Japanese Journal of Applied Physics **50** (2011) 05FD04 **BRIEF NOTE**
DOI: 10.1143/JJAP.50.05FD04

Metal–Insulator Transition Induced by Temperature in $Bi_2Te_{3-x}Cl_x$ Layered Compound

Nadir A. Abdullayev*, Nadir M. Abdullayev, Xayala V. Aliguliyeva, Samir Sh. Gahramanov, Taira G. Kerimova, Konul M. Mustafayeva, Sergey A. Nemov[1], and Vladimir N. Zverev[2]

Institute of Physics, National Academy of Sciences, 33 H. Javid av., AZ 1143 Baku, Azerbaijan
[1]*St. Petersburg State Polytechnical University, ul. Politekhnicheskaya, 29, St. Petersburg 195251, Russia*
[2]*Institute of Solid State Physics, Academy of Sciences, 2 Institutskaya ul., Chernogolovka 142432, Russia*

Received September 24, 2010; accepted February 24, 2011; published online May 20, 2011

It is shown, that doping by chlorine atoms changes the type of conductivity of Bi_2Te_3 from p- to n-type as well as the character of conductivity. In the direction perpendicular to the layers plane phonon assisted hopping conductivity is observed. The mechanism of charge transport in Bi_2Te_3 crystals doped by chlorine atoms is proposed.

Recently, interest to the doped $A_2^VB_3^{VI}$-group semiconductors has increased considerably.[1–3] On one hand, this interest is due to the peculiarities of energy spectrum and charge carriers scattering mechanism in such compounds. On the other hand, these materials can be used in thermoelectric transformers. In spite of the fact that Bi_2Te_3 is a semiconductor, the temperature dependence of conductivity has metallic character. It caused by presence of numerous antisite defects Bi ↔ Te forming a great number of local states in the band gap creating wide impurity bands overlapping with conduction and valence bands.

The Bi_2Te_3-type single crystals were grown by the Bridgman-Stockbarger method and by the method of directed vertical crystallization from the components taken in stoichiometric ratio and with the addition impurities. The directed zone crystallization was performed with a zone rate of 3×10^{-2} m/h. The X-ray diffraction studies for the samples were performed using a DRON-3M diffractometer.

The samples for investigations were obtained from single crystals ingots by the simple cleavage along the plane of the layers and were prepared in the form of rectangular plates of $(2–8) \times 10^{-4}$ m thick. The absolute values for resistivity in the plane of the layers ρ_{par} and perpendicularly to the layers ρ_{per} were determined by the improved four-probe Schnabel combination method.[4] The measurements were performed by the selective method with an ac frequency of 20 Hz; the current was not higher than 1×10^{-3} A.

This paper presents the results of studies of electrical conductivity, Hall effect and magnetoresistance in layered single crystals Bi_2Te_3, doped with chlorine, in the temperature range 0.5–300 K and magnetic fields up to 8 T. Single crystals have rhombohedral crystalline structure with space group D_{3d}^5 ($R\bar{3}m$).

Note, first of all, that the doping with halogen–chlorine has the donor effect. Apparently, in Bi_2Te_3 crystals doped with chlorine, chlorine atoms substitute the tellurium atoms in the lattice. Since the number of electrons in chlorine atom is one greater than that in tellurium, the chlorine atom gives one electron to the conduction band.

It has been shown (see Fig. 1), that in Bi_2Te_3:Cl crystals (curve 2) the anisotropy of electrical conductivity at $T = 300$ K is much higher than in undoped Bi_2Te_3 crystals ($\rho_{per}/\rho_{par} \sim 14$) and significantly increases with decreasing the temperature (at $T = 5$ K, $\rho_{per}/\rho_{par} \sim 400$). Note that the anisotropy of conductivity in undoped Bi_2Te_3 does not change with temperature (curve 1). This "metallic" character of behavior almost preserved in the layers plane. The absolute values of resistivities increase and weaken their temperature dependence only, indicating the increasing role of impurity scattering of charge carriers.

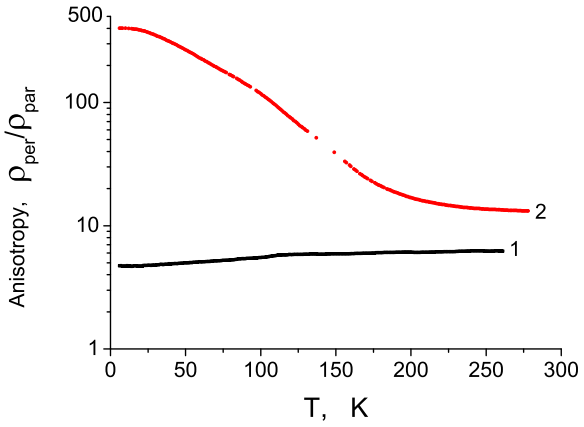

Fig. 1. (Color online) Temperature dependencies of resistivity anisotropy ρ_{per}/ρ_{par} in Bi_2Te_3 crystals: (1) undoped crystal, (2) Bi_2Te_3:Cl.

Conductivity perpendicular to the layers varies significantly (Fig. 2). In Bi_2Te_3 single crystals doped with chlorine (curve 2) the conductivity in the direction perpendicular to the layers acquires an activated character. As the temperature is lowered from 300 to 200 K the resistance decreases slightly. Then in temperature interval 200–18 K activated conductivity is observed — the resistance increases more than 5 times, below 18 K again there is a decrease of resistance with decreasing temperature.

Thus, in the direction perpendicular to the layers in the temperature behavior of conductivity some metal–insulator type transition is observed with "metallic" character at low temperatures and the "dielectric", or activated — at higher temperatures.

We assumed that as in graphite,[5] the conductivity of Bi_2Te_3:Cl samples in the direction perpendicular to the layers plane is realized via two competing channels: "metallic", σ_M, and "activated", σ_H. In this case the total conductivity σ is expressed as

$$\sigma = \sigma_M + \sigma_H, \quad (1)$$

where metallic conductivity is

$$\sigma_M = \rho_M^{-1} = (\rho_0 + AT)^{-1}. \quad (2)$$

*E-mail address: abnadir@mail.ru

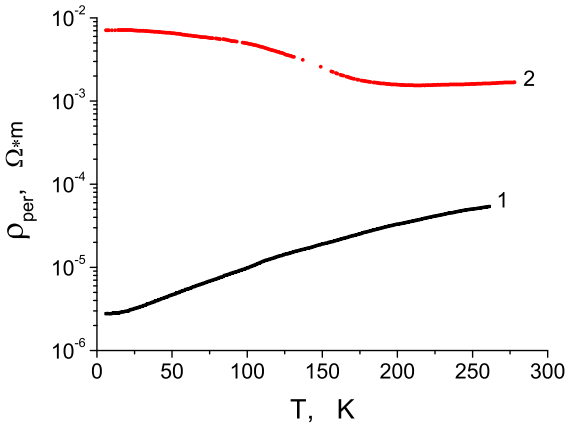

Fig. 2. (Color online) Temperature dependencies of the resistivity perpendicular to the layers, ρ_{per}, in Bi_2Te_3 crystals: (1) undoped crystal, (2) Bi_2Te_3:Cl.

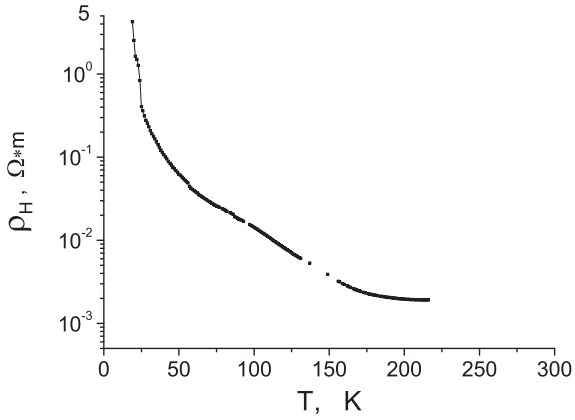

Fig. 3. The temperature dependence of the activation part of the resistivity $\rho_H(T)$.

The quantities ρ_0 and A can be determined by extrapolation $T \to 0$. From Fig. 2 follows: $\rho_0 \approx 7 \times 10^{-3}\,\Omega\,\mathrm{m}$, $A = 6.6 \times 10^{-6}\,\Omega\,\mathrm{m\,K^{-1}}$. Then, subtracting σ_M from resultant σ, activation part of conductivity σ_H and $\rho_H = \sigma_H^{-1}$ can be determined (Fig. 3).

Exponential increase of resistivity with decreasing temperature is well seen. Fitting by least square method of $\rho_H(T)$ function having the form:

$$\rho_H(T) = \rho_{H0} \exp\left(\frac{T_0}{T}\right)^x \tag{3}$$

gives $x = 1/2$ and $T_0 \approx 1100\,\mathrm{K}$. Thus, experimental data show that conductivity in the direction perpendicular to the layers plane in Bi_2Te_3 single crystals doped with chlorine atoms is well described by the expression

$$\rho_H(T) = \rho_{H0} \exp\left(\frac{1100}{T}\right)^{1/2} \tag{4}$$

in temperature interval $T = 25$–$150\,\mathrm{K}$ which is true for one dimensional variable range hopping conductivity.[6] Thus, the charge transport perpendicular to the layers is carried out simultaneously by two competing ways: "metal" way and "disordered" way, via phonon assisted hopping of charge carriers. The disorder is due to inhomogeneous doping, when the most of the impurity atoms is introduced into the interlayer spaces.

Carrier mobility in the plane of the layers, determined from the studies of electrical conductivity, Hall effect and magnetoresistance in Bi_2Te_3 ($\mu_H \approx 0.27\,\mathrm{m^2\,V^{-1}\,s^{-1}}$) and Bi_2Te_3:Cl ($\mu_H \approx 0.25\,\mathrm{m^2\,V^{-1}\,s^{-1}}$) are quite high. It confirms, on the one hand, that the scattering of holes by the defects is not dominant, and, on the other hand, that the chlorine atoms are introduced into the interlayer spaces during the doping. Such defects, practically have no effect on the electrical conductivity in the plane of the layers, but make it very difficult the charge transport in the direction perpendicular to the layers.

In summary, it was found that doping with chlorine atoms has the donor effect on Bi_2Te_3, single crystals, and leads to a significant increase in the anisotropy of conductivity which increases with decreasing temperature. It is shown that while in the layers plane the charge transport is realized through the impurity band, the charge transport perpendicular to the layers is mainly determined by thermally activated hopping over localized states. This is possible for an inhomogeneous doping. Apparently, the chlorine atoms are introduced into the interlayer spaces during the doping due to weak bonds between the layers planes. Interlayer distances can be changed, the restructuring of the band structure and the emergence of localized states can be realized in this case.

1) V. A. Kutasov, L. N. Luk'yanova, and P. P. Konstantinov: Semiconductors **34** (2000) 376.
2) M. K. Zhitinskaya, S. A. Nemov, and T. E. Svechnikova: Phys. Solid State **40** (1998) 1297.
3) N. A. Abdullaev, S. Sh. Kakhramanov, T. G. Kerimova, K. M. Mustafaeva, and S. A. Nemov: Semiconductors **43** (2009) 145.
4) P. Schnabel: Z. Angew. Phys. **22** (1967) 136 [in German].
5) N. A. Abdullayev and T. G. Kerimova: Physica B **404** (2009) 5215.
6) N. F. Mott and E. A. Davis: *Electron Processes in Noncrystalline Materials* (Clarendon, Oxford, U.K., 1971) p. 437.