THE FEATURES OF ELECTROCONDUCTIVITY IN LAYERED CRYSTALS

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ABSTRACT

It is shown, that anisotropy of conductivity not corresponded to the anisotropy of charge carrier effective masses (the conductivity along the planes of layers exceeds by some orders the conductivity in the direction of perpendicular layers) is taken place. Such anisotropy of conductivity can be explained by the the account the real structure, presence of the plane defects, defects of stacking fault being characteristic of layered crystals. Two types of localization of charge carriers are discussed.

Keywords: crystal, anisotropy of conductivity, stacking fault, Mott conductivity, localization,

I. INTRODUCTION

Nowadays it is known, that the anisotropy of conductivity not corresponded to the anisotropy of charge carriers effective masses, is practically characteristic of all layered crystals, for example, for *InSe* layered semiconductor $\rho_{\perp} / \rho_{II} \sim 10^2 \div 10^3$ [1] (here $\rho_{\perp}$ - resistuvity in the direction of perpendicular to the layers, and ρ_{II} - resistivity in the planes of layers), for $NbSe_2$ layered metal $\rho_{\perp} / \rho_{II} \sim 10^2$ [2] and for layered semimetal of graphite $\rho_{\perp} / \rho_{II} \sim 10^3 \div 10^5$ [3]. It is necessary to note, that due to the weakness of interlayer forces for the layered crystals, the presence of plenty of interlayer defects, defects of stacking faults and etc. The periodicity of wave functions in the direction of perpendicular to layers is broken, and it leads to the occurrence of localized states with the energies of layers being in the interval of band gap energy. As a result it turns out, that the of charge carriers mobility in layer planes is considerably more, than in the direction perpendicular to layers.

Electrical conductivity of single crystals of layered compounds - $CuFeTe_2$, $GeNi_3Te_5$ and Bi_2Te_3 tellurides has been investigated in various crystallographic directions with the purpose of an establishment of interrelation of charge transport processes with the real crystalline structure. At present time only Bi_2Te_3 single crystals among the investigated compounds have found widely used as high effective thermoelectrical transformers. Selected compounds for investigations have various type of conductivity: $CuFeTe_2$, is the semiconductor of *n* - type, Bi_2Te_3 – narrow-band semiconductor of *p*-type with the metallic conductivity in impurity zone, and $GeNi_3Te_5$ – is the metal. All these compounds have layered behavior of crystalline structure.

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II. EXPERIMENTAL RESULTS

By investigating the electrical properties of single crystals samples, the method of applying of contacts are of decisive importance there have been impaced requirements as to the direction of force lines of electric intensity in the sample, and to the contacts. In 1967 P.Schnabel [4] offered advanced, combined, the four-probe method for study of anisotropy electrical conductivity of layered crystal samples prepared in the form of thin plates. Such plates can be obtained easily from layered materials by natural spalling in the plane parallel to layers. For probe methods the force lines of of electric intensity are nonparallel and distributed nonhomogeneously distributed in the sample cross section. In this connection, at first it is necessary to calculate theoretically the distribution of electrical potential in the sample, then to find interrelation between the resistivity and experimentally measured values-current and voltage.

The investigation samples have been obtained from single crystal ingots, by single spalling along the surface, containing the layer plane. The samples are prepared in the a form of rectangular plate thickness $0{,}2 \div 0{,}8$ mm, sizes in layer plane $\sim 5 \times 7\,\text{mm}^2$. Indium contacts are applied on the freshly spalled surface in pairs on opposite surfaces of investigated sample of rectangular arrangement [4]. The measurements are carried out by the selective technique with alternating current in frequency 20 Hz, the value of the current does not exceed 1 mA. The electric intensity of the applied field ($E = 10 \div 100 V/cm$) corresponds to the ohmic range of the volt-ampere characteristic. The peculiar sizes of the investigated sample (sample thickness, contact diameter, distance between contacts and etc.) have been determined by the optical microscope.

The magnitudes of ρ_{II} - resistivity in the layer plane and $\rho_{\perp}$ - resistivity in the direction perpendicular to the

layers have been calculated by the relations given in work [4].

In figure 1 the temperature dependence of $CuFeTe_2$ single crystals resistivity in layer plane (ρ_{pa}) and in the direction perpendicular to layers (ρ_{per}), submitted in Arrenius coordinates are given. The "semiconductive" course of temperature dependence of the resistivity is obvious: with the decrease of temperature the exponential increase of the resistivity in both directions are observed.

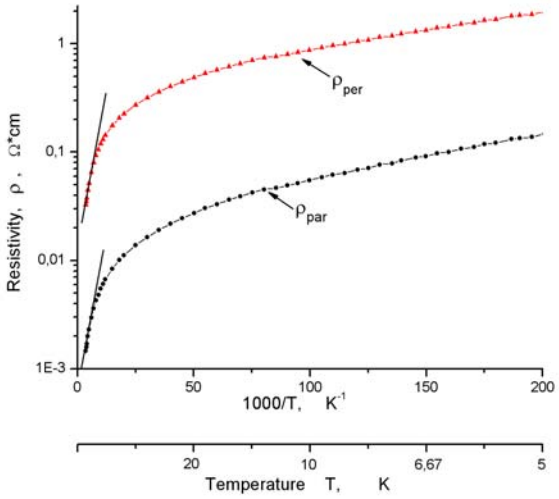

Fig.1. Temperature dependence of $CuFeTe_2$ resistivity

The presence of two ranges resistivity of change with the decrease temperature decrease is characteristic of two $\rho(T)$ dependences $\rho(T)$. Decreasing rather temperature the exponential increasing of $\rho_{II}(T)$ and $\rho_{\perp}(T)$ resistivities are observed in rather high temperatures 150 K < T < 300 K. In this temperature range the conductivity of thermoexcited charge carriers in the allowed zone have been dominated. The temperature decrease is accompanied by fast decrease of of charge carriers, so-called concentration freezing –out range of charge carriers impurity. The obtained activation energy of the charge carriers impurity is approximately equal to 23 meV both for $\rho_{II}(T)$ and $\rho_{\perp}(T)$, which corresponds to the data of [5]. According to [5], from high temperature (200K < T < 300K) investigations of $CuFeTe_2$ electrical conductivity of it follows, that the activation energy of impurity states is in 10-25 meV.

Low temperature range of the electrical conductivity (T < 150 K) is of great interest. It is a range of continuous reduction of the activation energy of conductivity. The analysis of functional temperature dependence of resistance has revealed that experimental points can be to straighten with great precision in Mott coordinates. It gives us an opportunity to assume, that in the mentioned temperature range the charge transport by along and across to layers in $CuFeTe_2$ single crystals is carried out by means of hopping conductivity of charge carriers between the localized states lying in energy narrow zone of energies near to Fermi level. In this case electrical conductivity is described by known Mott expression [6]:

$$\rho = \rho_0 \exp(T_0 / T)^{1/4} \qquad (1)$$

where $T_0 = \beta / kg(\mu)a^3$, $g(\mu)$ -- density of the localized states at the Fermi level, a - radius of the localized states near to Fermi level, β - number dependent on dimensionality of the task, k - Boltzmann constant.

The temperature parameter $T_0 = 6 \cdot 10^3 K$ has been determined (for direction perpendicular to layers the T_0 value is the same) from the slopes of the straight line of $\lg \rho_{\text{Ш}}$ versus $T^{-1/4}$. Taking $\beta = 21$ [6], and radius of the localized states equal to peculiar radius of Coulomb states of $A^{III}B^{III}C_2^{VI}$ group crystals $a = 20A^0$ [7] one can estimate the density of the localized states near Fermi level in $CuFeTe_2$ single crystals: $g(\mu) = 5*10^{21} eV^{-1} * cm^{-3}$. Such abundance of the localized states in the band gap is characteristic of $A^{III}B^{VI}$ [1] and $A^{III}B^{III}C_2^{VI}$ [7] group of crystals, crystallized in layered and chained structures. Anisotropy of bonding forces in layered structures promotes the occurrence of numerous defects of stacking fault, impurities of introduction, vacancies and dislocations. In leads to change periodicity of crystalline structure, occurrence of localized states of the energies included in the interval of band gap energies in ideal crystal. The magnitude of density of the localized states wonderfully correlates with the magnitude of of free electron concentration at 300K [5] that probably testifies to the nature of occurrence of so high concentration of charge carriers in $CuFeTe_2$.

Using the relation [6]:

$$\frac{R}{a} = \frac{3}{8}\left(\frac{T_0}{T}\right)^{1/4} \qquad (2)$$

one can estimate R average hopping length of charge carriers in the localized states near Fermi level at given temperature T. As we see, in the range of applicability of (1) the average hopping length of charge carriers increases with decreasing temperature, therefore such conductivity refers to as hopping conductivity with variable range hopping. It is connected that with decreasing of temperature the probability jumps of charge carriers jump to spatially more removed once, but energetically close centers of localization has been grown. The charge carrier, as a rule, hopping to such state, what W activation energy is the least probable value. According to [6] one can estimate the activation energy from:

$$W = \frac{3}{4\pi R^3 g(\mu)} \qquad (3)$$

From the relations (2) and (3) $R = 22A^0$ the average length of carrier jump and $W = 4{,}48 meV$ energy spread

of the localized states were calculated at temperature T=80K. At T=10K the average length of carrier jump already is much more $R = 37A^0$, and energy spread of the localized states is $W = 0{,}94 мэВ$.

In fig.2 there have been presented the temperature dependence of resistivity of $GeNi_3Te_5$ layered single crystals. The temperature dependence of resistivity typical for metallic conduction is well distinct: the value of resistivity linearly decreases with decreasing temperature both in layer plane (ρ_{par}), and perpendicular to layers (ρ_{per}).

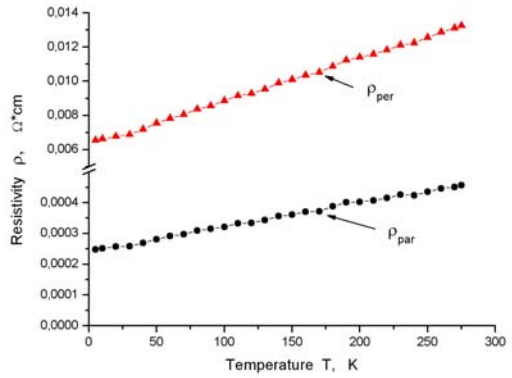

Fig. 2. Temperature dependence of resistivity $GeNi_3Te_5$.

The temperature coefficients of resistivity in layer plane and perpendicular to there are equal to $\alpha_{par} = 8{,}2 \times 10^{-7}\ Ohм * cm / K$ and $\alpha_{per} = 2{,}5 \times 10^{-5}\ Ohм * cm / K$., respectively.

As it is shown from fig.2 the anisotropy of conductivity is considerable and falls slowly with temperature (from 29 at 275 K up to 26,4 at 5 K). Such anisotropy of conductivity not corresponding to the anisotropy of effective masses of charge carriers, as it is mentioned above, is characteristic of practically for all layered crystals. For layered crystals owing to weakness of interlayer forces it is peculiar the presence of plenty of interlayer defects, defects of stacking fault and etc. These defects not influencing practically on the movement of charge carriers in the plane of layers, have a considerable influence on the movement of charge carriers in the direction perpendicular to layers.

If the electrical resistance would be defined by only dispersion of charge carriers on phonons, at very low temperatures ($T \to 0^0 K$) the resistance practically would be zero. Actually there are various leads to change of periodicity of the lattice (dislocation, vacancy, impurities of alien atoms etc.) and that is why except the dispersion on phonons, the carriers undergo other kinds of dispersion. It brings about that at low temperatures, at which the phonon dispersion mechanism can be neglected, the crystals have resistance so-called as residual resistance. Thus, the value of residual resistance in metals characterizes the purity degree of cleanliness and perfection of crystal structure of sample under the investigation. So, the value of residual resistance in the direction perpendicular to layers ($\rho_{per}\ (T = 4{,}2K) = 6{,}4 \times 10^{-3}$ Ом * cm) exceeds considerably the value of residual resistance in the plane of layers ($\rho_{par}\ (T = 4{,}2K) = 2{,}5 \times 10^{-4}$ Ом * cm).

We also investigate the electrical conductivity of layered Bi_2Te_3. The calculated absolute value of resistivity of Bi_2Te_3 layered single crystals at 5K < T < 300K are given in fig.3. As it is shown from figure, in all investigated range of temperature the values of resistivity both in plane of layers and perpendicular to layers with decreasing temperature decreases monotonically, showing "metallic" behaviorof temperature dependence of the electrical conductivity. Such temperature behavior of electrical conductivity in semiconductor testifies to

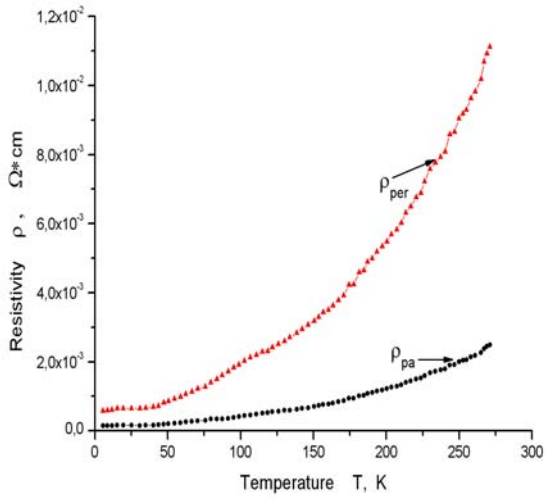

Fig. 3. Temperature dependence of resistivity Bi_2Te_3.

presence of wide impurity zones in the band gap.The impurity concentration in Bi_2Te_3 appears to be, that in the band gap the whole area of allowed states (impurity zone) is formed, which at rather large concentrations of impurity can be overlapped by intrinsic band of the pure crystal.

It is known, that stoichiometric Bi_2Te_3 is characterized by the presence of own dot defects of structure due to the transition of Bi atoms in Te position in the lattice. As such antistructural defects are acceptors, bismuth telluride crystals initially have a high hole concentration as $p \sim 10^{18} cm^{-3}$. Because of high dielectric constant ($\varepsilon = 85$), the condition of strong doping is already carried out at $n \sim 10^{17} cm^{-3}$ impurity concentrations, which causes metallic conduction of samples. From of Hall voltage measurements follow, that charge carriers concentration in investigated samples changed within $(2 \div 5) * 10^{18} cm^{-3}$ that exceeds considerably the concentrations of charge carriers sufficient for realization of condition of strong doping.

In the investigated samples $\rho_{\perp} / \rho_{II} \sim 4 \div 4{,}5$ conductivity anisotropy is taken place. With the change of temperature the anisotropy of conductivity practically does not change. Such anisotropy of conductivity in Bi_2Te_3, not corresponding to anisotropy of carriers effective masses, can be explained, as it is mentioned above, only at the expense of the real crystalline structure.

Investigation results of Bi_2Te_3 single crystals conductivity at (0,4 K < T < 5 K) below liquid helium temperatures are of great interest. As it is shown from fig. 3, at temperatures below $20 \div 30$ K the temperature dependence of electrical conductivity does not change. At the top of fig.4 the temperature behavior of Bi_2Te_3 samples resistance in the plane of layer in the lowest temperature ranges (T < 1 K) is shown.

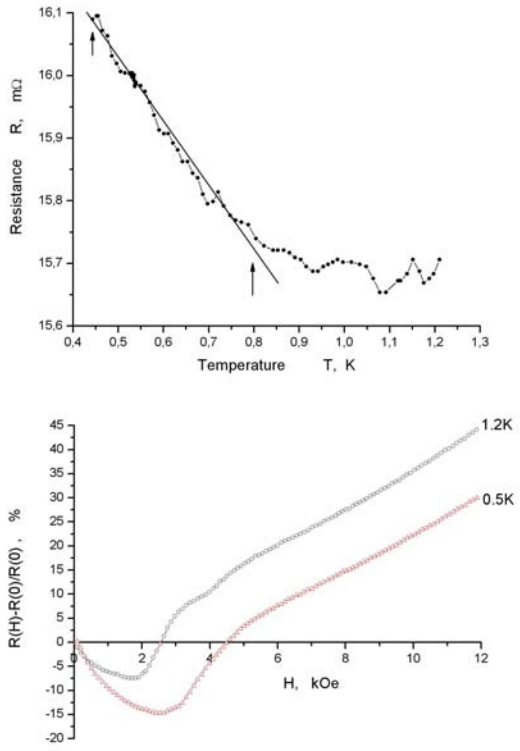

Fig. 4. Top) Temperature dependence of resistivity Bi_2Te_3 at T < 1K.
Bottom) Negative magnetoresistance of Bi_2Te_3 at T=1,2K and T=0,5K.

It is shown, that below mentioned temperature with decreasing temperature some increase of of Bi_2Te_3 sample resistance is taken place (3-10 % of value varies from sample to sample). Such temperature behavior of Bi_2Te_3 samples resistance is probably caused by localization of charge carriers at low temperatures, which is characteristic of the quantum allowance to conductivity in approach of noninteracting electrons, due to interference of trajectory amplitudes with self-crossing of dispersion carriers in impurities and structural defects (so-called the effect of weak localization). In order to actually to occur the interference effects, condition it is necessary to fulfill the:

$$\tau << \tau_{\varphi} \qquad (4)$$

where τ - time between two sequential elastic collisions (for example, dispersions in impurities), and τ_{φ} - time between two sequential acts of inelastic collisions (for example, electrons by electrons or by phonons). The inelastic collisions bring about to phase relaxation and leads to change of amplitudes coherence. The realization of condition (4) is possible only in the range of very low temperatures (large τ_{φ}) and within "dirty" metal (small τ).

The destruction of carriers localization by weak magnetic field and appearance of negative magnetoresistance is the direct proof of existence of existence of weak localization (quantum interference additive to conductivity). At the presence of magnetic field the difference of phases appears at interfering amplitudes of trajectory dispersion with self-crossing. The appearance of an additional difference of phases brings to leads to change coherence and destruction of interference, i.e. to reduction of resistance. Thus, the quantum interference allowance the to conductivity leads to negative magnetoresistance.

For the above-mentioned reason we have carried out the magnetoresistance investigations of Bi_2Te_3 samples. Negative magnetoresistance appears to be was observed. As it is shown from fig.4 (below), the integrated slope of resistance in the range of negative magnetoresistance increases with lowering temperature T. It is necessary to note that negative magnetoresistance has been observed immediately since the smallest values of magnetic fields. With decreasing temperature the range of fields, at which negative magnetoresistance is observed, increases to large fields. At T = 0,5 K the maximal value of maximum negative magnetoresistance reaches at magnetic field of $H \sim 2{,}54 \kappa Oe$ equal to $\sim 15\%$. In the field $H \sim 4{,}5 \kappa Oe$ the change of sign occurs and magnetoresistance becomes positive.

III. CONCLUSIONS

Thus, from the obtained experimental results, follow that in $CuFeTe_2$, $GeNi_3Te_5$ and Bi_2Te_3 layered single crystals despite of distinction of mechanisms of charge carriers transport, significant anisotropy of conductivity is taken place. Observed anisotropy of conductivity in these crystals is possible to explain only within the real structure of crystals. As a rule, the anisotropy of conductivity in layered crystals varies strongly with temperature (more, than by an order ofvalue) at simultaneous effect in the same temperatures range of various mechanisms of charge carriers transport in different crystallographic directions, as it takes place, for example, in graphite [3] and *InSe* [1]. The value of conductivity anisotropy in investigated crystals varies rather weakly in value in all investigated temperature range $5K \div 300K$, that testifies, on the one hand, to identity the mechanism of charge carriers transport in different crystallographic directions. And on the other hand, it specifies that the anisotropy of conductivity,

despite of change of the of charge carriers transport mechanism from impurity conductivity on extended states to hopping one on the localized states, is due to the same factors - anisotropy of effective masses of electrons and influence of plane defects, defects of stacking faults, which are characteristic layered crystals.

There have been revealed and investigated two types of localization of charge carriers. Strong one, observed at higher temperatures, exhibited by hopping of charge carriers in the localized states and weak localization one, observed at very low temperatures (T < 1K), caused by interference of scattering amplitudes of charge carriers. It is important to note, that the basic condition of both effects is the large density of the localized states, which is characteristic, of layered crystals as it is above mentioned.

REFERENCES

1. *G.L. Belenkii, N.A. Abdullayev, V.N. Zverev, V.Ya. Shteinsraiber.* JETF Letters. **47**, 10, 498 (1988). (in Russian)
2. *J. Edwards and R.F. Frindt.* J. Phys. Chem. Solids. **32**, 9, 2217 (1971).
3. *C. Uher and L.M. Sander.* Phys. Rev. B. **27,** 2, 1326 (1983).
4. *P. Schnabel.* Zeits. Angew. Phys. **22**, 2, 136 (1967).
5. *A.A. Vaypolin, V.D. Prochuhan, Yu. V. Rud, V.E. Skoryukin.* Inorgan. Mat. **20**, 4, 578 (1984).
6. *N.F. Mott.* Phyl. Mag. **19**, 835 (1969).
7. *F.N. Abdullayev, T.G. Kerimova, N.À. Abdullayev.* Solid St. Phys., **47**, 7, 1180, (2005).