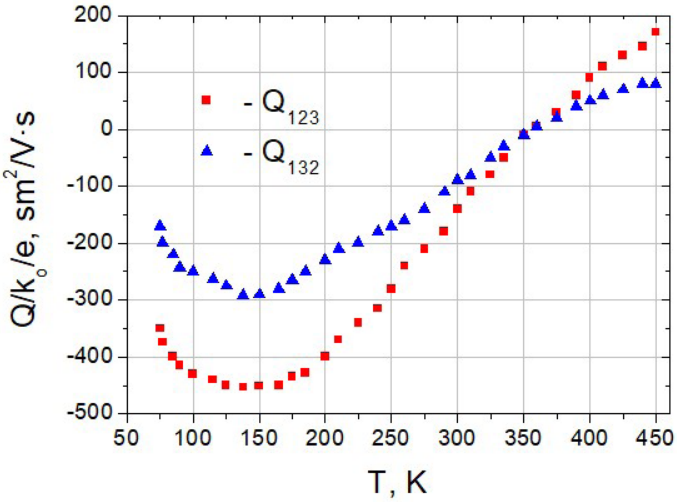

Fig. 1. Temperature dependence of the Nernst–Ettingsgazuen coefficient for a Bi_2Te_3 crystal$_2Te_3$ with a hole concentration *of* $1 \times 10^{10-19}$ *cm*$^{-3}$.

Note that the thermopower coefficient is isotropic and increases linearly with the temperature in the range of 85–250 K. The differences in the values of the Seebeck coefficients in the cleavage plane (α_{11}) and along the inversion-rotation axis $\bar{3}$ (α_{33}) are several MV/K, which does not exceed the measurement error. This result indicates that there is no noticeable anisotropy in the energy dependence of the hole relaxation time $\tau(\varepsilon)$ in Bi_2Te_3.

Discussion of experimental data

First of all, we note that measuring the four main kinetic coefficients R, σ, α, Q and their temperature dependences allows us to determine the main parameters of the band and structure of semiconductors, as well as the dominant scattering mechanisms in a single-band model (Zhitinskaya et al. 1966), and to conduct a correct analysis of experimental data for several types of current carriers.

Let us take a closer look at the obtained data. Let us start with the Hall effect. Both components of the Hall coefficient tensor R_{123} and R_{132} in hole chalcogenide materials $Bi_{1-x}Sb_xTe_{1-y}Se_y$ (including in Bi_2Te_3) (Goltsman et al. 1972; Sologub et al. 1975) grow with increasing temperature. Therefore, in the materials of group $A_2^{V}B_3^{VI}$, it is customary to determine the concentration of holes p from the larger component of the Hall tensor R_{77} at a temperature of 77 K. In p-Bi_2Te_3 there is a large component of the Hall tensor R_{132}. The concentration of holes is calculated by the formula

$$p = \left(eR_{77}\right)^{-1} \tag{1}$$

The concentration determined in this way is called the Hall concentration of holes and is used in all calculations of the parameters of the zone structure.

Note that Formula (1) does not take into account the hall factor associated with the anisotropy of the effective mass (it is approximately 0.7–0.8 for the coefficient R_{132} in p-Bi_2Te_3 (Goltsman et al. 1972). Thus, the real concentration of holes is about 20–30% more.

The Bi_2Te_3 single crystals studied by us had a Hall concentration of holes $p \approx 1 \times 10^{19}$ cm^{-3}, the maximum was observed in unalloyed bismuth telluride crystals obtained by deviation from the stoichiometric composition (Goltsman et al. 1972).

Our data on the Hall effect are consistent with the literature data (Goltsman et al. 1972). Both components of the Hall tensor R_{123} and R_{132} grow with increasing temperature from the value of R_{77} to R_{300} (at room temperature) by about 1.4 times.

Let us discuss in more detail the data on the Nernst–Ettingshausen transverse effect, which are presented in Figure 1 as a temperature dependence of the Nernst–Ettingshausen coefficient Q divided by a multiplier k_0/e (where k_0 is the Boltzmann constant, e is the electron charge modulus).

In this form, experimental data on the Nernst–Ettingshausen transverse effect are usually presented. The fact is that the coefficient $Q/(k_0/e)$ has a dimension of $cm^2/V{\cdot}s$, and its module is called the Nernst mobility. In such units of measurement, it is convenient to compare the Nernst and Hall mobility (Rσ).

As can be seen from Figure 1, both components of the Nernst–Ettingsgazuen tensor Q_{123} and Q_{132} are negative at $T \le 350$ K. This means that in the studied temperature range according to the formula for Q, valid for degenerate statistics

$$Q = \frac{k_0}{e} R\sigma \frac{\pi^2}{3} \frac{k_0 T}{\mu} \left.\frac{\partial \ln \tau}{\partial \ln \varepsilon}\right|_{\varepsilon=\mu}. \tag{2}$$

So, the energy dependence of the relaxation time of holes $\tau(\varepsilon)$ is a function decreasing with energy ε. This dependence has only two mechanisms of current carriers scattering: on acoustic phonons and interband scattering.

Note that the idea of interband scattering was introduced by N. V. Kolomoets (Zhitinskaya et al. 1966). The inclusion of this mechanism of hole scattering in samples with a chemical potential located near the top of the additional extremum of the valence band, that is, under the condition of $\mu \approx \Delta E_v$ in the region of nitrogen temperatures, can lead to features in the temperature dependence of the Nernst mobility. The fact that the interband scattering is characterized by the large negative value of the derivative $\left.\frac{\partial \ln \tau}{\partial \ln \varepsilon}\right|_{\varepsilon=\mu}$,

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as the relaxation time of "light" holes from the main extremum, in this case it is described by the expression according to (Kolomoets 1966):

$$\tau^{-1}(\varepsilon) = \tau_0^{-1} \begin{cases} \sqrt{\varepsilon}\ by\ \varepsilon < \Delta E_v \\ \sqrt{\varepsilon} + w_{12}\sqrt{\varepsilon - \Delta E_v}\ by\ \varepsilon > \Delta E_v \end{cases}, \tag{3}$$

where τ_0 is a constant coefficient in expression for the relaxation time of light holes when scattering by acoustic phonons $= \tau_0 \varepsilon^{-0,5}$; $w_{12} = \left(m_2^* / m_1^*\right)^{3/2} \left(\Xi_{12} / \Xi_{11}\right)^2$ is a parameter characterizing the probability of an interband transition of holes from the main to the additional extremum; m_1^* and m_2^* are the effective masses of the density of the states of holes in the first and second zones; Ξ_{11} and Ξ_{12} are the constants of the deformation potential for intraband and interband scattering of holes. Using the data on the four kinetic coefficients R, σ, α and Q, we will estimate the scattering parameter r, which is included in the expressed $\tau = \tau_0\, \varepsilon^{r-0,5}$ as part of a single-band model. Since the coefficients α and Q are equal, respectively

$$\alpha = \frac{k_0}{e}\frac{\pi^2}{3}\frac{k_0 T}{\mu}(r+1), \tag{4}$$

$$Q = \frac{k_0}{e}\frac{\pi^2}{3}\frac{k_0 T}{\mu} R\sigma\left(r - \frac{1}{2}\right), \tag{5}$$

we get an expression for their relationship

$$\frac{Q_{123}}{\alpha_{11} R_{123} \sigma_{11}} = \frac{r - 1/2}{r+1}, \tag{6}$$

where index 3 means the direction along the trigonal axis $\overline{3}$.

Denoting the experimental values of the relation by x

$$\frac{Q_{123}}{k_0/e} : \frac{\alpha_{11}}{k_0 e} \times R_{123}\sigma_{11} = x \tag{7}$$

we obtain an equation for determining the scattering parameter r

$$r = \frac{0,5 + x}{1 - x}. \tag{8}$$

The value of r obtained from experimental data is shown in Table 1, from which it can be seen that in the low temperature region the parameter r is close to zero. This means that in bismuth telluride at temperatures of 77 K and above, hole scattering on long-wave acoustic phonons dominates (parameter r = 0) and there are no signs of the inclusion of a new interband hole scattering mechanism.

As can be seen from Table 1, the parameter r does not decrease, rather, it shows a slight increase. So, there are no large modulo negative values of the scattering parameter characteristic of the interband scattering of holes. Thus, interband hole scattering is inefficient in p-Bi_2Te_3.

Perhaps, this is due to the fact that the transfer phenomena involve holes with slightly different effective masses of the density of states $m_1^* \sim (0,5-0,6)\, m_0$ and $m_2^* \sim (0,9-1,2)\, m_0$, where m_0 is the mass of a free electron. Estimates of effective masses are made for the two-band model (Goltsman et al. 1972; Sologub et al. 1975). In addition, the thermal blurring of the Fermi distribution function k_0T is comparable to the energy gap ΔE_v in the two-band model and the chemical potential μ, which eliminates the features in the energy dependence of the relaxation time of holes. Theoretical calculations of Bi_2Te_3 performed from the first principles confirm the complex structure of the valence band (Scheidemantel et al. 2003).

In conclusion, we note that at temperatures T > 250 K, non-basic carriers (electrons) appear and, in accordance with the theory of kinetic phenomena, the Hall coefficients and thermal EMF decrease, and the electrical conductivity increases. The Nernst–Ettingshausen coefficient at the same time sharply decreases in modulus and at temperatures T = 350 K it changes its sign to positive.

Conclusion

Thus, as a result of studies of the specific electrical conductivity, Hall coefficients, Seebeck coefficients and the Nernst-Ettingshausen transverse effect on a single crystal p-Bi_2Te_3 at temperatures of 77–350 K, it was found that the dominant mechanism of hole scattering is the scattering by long-wave acoustic phonons.

Due to the location of the chemical potential level μ in the studied crystal with a hole concentration of 1×10^{19} sm^{-3} near the top of the additional extremum ($\mu = \Delta E_v$) interband scattering was expected, however, it was not detected. Perhaps this is due to the fact that the holes involved in the transfer phenomena have slightly different effective masses, and the amount of thermal blurring of the Fermi distribution function k0T is comparable to the values of μ and ΔE_v.

The observed deviations of the experimental data on kinetic coefficients from the calculation results in the single-band approximation are associated with the complex structure of the valence band and the participation in the transfer phenomena of several groups of current carriers with different effective masses.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

The authors have made an equal contribution to the preparation of the text.

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