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Thermoelectric and Galvanomagnetic Properties of the Alloy Bi_2Te_3 + 0.04 Weight% Ni in the Temperature Range 77 ÷ 300 K

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Abstract: The article introduces Hi input to p -type Bi_2Te_3 thermoelectric materials under inert gas pressure and presents the results of the study of electrical conductivity, Hall coefficients, thermoelectric and galvanomagnetic properties in the temperature range 77 ÷ 300K. The study of thermoelectric properties has shown that in order to explain the temperature dependence of the heat transfer parameter and the ratio of thermoelectric power to temperature, it is necessary to take into account the complex structure of the valence zone and the contribution of heavy cavitation in transport. It is shown that in order to explain the temperature dependences of the scattering parameter and the ratio of thermoelectric power to temperature, it is necessary to take into account the complex structure of the valence band and the contribution of heavy holes to transport phenomena. The estimates of the band parameters in the framework of the two-band model give the values of the effective mass of holes on the order of the mass of a free electron and the energy gap between nonequivalent extrema on the order of several hundredths of an eV.

Keywords: Single Crystal, Thermal Conductivity, Scattering, Mobility, Thermoelectric Power, Degeneracy, Effective Mass, Density of States

1. Introduction

Solid solutions based on bismuth and antimony is the best thermoelectric materials for the low-temperature temperature range (200 ÷ 600K). Therefore, a comprehensive study of their properties is of great scientific and practical interest.

The increase in conversion efficiency is primarily associated with an increase in the efficiency of thermoelectric materials (z). One of the widely used methods for increasing z is the formation of solid solutions of elementary semiconductor substances and their compounds. In this case, an active influence on the scattering mechanism and the energy spectrum of electrons and phonons is carried out: expansion of the band gap, change in the effective mass of current carriers and a decrease in the thermal conductivity of the lattice. In this way, on single crystals and coarse-grained polycrystals of solid solutions based on antimony and bismuth tellurides - Sb_2Te_3 - Bi_2Te_3 of p-type conductivity, z values equal to $(3\div3,4)\times10^{-3}K^{-1}$ [1, 13].

It is known that a decrease in the resistivity is associated with a decrease in the polarity of the covalent bond, which causes an increase in the mobility of charge carriers, and an increase in the Seebeck coefficient is associated with an increase in the density of states near the Fermi level. An increase in the degree of its disordering also contributes to a decrease in the thermal conductivity of a material.

The mobility is determined by the scattering of carriers by temperature fluctuations of the periodic potential in the crystal lattice. The change in potential is most pronounced in ionic crystals, where atoms with positive and negative charges alternate. The covalent bond in the crystal has a positive effect on the mobility, because in such a crystal, the interatomic bond is strongly expressed due to less pronounced temperature fluctuations of the crystal lattice potential.

The value of thermal conductivity is in the denominator of the expression that determines the thermoelectric efficiency. Therefore, it is important to obtain the minimum values of the thermal conductivity without impairing the electrical conductivity [14]. The value of thermal conductivity directly depends on the frequency of thermal vibrations of the lattice [11]. The scattering of charge carriers in bismuth telluride occurs on acoustic phonons [2-3], which is consistent with experiment [4].

2. Experience and Methods

In order to identify the scattering mechanisms of charge carriers and qualitatively establish the model of the band structure of the Bi_2Te_3 + 0.04 wt% Ni alloy, we investigated the thermoelectric power and electrical conductivity in the temperature range 77 ÷ 300 K and their changes in a constant magnetic field in the same temperature range. The Hall mobility of charge carriers and the Hall coefficient are also calculated. Figure 1 shows the temperature dependence of the thermopower (α). Figure 1 shows that at T<180 K the change is linear, which corresponds to the degenerate state of the electron gas and is described by the formula [5]

$$\alpha = \frac{2\pi^{\frac{2}{3}}k_0^2 m^* T}{3^{\frac{5}{3}} e\hbar^2 p^{\frac{2}{3}}}\left(r + \frac{3}{2}\right) \quad (1)$$

where: k_0 is the Boltzmann constant, m* is the effective mass of the density of states, e- is the electron charge, ħ- is the Planck constant, p- is the concentration of charge carriers, r is the scattering parameter and r = -1/2 in the case of scattering by acoustic phonons, 3/2 - scattering on impurity ions, 1/2 scattering on optical phonons below the Debye temperature.

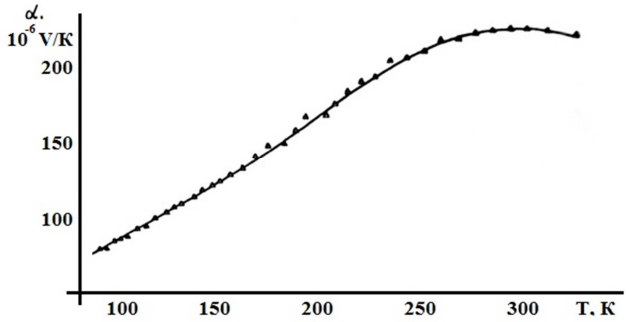

Figure 1. *Temperature dependence of the Seebeck coefficient for the Bi_2Te_3 + 0.04 wt% Ni alloy.*

At temperatures T>180 K, a faster increase in the thermoelectric power is observed than follows from formula (1), continuing up to values of T=250÷260 K, upon reaching which saturation occurs and then the thermoelectric power decreases. We interpret this behavior of the thermopower by the presence of a complex valence band characteristic of Bi_2Te_3 on the alloy under study [12]. The valence band of Bi_2Te_3 is split into 2 subbands with an energy gap between us ε = 0.02 eV [6-7]. At low temperatures T <200 K, the first subband, the subband of "light" holes with a lower effective mass of the density of states and with a higher Hall mobility R_h, is mainly involved in the conduction processes. Moreover, the state of charge carriers is degenerate due to high values of concentrations p and low temperatures T; with increasing temperature, some of the "light" holes pass into the second subband - the subband of heavy holes with a higher effective mass of the density of states and lower mobility with a nondegenerate state of carriers. In this case, the total thermoelectric power is determined as [16, 17]:

$$\alpha_{\text{общ}} = \frac{\alpha_1\sigma_1 + \alpha_2\sigma_2}{\sigma_1 + \sigma_2} \quad (2)$$

Where

$$\alpha_1 = \frac{2\pi^{2/3}k_0^2 m^* T}{3^{5/3} e\hbar^2 p^{2/3}}\left(r + {}^3/_2\right)$$

$$\alpha_2 = \frac{k_0}{e}\left[r + {}^5/_2 + \ln\frac{2(2\pi m^* k_0 T)^{3/2}}{\hbar^3 p}\right]$$

$$\sigma_1 = 2e\left(\frac{2\pi m_0 k_0 T}{h^2}\right)^{3/2} F_0(\mu^*) U_1 \left(\frac{m_1^*}{m_0}\right)^{3/2}$$

$$\sigma_2 = 2e\left(\frac{2\pi m_0 k_0 T}{h^2}\right)^{3/2} F_0(\mu^* - \Delta\varepsilon) U_2 \left(\frac{m_2^*}{m_0}\right)^{3/2}$$

Here α_1, α_2, σ_1, σ_2, thermoelectric power and electrical conductivity of the first and second subbands, respectively, μ* is the reduced Fermi level, Δε is the energy gap

$$F_r = \int_0^\infty x \frac{1}{e^x + 1} dx.$$

The participation of "heavy" holes of the second subband in conduction processes leads to an increase in the values of the total thermopower α relative to the thermopower of charge carriers of the first subband at certain temperatures. This behavior of the total thermopower continues until reaching temperatures at which the participation of charge carriers of the second sign, i.e. electrons begins to affect the value of α_{total}. In this case, the total thermopower is defined as

$$\alpha_{\text{total}} = \frac{\sum \alpha_p \sigma_p - \alpha_n \sigma_n}{\sum(\sigma_p + \sigma_n)} \quad (3)$$

where α_n, σ_n respectively, thermopower and electrical conductivity of electrons in the conduction band.

The manifestation of the participation of electrons in the conduction process leads to a slowdown in the growth of the thermopower, then to saturation and a decrease in its values with a further increase in temperature. The decrease in the values of the thermopower can also be significantly influenced by the approach of the research temperature to the region of intrinsic conductivity, which causes an exponential drop in the value of the thermopower [5].

The nature of the non-standard structure of the valence band for the material under study is also confirmed by the dependence of the Hall coefficient on temperature (Figure 2). As is known for substances with a complex band structure, such as Be_2Te_2, Sb_2Te_3, etc [8]. (the presence of charge carriers of two types of sign) the Hall coefficient is determined

under the assumption of spherical bands and the same mechanism of hole scattering as

$$R = \frac{A}{peC_0}\frac{p_1\mu_1^2+p_2\mu_2^2}{(p_1\mu_1+p_2\mu_2)} \quad (4)$$

where A is the coefficient that determines the mechanism of hole scattering, p_1, μ_1, p_2, μ_2, respectively, the concentration and mobility of carriers in subbands, C_0-is the specific heat capacity [7-9].

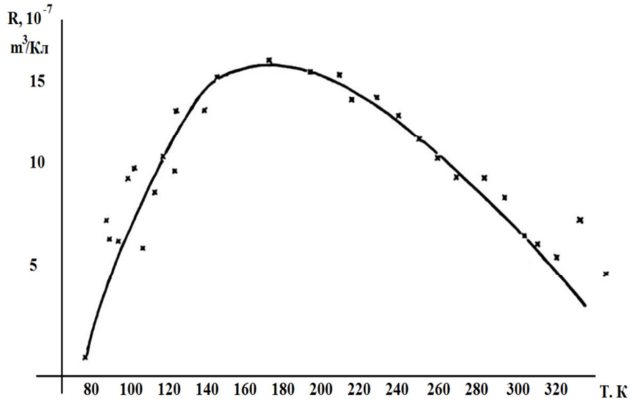

Figure 2. *Dependence of the Hall coefficient on temperature for the Bi_2Te_3+ 0.04 wt% Ni alloy.*

At low temperatures (T <100 K), it can be assumed that

$$R = R_0\frac{(1+p_2/p_1)[1+(p_2/p_1)b^2]}{[1+(p_2/p_1)b]^2} \quad (5)$$

Where $b = \frac{\mu_2}{\mu_1}$ $R_0 = \frac{A}{peC_o}$

Where $p = p_1 + p_2$ (p_1 and p_2 are the concentration of heavy and light holes, respectively)

With a sufficient degree of reliability, it can be assumed that there is an insignificant dependence of "b" on temperature, and then

$$R \approx R_0(\frac{p_2}{p_1}) \quad (6)$$

which leads to an increase in R_x with increasing temperature, due to an increase in holes in the second subband and a decrease in the first.

The maximum values of the Hall coefficient are achieved when the values of electrical conductivities $\sigma_1 = \sigma_2$ in the subzones are equal, while

$$R_{max} = R_0\frac{(1+b^I)^2}{4b^I} \quad (7)$$

After reaching the maximum value, the R_x value is determined, like the rest of the kinetic coefficients, mainly by carriers of the second subband, and an increase in their concentration leads to a decrease in $R_x$values according to the expression

$$R_x = \frac{A}{peC_0}$$

Note that for semiconductor materials with a complex band structure at a temperature at which the maximum R_x, is reached by a combination of the parameters R_x, α_{total}, and σ_{total}, it is possible to determine some band parameters, such as,, $\frac{\mu_2}{\mu_1}, \frac{p_2}{p_1}, \Delta\varepsilon$.

The theory for a two-band model of the structure of the valence band gives the following expression for the mobility of charge carriers:

$$\mu = \frac{\mu_1 p_1+\mu_2 p_2}{p} \quad (8)$$

Where μ_1, μ_2 are the hole mobilities in the corresponding subbands, and p_1, p_2 is the concentration.

As is known, in the general case, the mobility of charge carriers

$$\mu = \frac{\sqrt{\pi}}{\Gamma(r+3/2)}\frac{F_{r+1/2}(\mu^*)}{F_{1/2}(\mu^*)}\mu_0. \quad (9)$$

$$\mu_0 = \frac{2e}{3m^*}\tau_0(k_0T)^r\left(r+\tfrac{3}{2}\right)\frac{\Gamma(r+3/2)}{\Gamma(3/2)} \quad (10)$$

Where $\Gamma(s) = \int_0^\infty x^{s-1}e^{-x}\,dx$- Gamma Function.

s- it is an index that runs through all possible microstates of the system.

$F_s(\mu^*) = \int_0^\infty x^s[\exp(x-\mu^*)+1]^{-1}\,dx$ – Fermi integral.

As is known from (10), the mobility of current carriers depends on the degree of degeneracy of the electron gas, the effective mass of the density of states, the scattering mechanism, and temperature; therefore, its calculation from measurements of the Hall effect, electrical conductivity, and thermoelectric power is difficult due to the difficulty of determining $\frac{m^*}{m_0}$, r etc.

One of the ways to directly calculate the mobility, without determining the above parameters, is to use the effect of changing the resistance in a magnetic field, the graph of the change in which is shown in Figure 3.

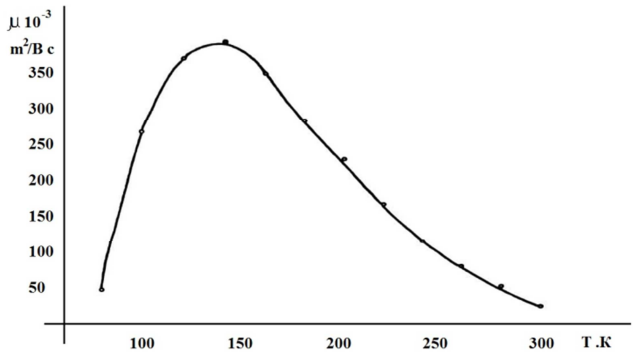

Figure 3. *Dependence of the charge carrier mobility on temperature for the Bi_2Te_3 + 0.04 wt% Ni alloy.*

The change in resistivity in a magnetic field is a function of the mobility, strength (induction) of the magnetic field and the degree of degeneracy of charge carriers [15];

$$\rho_{(H)} = \rho_{(0)}\left[1+\left(\frac{\mu H}{C}\right)^2 A\right] \quad (11)$$

$$A = \frac{(F_{3/2}\mu^*)^2}{F_{r+1}^4}\left[F_{r+1}(\mu^*)F_{3r+1}(\mu^*) - F^2_{2r+1/2}(\mu^*)\right] \quad 12)$$

For nondegenerate semiconductors (in the case for the second subband)

$$A = b_2 - a_r^2 \quad (13)$$

$$a_r = \frac{3\sqrt{\pi}}{4}\frac{\Gamma(2r+\frac{3}{2})}{\Gamma^2(r+2)} \quad (14)$$

$$b = \frac{9}{16}\pi\frac{\Gamma(3r+1)}{\Gamma^3(r+2)} \quad (15)$$

In the case of strong or weak degeneracy of the electronic spectrum of carriers (for the first subband and in the range of action of both subbands)

$$A = \frac{\pi^2}{3}\left(\frac{1}{\mu}*\right)^2\left(r-\frac{1}{2}\right)^2 \quad (16)$$

If we assume that for the composition under study, in the region of low temperatures, carrier scattering occurs on acoustic vibrations, as for Bi_2Te_3 (i.e., in expressions (14-16) r = 0), then for a nondegenerate state of charge carriers

$$A = \frac{9}{10}\pi\cdot\frac{\Gamma 1}{\Gamma^3 2} - \frac{9\pi^2}{64} = B,$$

for a weakly and relatively strongly degenerate state $A = +\pi^2\cdot\frac{1}{4}\left(\frac{1}{\mu^*}\right)^2$

Change in resistivity in a magnetic field

$$\frac{\Delta\rho}{\rho} = +\frac{\mu H^2}{c}\frac{\pi^2}{12}\frac{1}{\mu^{*2}} \quad (17)$$

for the scope of the first subzone and

$$\frac{\Delta\rho}{\rho} = \frac{\mu H^2}{\mathrm{C}}B \quad (18)$$

for the preferential action of the second sub-zone. Thus, as can be seen from the formulas for $\frac{\Delta\rho}{\rho}$, its change is determined by the temperature dependence of the mobility of charge carriers. Taking into account the two-zone model of the structure of the valence band, the growth of $\frac{\Delta\rho}{\rho}$ in the temperature range 80–150 K is caused by two reasons. First, an increase in the mobility in the temperature range T <150 and, second, a decrease in the carrier concentration of the first zone and a corresponding decrease in the total mobility.

In the temperature range T> 150 K, a decrease in the values of $\frac{\Delta\rho}{\rho}$ is caused by a decrease in the mobility of charge carriers of the second subband due to an increase in the effective mass of the density of states, a decrease in the mobility due to scattering by acoustic lattice vibrations.

The presented data on the change in $\frac{\Delta\rho}{\rho}$ are confirmed by the data on the determination of the mobility, calculated from the simultaneous determination by the Hall effect and electrical conductivity. Indeed, in the temperature range T<150 K, an increase in the values ($\frac{\Delta\rho}{\rho}$) is observed, and above T>150 K, their decrease (Figure 4) [18-20]. This behavior ($\frac{\Delta\rho}{\rho}$) for Bi_2Te_3 and solid solutions based on it is explained in the literature only by a change in the scattering parameter r.

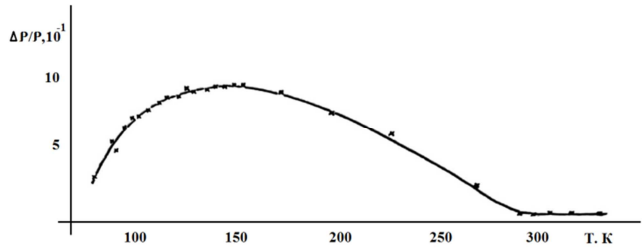

Figure 4. *Dependence of the change in resistivity in a magnetic field on temperature for the Bi_2Te_3 + 0.04 wt% Ni alloy.*

3. Conclusions

Studies of thermoelectric power, electrical conductivity and Hall coefficient showed that the alloy of solid solution Bi_2Te_3 + 0.04 wt% Ni retained the energy spectrum of charge carriers inherent to the p-type of bismuth sesqui telluride.

In the temperature range 80–150 K, the subband of light holes with a lower effective mass of the density of states and, accordingly, a higher carrier mobility is involved in the conduction processes, and at temperatures T>200 K the main contribution to the value of thermoelectric parameters is made by “heavy” holes.

The scattering mechanism of charge carriers (both "light" and "heavy" holes0 is mainly on acoustic vibrations of the lattice. The results of studies on the determination of the scattering mechanism of charge carriers from thermoelectric parameters are in good agreement with the data on the change in resistance in a magnetic field.

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