Semiconductors, 2022, Vol. 56, No. 14

Temperature dependences of electrical conductivity and magnetic susceptibility of crystals of solid solution Sb_2Te_3-Bi_2Te_3

© N.P. Stepanov[1,3], V.Y. Nalivkin[1], A.K. Gilfanov[1], A.A. Kalashnikov[2], E.N. Trubitsyna[3]

[1] Transbaikal State University,
672036 Chita, Russia
[2] Trans-Baikal Institute of Railway Transport,
672040 Chita, Russia
[3] Zabaikalsky Institute of Entrepreneurship,
672000 Chita, Russia
E-mail: np-stepanov@mail.ru

Received August 12, 2021
Revised August 28, 2021
Accepted August 28, 2021

Solid solutions Bi_2Te_3-Sb_2Te_3 continue to be the subject of numerous and versatile experimental studies due to their practical importance for thermoelectric materials science. In this regard, the problem of studying the regularities of changes in the state of the electronic system of these semiconductors from composition and temperature remains urgent. This paper presents the results of studying the temperature dependences of the magnetic susceptibility of Bi_2Te_3-Sb_2Te_3 crystals containing 10, 25, 40, 50, 60 mol.% Sb_2Te_3. The correlation of the behavior of the temperature dependences of the magnetic susceptibility and electrical conductivity is analyzed.

Keywords: magnetic susceptibility, diamagnetic susceptibility, temperature dependence of electrical conductivity.

DOI: 10.21883/SC.2022.14.53857.17

1. Introduction

The research into crystals of Bi_2Te_3-Sb_2Te_3 solid solutions, which were proposed to be used as thermoelectric materials as early as in the 1950s and feature a unique combination of properties that make them one of the leading materials in current commercial production of thermoelectric devices [1], is still ongoing. The dependences of their physical characteristics on the composition of solid solutions, the temperature, and the dopant impurity type and amount are being examined. In certain cases, anomalous variations of quantities affecting directly the thermoelectric efficiency of Bi_2Te_3-Sb_2Te_3 crystals with a complex structure of the valence band are observed [2]. Specifically, group III impurities, such as gallium Ga, indium In, or thallium Tl, introduced into *p*-type Bi_2Te_3-Sb_2Te_3 crystals reduce the hole density instead of raising it [2,3]. In view of this, studies focused on examining thoroughly the patterns of variation (most importantly, variation with temperature and composition) of the electron system state in Bi_2Te_3-Sb_2Te_3 crystals remain to be relevant. The aim of the present study is to investigate the patterns of variation of the magnetic susceptibility of Bi_2Te_3-Sb_2Te_3 crystals with temperature and ratio of components in the composition of the solid solution and to interpret them with account for the trends of variation of the temperature dependences of electric conductivity.

2. Crystals, samples, experimental procedure

Single crystals of Bi_2Te_3-Sb_2Te_3 solid solutions containing 10, 25, 40, 50, 60 mol% of Sb_2Te_3 and grown by the Czochralski method at the Baikov Institute of Metallurgy and Materials Science were examined. The initial materials were Te, Sb, Bi containing 99.9999 wt% of the base substance. The chemical composition of the grown single crystals was determined by atomic adsorption spectrometry. The quality of single crystals was verified by X-ray diffraction topography [4].

Bi_2Te_3-Sb_2Te_3 solid solutions are uniaxial crystals. Bi_2Te_3 crystals feature a rhombohedral structure with space group D^5_{3d} ($R3m$), and their structure may be presented as a set of layers perpendicular to third-order symmetry axis C_3 [1]. A crystal may be cleaved along these layers (i.e., along the cleavage plane perpendicular to C_3). Samples for magnetic measurements were cut from ingots with a mass of 200−300 g by spark cutting and subjected to etch cleaning. The characteristic size of samples for magnetic measurements was $2 \times 2 \times 4$ mm.

The results of measurements of the magnetic susceptibility at temperatures ranging from 2 to 400 K performed in magnetic fields up to 30 kOe using a superconducting quantum interference device (SQUID magnetometer) with magnetic field vector H being oriented as $H \parallel C_3$ relative to C_3 are also reported in the present study. The dependence of susceptibility of all the studied samples on the field intensity remained linear up to 30 kOe. The value of $\chi_{\parallel}$ is determined at H || C_3. In the present study, temperature dependences of the magnetic susceptibility of crystals of Bi_2Te_3-Sb_2Te_3 solid solutions were measured in the range of 2–400 K using a measurement instrument produced by Quantum Design (USA). Its complete designation is the Magnetic Property Measurement System (MPMS MultiVu). The magnetic moment of the sample was measured in the course of the study by recording the SQUID sensor output data while the sample moved upward from the initial position through the QUID coils. The voltage values, which are read out as a function of the sample position in the SQUID coils, are the unprocessed data of a single measurement. At each position of the sample in the coils, MPMS MultiVu reads out the output SQUID voltage several times. Data from a certain number of scans may then be averaged to exclude random errors. The magnetic moment calibration for MPMS is performed by measuring the signal from a palladium reference in the corresponding magnetic field range. This reference is a cylinder $\sim$ 3 mm in diameter and 3 mm in height. A measurement error no higher than 0.1% could be achieved in the studies of samples with the indicated sizes.

3. Discussion of experimental results

It follows from the experimental data presented in Fig. 1 that the increase in diamagnetic susceptibility in the 2–15 K temperature range is the most common feature of temperature dependences of the magnetic susceptibility that is typical of all the studied crystals of Bi_2Te_3-Sb_2Te_3 solid solutions. This increase may be associated with the disalignment of magnetic moments of the paramagnetic impurity that is still present in trace amounts in crystals containing 99.9999% of the base substance. If the above assumption is true, the effect of the paramagnetic impurity vanishes when the temperature increases to 15 K, and the magnetic susceptibility at higher temperatures is shaped by the contributions from the ion core and free carriers. However, it is also possible that other factors contribute to the increase in diamagnetic susceptibility at low temperatures. The experiments in [3] revealed that the electric conductivity of Bi_2Te_3-Sb_2Te_3 crystals in most cases has a weak temperature dependence in the region of 15 K. In accordance with the Bloch–Grüneisen approach, which characterizes well the temperature behavior of resistivity of metals, the relaxation time should decrease rapidly (in proportion to the fifth power of temperature) as the temperature increases in the region where it is roughly equal to one tenth of the Debye temperature. This is attributable to the intensification of lattice vibrations, which leads to a reduction in electric conductivity of crystals with a small contribution of impurity scattering. The Debye temperature for Bi_2Te_3 crystals is 155 K. Thus, the weak temperature dependence of electric conductivity observed in Bi_2Te_3 crystals in the 4–15 K range (notably, the conductivity even increases slightly with temperature in certain cases)

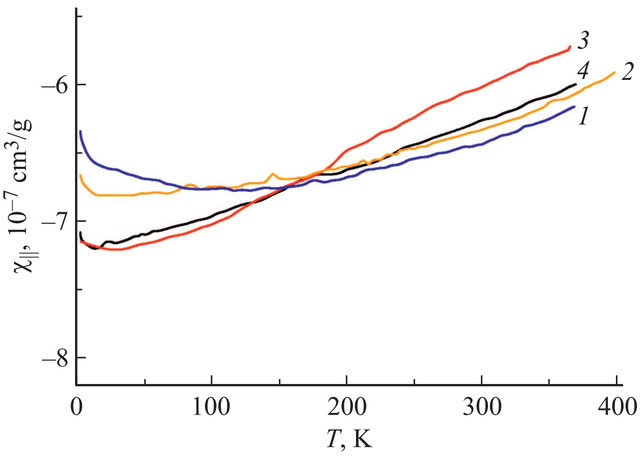

Figure 1. Temperature dependence of magnetic susceptibility $\chi_{||}$ for various values of x in the composition of crystals of the $(Bi_{2-x}Sb_x)Te_3$ solid solution: *1* — 0.2, *2* — 0.5, *3* — 1.2, *4* — 1.0. The susceptibility was measured in a field of 10 kOe.

is indicative of the presence of additional mechanisms of carrier scattering and of the probable growth of the free hole density, which may be induced by the transition of electrons to acceptor impurity levels located in the immediate vicinity of the valence band top. Note also that, as follows from Fig. 1, the diamagnetic susceptibility in the Bi_2Te_3-Sb_2Te_3 crystal containing 10% of Bi_2Te_3 ceases to increase with temperature at 80 K. According to the data from [1], this is the temperature at which the Hall coefficient in Bi_2Te_3 stops decreasing and starts growing anomalously up to the temperatures of transition to intrinsic conductivity. If variations of the electric conductivity and the magnetic susceptibility at low temperatures have the same physical cause, it is likely that the increase in diamagnetic susceptibility of Bi_2Te_3-Sb_2Te_3 crystals in the 4–15 K range is attributable in part to an increase in light hole density. The magnetic response of light holes is then diamagnetic in nature.

The observed variation of the magnetic susceptibility of crystals at 15 K with percentage concentration of antimony telluride is another fact in favor of the assumption that the response of light holes to an external magnetic field in Bi_2Te_3-Sb_2Te_3 crystals is diamagnetic in nature. Specifically, it can be seen from Fig. 1 that the diamagnetic susceptibility at a temperature of 15 K increases when the concentration of Sb_2Te_3 in Bi_2Te_3-Sb_2Te_3 crystals reaches 60 mol%. This may be induced by an increase in light diamagnetic hole density. It can be seen from Fig. 2 that the electric conductivity of Bi_2Te_3-Sb_2Te_3 crystals increases with concentration of Sb_2Te_3 in the composition of the solid solution [5]. This conductivity variation is especially well-pronounced at low temperatures and is associated with an increase in light hole density. Indeed, it follows from the table that the hole densities determined based on the Hall effect at a temperature of 78 K increase with percentage concentration of Sb_2Te_3. Thus, an increase in electric

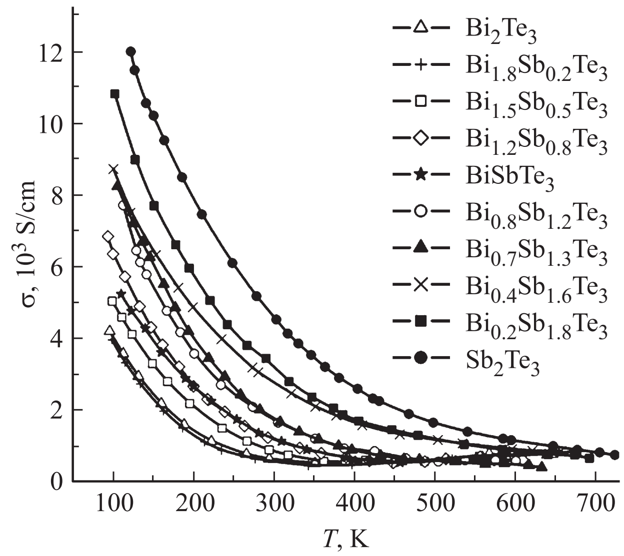

Figure 2. Dependences of the electric conductivity on the composition and the temperature of crystals of the Bi_2Te_3-Sb_2Te_3 solid solution [4]. The electric conductivity was determined in the direction perpendicular to trigonal crystal axis C_3.

conductivity and free carrier density is accompanied by an increase in diamagnetic susceptibility of a crystal. This also provides an indication of the resultant diamagnetic susceptibility of light holes.

Note that the analyzed experimental data characterize the temperature variation of the electron system state specifically in the valence band. The growth of electric conductivity and light hole density with concentration of antimony telluride in the Bi_2Te_3-Sb_2Te_3 solid solution indicates that the chemical potential level shifts deeper into the valence band, thus increasing the number of unoccupied states in this band. The diamagnetic susceptibility of a crystal also increases in the process. This experimental fact does not agree with the concept of probable prevalence of the diamagnetic contribution of the fully occupied valence band, since the diamagnetic crystal response should then decrease in the case of incomplete filling; as follows from Fig. 1, this response

Composition and magnetic susceptibility χ of Bi_2Te_3-Sb_2Te_3 crystals, $T = 291$ K, and hole density p measured at a temperature of 78 K

Composition of crystals	% Sb_2Te_3 in Bi_2Te_3	$\chi_\perp \cdot 10^6$, cm^3/g	$\chi_\parallel \cdot 10^6$, cm^3/g	$p \cdot 10^{-19}$, cm^{-3}
Bi_2Te_3	0	−0.423	−0.676	
$Bi_{1.8}Sb_{0.2}Te_3$	10	−0.456	−0.744	0.8
$Bi_{1.5}Sb_{0.5}Te_3$	25	−0.433	−0.686	0.9
$BiSbTe_3$	50	−0.412	−0.623	1.6
$Bi_{0.8}Sb_{1.2}Te_3$	60	−0.407	−0.596	2.3
$Bi_{0.6}Sb_{1.4}Te_3$	70	−0.368	−0.457	4.2
$Bi_{0.4}Sb_{1.6}Te_3$	80	−0.342	−0.357	4.8

does, on the contrary, increase as the Sb_2Te_3 concentration grows.

The experimental data in Fig. 1 provide one more indication that the response of light holes in Bi_2Te_3-Sb_2Te_3 crystals is diamagnetic in nature. It follows from the comparison of temperature dependences of the magnetic susceptibility and the electric conductivity. Specifically, Figures 1 and 2 demonstrate that the temperature intervals of reduction of the resulting diamagnetic susceptibility of crystals and the electric conductivity are the same. It is known that the electric conductivity of Bi_2Te_3-Sb_2Te_3 crystals decreases in the temperature interval where an anomalous behavior of the Hall coefficient (i.e., its growth with temperature) is manifested. This interval ends with the transition to intrinsic conductivity at a temperature of ~ 300 K in Bi_2Te_3 crystals and at 600 K in Sb_2Te_3 crystals [1]. The most plausible explanation of the anomalous temperature dependence of the Hall coefficient in Bi_2Te_3-Sb_2Te_3 crystals involves the process of redistribution of holes between the extrema of the valence band. Owing to this redistribution, the density of light mobile holes decreases at higher temperatures, while the density of heavy low-mobility holes increases with temperature. Experimental reflection spectra of the Bi_2Te_3-Sb_2Te_3 crystal, which contained 60% of antimony telluride, measured at different temperatures were examined in [6]. These spectra demonstrate that the energy of interband transitions from the chemical potential level to the conduction band decreases at higher temperatures, since this level shifts to the valence band top (probably owing to the redistribution of holes between the nonequivalent extrema of the valence band). It is fair to say that the data of optical studies provide experimental confirmation of the existence of redistribution of holes in the valence band of Bi_2Te_3-Sb_2Te_3 crystals, which gives rise to the anomalous temperature dependence of the Hall coefficient.

Thus, the process of redistribution of holes should also contribute to the reduction in electric conductivity at higher temperatures that is seen in Fig. 2. The analysis performed in [7] reveals that the reduction in electric conductivity of Bi_2Te_3-Sb_2Te_3 crystals at higher temperatures is too significant to be attributed solely to the reduction in relaxation time of carriers and to the increase in their effective mass. The influence of redistribution of free carriers between the extrema of the valence band, which reduces the density of light mobile holes that produce the primary contribution to the electric conductivity, should also be taken into account. Since free carriers also contribute to the magnetic susceptibility of a crystal, the same process affects the shape of the temperature dependence of the magnetic susceptibility. Indeed, it follows from Fig. 1 that the diamagnetic susceptibility of Bi_2Te_3-Sb_2Te_3 crystals containing 50 and 60 mol% of Sb_2Te_3 decreases in the temperature interval from 15 to 400 K. This may be associated with a reduction in density of light diamagnetic holes. Therefore, comparing the shapes of temperature dependences of the electric conductivity and the magnetic susceptibility, one may also conclude that the response of light holes in Bi_2Te_3-Sb_2Te_3 crystals is diamagnetic in nature.

4. Conclusion

We note in conclusion that the studied correlation between the temperature dependences of the magnetic susceptibility and the electric conductivity is induced by the response of Bi_2Te_3-Sb_2Te_3 crystals to electric, magnetic, and electromagnetic fields and allows one to use the temperature dependences of the magnetic susceptibility to examine in detail the processes in the electron system of these crystals and the variation of their intensity with Sb_2Te_3 concentration and temperature. The reported diamagnetic nature of the magnetic susceptibility of light holes is crucial for interpreting the temperature dependences of the magnetic susceptibility of Bi_2Te_3-Sb_2Te_3 crystals containing more than 60 mol% of Sb_2Te_3 that are distinguished by specific patterns of dependence of the electric conductivity on temperature. The probable causes of emergence of these features were analyzed in [8]. Owing to the elevated Sb_2Te_3 concentration, these crystals feature higher free carrier densities and, consequently, higher plasmon energies that approach the band gap energy, thus enhancing the electron–plasmon interaction. This interaction, alongside with the electron–phonon one, exerts influence on the electron system of a crystal [9,10], inducing the emerge of specific patterns of variation of certain physical quantities characterizing the state of the electron system.

Funding

This study was supported by grant 15-2021 from the Transbaikal State University given by the Council for Research and Innovation and aimed at facilitating the activity of scientific units.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] B.M. Gol'tsman, V.A. Kudinov, I.A. Smirnov. *Poluprovodnikovye termoelektricheskie materialy na osnove Vi_2Te* (M., Nauka, 1972) (in Russian).
[2] V.A. Kulbachinskii, V.G. Kytin, P.M. Tarasov. J. Exp. Theor. Phys., **110** (4), 618 (2010).
[3] A.A. Kudryashov. Candidate's Dissertation in Mathematics and Physics: 01.04.09, Low Temperature Physics (M., Mosk. Gos. Univ., 2016) (in Russian).
[4] I.Kh. Abrikosov, L.D. Ivanova, O.G. Karpinskii, T.E. Svechnikova, S.N. Chizhevskaya. Neorg. Mater., **13** (4), 641 (1977) (in Russian).
[5] L.D. Ivanova, Yu.V. Granatkina. Inorg. Mater., **36**, 672 (2000).
[6] N.P. Stepanov, A.A. Kalashnikov, O.N. Uryupin. Semiconductors, **55** (7), 637 (2021).
[7] N.P. Stepanov, A.S. Lozovskaya, L.E. Stepanova. Russ. Phys. J., **61** (8), 1429 (2018).
[8] N.P. Stepanov. Semiconductors, **54** (1), 11 (2020).
[9] N.S. Baryshev. Fiz. Tekh. Poluprovodn., **9** (10), 2023 (1975) (in Russian).
[10] Ch. Kittel. *Introduction to Solid State Physics* (M., Nauka, 1978), Chap. 6, p. 742 (in Russian).

For the continuation of the publication of the Conference materials see No. 1/22