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Energy bands splitting with interlayer broadening in Bi_2Te_3<Ni>

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As a result of the developed technology, an ordered array of nanoislands was formed in the process of self-organization on the *Bi_2Te_3<Ni> (0001)* plane. Penetrating mainly into the interlayer space impurities create bulk periodic superstructures, and consisting of arrays of nanoislands between packet of layers, which, as a result, move apart. The symmetry of the *Bi_2Te_3* crystal forbids the mixing of the states $|s\rangle$ and $|d_z^\eta\rangle$ with $|p_x\rangle$ and $|p_y\rangle$, and $|d_z^\eta\rangle$ with the other d-states at high-symmetry points of the Brillouin zone, while mixing of all states is allowed at low-symmetry points. As a result, an increase in the potential barrier due interlayer broadening is accompanied by a shift and splitting (ΔE ~ 20 meV) of some bands and the formation of an energy gap.

Keywords: energy bands, self-organization, magnetoresistance oscillation.

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Introduction

The tested material is a superstructure with a set of basic five-layer packages (quintet) and an array of nanoparticles - INSE (interlayer nanostructural elements) on interlayer surfaces (Fig. 1). Nanoparticles - nanoclusters on the cleaved or interlayer *Bi_2Te_3* surface are created by the self-assembly method. During the formation of superstructures in doped *Bi_2Te_3*, an extreme temperature dependence of the kinetic properties is possible [1, 2]. Electronic confinement in nanoparticles leads to unique quantum properties as the effect on the electrons interact with each other, and on external influences, such as electric and magnetic fields.

The height dimensions of the interlayer nanostructures indicate the inhomogeneity of the INSE distribution in different van der Waals gaps depending on the defectiveness of the crystal packing. Apparently the largest INSE may aggregate in the cavities, which ending edge dislocations and other large defects of layers, where the elastic stresses are strongest. When a crystal is cleaved, it is precisely such a crotch that opens where INSE observed up to 16 nm. The width of defect cavities with nanoislands has distances of the order of nanometers, which, as usual, are formed with a frequency of ~500-1000 quintets, and the broadening of van der Waals gaps, due to the penetration of impurities with a small atomic radius (for example, copper or nickel), has dimensions of the order of fractions of an angstrom. Aggregation of impurity and superstoichiometric inclusions in these spaces should reduce the crystal energy and elastic stresses. Penetration of key elements from quintets into defective and van der Waals gaps may lie through screw dislocations. Presumably, they are concentrated at the ends of screw dislocations and other defect centers, creating a nanoislands in the defect interlayer space, since open valence (broken) bonds of screw dislocations appear, and the rest of the van der Waals surface is chemically inert.

I. Experiment and discussion

Nickel has a small ionic radius; therefore, its atoms easily diffuse into the interlayer space of bismuth chalcogenides. Images in Fig.1., obtained on a scanning probe microscope are shown: an array of nanoislands on a *3D* scale - a) and a *2D* scale - b), a profilogram showing the height and width of nanoislands - c); *X*-ray diffraction pattern of a freshly cleaved *Bi_2Te_3<Ni>* surface -d). The open valence bonds of chalcogen vacancies can combine

with nickel impurity and create compounds found on the surface, as on Fig.1.d), which shows that in addition to *Ni*, $NiTe_2$ and *NiTe* are present on the (0001) surface.

The migration and interaction of atoms with each other leads to the formation of islands in the framework of a process that has a "bottom-up" direction. The main reason for the formation of stressed islands on the surface is the relaxation of elastic stresses at the edges of the layers and the interaction of the islands through the stresses they create in the crystal. The shape of islands can change significantly during postgrowth annealing. Fig.1.a) shows the final result of the dynamics of the formation of large islands from small ones. The dynamics of the formation of nanofragments is such that nanoislands similar to QDs initially appear, and later, in the course of evolution, the islands can approach each other, forming bridges with the preservation of their shapes and heights.

As a result of the developed technology, an ordered array of nanoislands was formed in the process of self-organization on the *(0001)* plane. Particle aggregation leads to a decrease in the distribution density and the appearance of large nanoobjects. Nanoobjects are formed from particles in the process of diffusion at temperatures of 500–600 K. Penetrating mainly into the interlayer space impurities create bulk periodic superstructures consisting of arrays of nanoislands between layers, which, as a result, move apart. The enhancement of anisotropy during the self-assembly of nanoislands leads to an increase in the role of "bending" vibrations in the thermal properties of the crystal **[3,4].** The details of the contacts of Bi_2Te_3<Ni> layers with each other and with INSE not entirely clear, but due to an increase in the anisotropy of electrical conductivity by a factor of 4 [**5**], in comparison with undoped crystals, their influence on the overall conductivity of the sample can be significant. It is assumed that the increased resistance across the layers compared to an undoped crystal is due to the fact that for some of them the contacts with neighboring layers are either interrupted or are energy barriers. The nature of the energy barriers that appear at the edge of the planes can possibly modify the electronic properties of atoms located on the interlayer surface of the crystal.

The difference in size and another type of inhomogeneity lead to a spread of energy levels corresponding to different localized states, so the transitions of charge carriers between localization centers are accompanied by absorption or emission of phonons [**6**]. Since the distance between the centers does not allow the transfer of phonons, the phonon component of the thermal conductivity decreases accordingly. In addition, the mechanism of expansion of the interlayer space is triggered, which prevents the transfer of vibrational energy between layers - phonon confinement, which also leads to a decrease in phonon thermal conductivity. Extending the van der Waals space without destroying the topologically protected states [**7**] shifts them into an inner quintet [**8**]. Interlayer broadening, which reduces the dimension of the structure, can lead to the formation of a new parabolic state at the bottom of the conduction band, which is interpreted as a two-dimensional electron gas coexisting with the surface topological state [**8**], which, by increasing the density of states near the Fermi level, should lead to an additional increase in the thermoelectric power [**9-11**].

As is known [**12,13**], the transverse conductivity is due to the partial overlap of electron orbitals oriented perpendicular to the basal plane and forming weak van der Waals bonds between adjacent layers. There is a

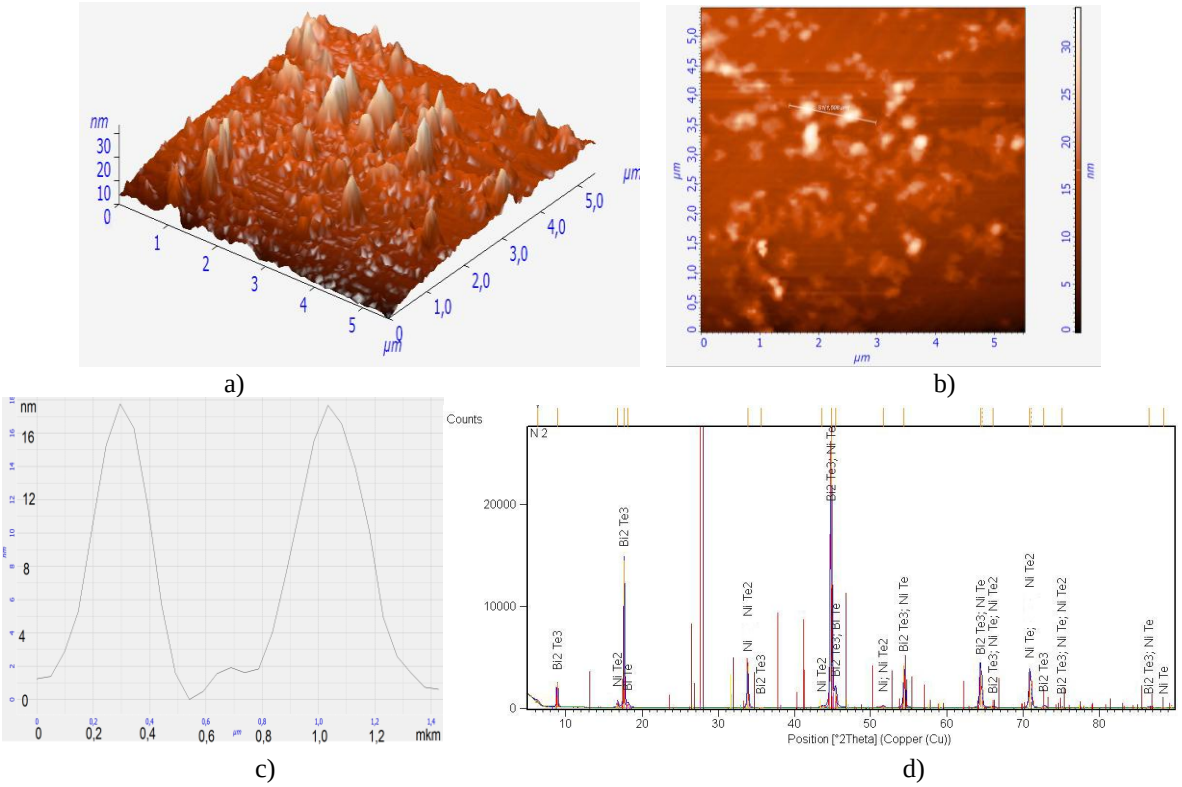


Fig. 1. a) - Bi_2Te_3<Ni> *(0001)* surface AFM image of array of nanoislands on a *3D* scale; b) - AFM image on *2D* scale; c) - profilogram of the highlighted line on b); d) - *X*-ray diffraction pattern of a freshly cleaved Bi_2Te_3<Ni> surface.

difference in the behavior of the zones in the direction perpendicular to the layers of the quintet and those lying in its plane. In the first case, the dispersion of the energy bands is much smaller than in the second. This corresponds to a lower mobility of charge carriers in the direction perpendicular to the layers compared to other directions in the crystal. The layering of the crystal structure affects the form of the energy spectrum, and in the directions perpendicular to the layers the zones are flatter than in other directions. An increase in the conductivity anisotropy due to the expansion of the interlayer distance and an increase in the height of the interlayer barrier, is reduces the overlap of the wave functions of different layers, weakens the dispersion, and brings the energy spectrum of the crystal to a more two-dimensional form. This is confirmed by an abnormal increase in carrier mobility by more than 5 times in the direction of the layers in the samples doped with copper [1]. It was shown in [**8**] that the expansion of the van der Waals gap leads to the formation of a two-dimensional state of an electron gas, formed predominantly by the p_z-orbitals of the atoms Bi.

The sharp increase in the carrier mobility, which indicates the presence of two-dimensional electron gas, indicates the formation of edge states, which can be transformed into an electron gas gapless surface states and TI, with a linear dispersion.

If the atoms located on the edge of the basal plane move away from each other, then the electron valence densities turn out to be even more drawn into the layers. But the five-layer structure of the packet is not changed and the potential relief as well, so the energy bands associated with the atomic states, placed in the plane of the quintet are unchanged. The energy bands corresponding to the electronic states located in the direction perpendicular to the layers are sensitive to changes in the interlayer potential barrier. The symmetry of the Bi_2Te_3 crystal forbids the mixing of the states $|s>$ and $|d_z^n>$ with $|p_x>$ and $|p_y>$, and $|d_z^n>$ with the other d-states at high-symmetry points of the Brillouin zone [**14**], while mixing of all states is allowed at low-symmetry points. As a result, an increase in the potential barrier is accompanied by a shift and splitting ($\Delta E \sim 20$ meV) of some bands and the formation of an energy gap. The shift of some bands can cross the level of ionized impurities and reach the level of an additional subband [2,**15,16**] with a large effective hole mass ~2.4 m_0 located ~20 meV below the top of the valence band. Overlaps of the above bands can lead to a resonant increase in the density of states at these energy levels and possible unstable states up to quantum phase transitions.

In [**8**] refers to the appearance of surface states in the gap of the valence band during moving apart quintets for which are mainly responsible p_z-orbitals of the chalcogen, and the likelihood of inducing topological states for sufficiently large band gap (Fig.2). The shift of the topological state to the second five-layer block, the appearance of states of both a parabolic form, which forms a two-dimensional electron gas localized in the outer five-layer block, and an M-shaped state in the valence band, localized in the vicinity of the broadened van der Waals gap, were explained by the effect of van der Waals gap broadening, the generality of this effect for all layered topological insulators is shown.

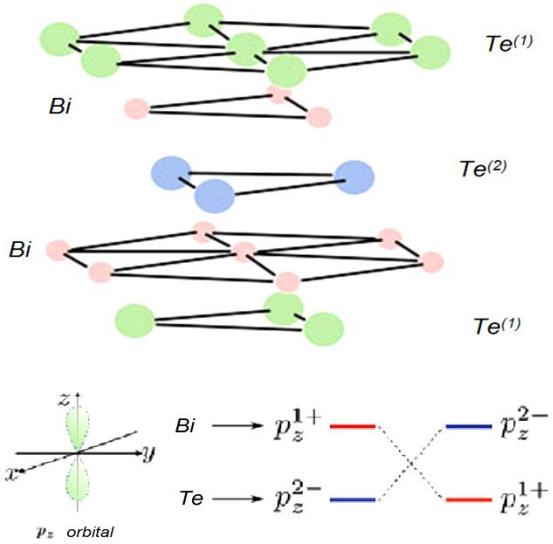
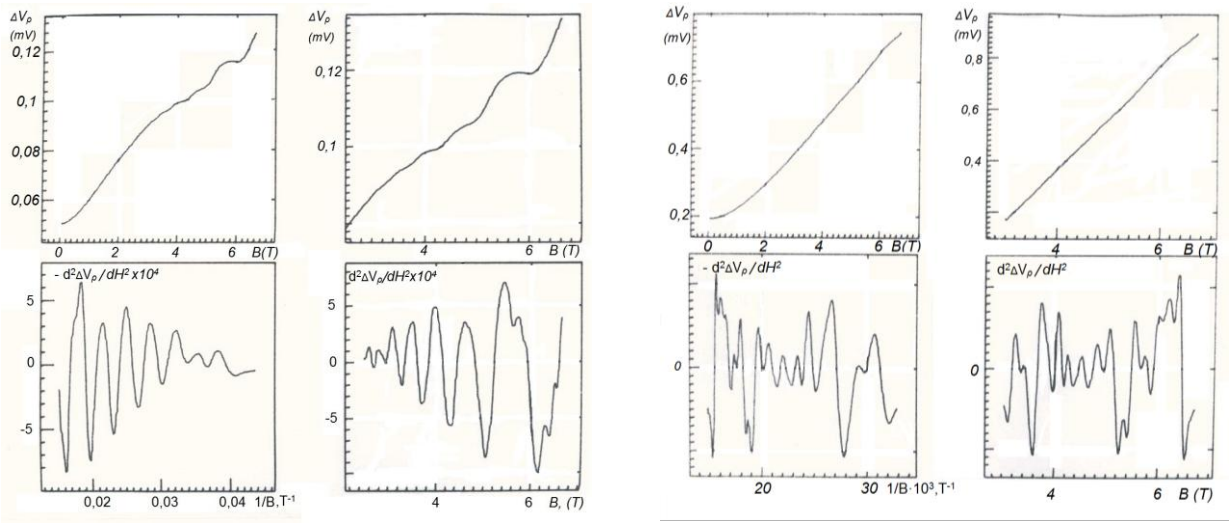


Fig. 2. Important role of *B*i an *Te* p_z-orbitals.

The charge carriers can migrate into quintets and accumulate at the edges of the layers. The electric field generated at the edges of quintets and INSE leads to band bending, and several energy levels can form in the resulting quantum well. The size of the potential well at the edge of the quintet in the direction perpendicular to the layers is on the order of or less than the de Broglie wavelength of the electrons, so the motion of charge carriers in this direction can be quantized. At the same time, they can move freely along the quintet boundary, i.e., behave as two-dimensional ones, but the scattering of charge carriers on potential barriers of the layer boundaries can also increase if these quantized levels are not filled, i.e., when the Fermi level is above these edge levels. The manifestation of the filling and quantization of the edge levels can be an increase in the value of the longitudinal mobility of charge carriers [**17, 18**] associated with the generation of topologically protected metallic states resulting from the splitting off from the edges of the forbidden gap due to the strong spin-orbit interaction of the inverted zones of the semimetal and chalcogen, with their inherent suppression of backscattering.

In the presence of a strong perpendicular magnetic field, an electron gas splits into discrete Landau levels; the separation between the Landau levels increases with the increasing magnetic field. As the magnetic field increases, the Landau levels cut through the Fermi surface one by one. Because Shubnikov-de Haas oscillation only responds to a perpendicular magnetic field, a two-dimensional electron gas has no Shubnikov-de Haas oscillation for in-plane magnetic fields, while a three-dimensional electron gas can have Shubnikov-de Haas oscillation for magnetic field applied along any directions. This makes the angle dependence of Shubnikov-de Haas oscillation a convenient tool to identify the dimension of carriers. The Shubnikov-de Haas oscillation measured in a Bi_2Te_3<*Ni*> crystal shows that the bulk states dominate the transport, because it can be measured for arbitrary magnetic field direction (Fig. 3).



a) b)

Fig. 3. Magnetoresistant and its second derivative curves of Bi_2Te_3<Ni>,
a) orientation of magnetic field perpendicular to plane of surface $B \parallel C \perp I$, T = 4,2K;
b) orientation of magnetic field parallel to plane of surface $B \perp C \perp I$, T = 4,2K.

The formation of an energy barrier at the edge of the layers and the probability of tunneling through such a barrier would lead to a very small contribution to the total conductivity of the crystal system. However, magnetic *Ni* atoms breaks time-reversal symmetry and that opens a gap of Dirac surface state. The Dirac fermion in the surface state becomes massive and leads to many interesting properties. To understand the intrinsic physical properties of the magnetic element doped topological insulator, especially the role of the magnetic element and the related magnetic interaction coupling, it could be helpful to continue this investigations [**19**], because our results might be also related to the ferromagnetism of magnetic elements.

Conclusions

As we can see, both an increase in the potential barrier between the layers, which leads to the splitting of some bands in the bulk of the layers and overlap with an impurity level and a subband with a large effective mass, leads to magnetoresistant oscillations with different frequency.

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[1] S.Sh. Kahramanov. *Self-intercalation in Bi_2Te_3<Cu>*. Inorganic Materials. 44(1), 13 (2008); https://doi.org/10.1134/S0020168508010032.
[2] B.M. Goldsman, V.A. Kudinov. I.A. Smirnov. *Poluprovodnikovye termoelektricheskie materialy na osnove Bi_2Te_3*. Moscow: Nauka, 320 (1977). (in Russian).
[3] G.L.Belenkii, E.Yu.Salaev, R.A.Suleimanov, N.A.Abdullayev and V.Ya. Shteinshraiber. *The nature of negative linear expansion of layer crystals C, BN, GaS, GaSe, InSe*. Solid State Commun, 53(11), 967-971 (1985). https://doi.org/10.1016/0038-1098(85)90470-3.
[4] N.A. Abdullayev, R.A. Suleimanov, M.A. Aldzhanov, and L.N. Alieva. *On the Role of Flexural Vibrations in Heat Transfer in Layered Crystals.* Physics of the Solid State, 44(10), 1859–1863 (2002). https://doi.org/10.1134/1.1514773.
[5] N.A. Abdullayev, S.Sh. Kahramanov, T.G. Kerimova, K.M. Mustafayeva, S.A. Nemov, *Conductivity anisotropy in the doped Bi_2Te_3 single crystals.* Semiconductors, 43(2), 145 (2009); https://doi.org/10.1134/S1063782609020043.
[6] G.L. Belenkii, N.A. Abdullayev, V.N. Zverev, V.Ya. Shteinshraiber. Nature of the conductivity anisotropy and distinctive features in the localization of electrons in layered indium selenide. JETP LETTERS 47(10), 584-587 (1988). http://www.jetpletters.ru/ps/1097/article_16573.pdf.
[7] A. Kundu, A. Zazunov, A.L. Yeyati, T. Martin, R. Egger. *Energy spectrum and broken spin-surface locking in topological insulator quantum dots*. Phys. Rev. B, 83(12), 125429 (2011); https://doi.org/10.1103/PhysRevB.83.125429.

[8] T.V. Menshchikova, S.V. Eremeev, E.V. Chulkov. *On the origin of two-dimensional electron gas states at the surface of topological insulators*. JETP Letters, 94(2), 106 (2011); https://doi.org/10.1134/S0021364011140104.
[9] M.S. Dresselhaus, G. Chen, M.Y. Tang, R.G. Yang, H. Lee, D.Z. Wang, Z.F. Ren, J.P. Fleurial, P. Gogna. *New Directions for Low-Dimensional Thermoelectric Materials*. Advanced Materials, 19(8), 1043 (2007); https://doi.org/10.1002/adma.200600527.
[10] J.P. Heremans. *Low-Dimensional Thermoelectricity*. Acta Physica Polonica A, 108(4), 609 (2005); https://doi.org/10.12693/APhysPolA.108.609.
[11] A.A. Balandin, O.L. Lazarenkova. *Mechanism for thermoelectric figure-of-merit enhancement in regimented quantum dot superlattices*. Applied Physics Letters, 82(3), 415 (2003); https://doi.org/10.1063/1.1539905.
[12] E.V. Oleshko, V.N. Korolyshin, *Quasirelativistic band structure of bismuth telluride*. *Sov. Phys. Solid State*, 27 (9), 1723 (1985).
[13] E.V. Oleshko, V.N. Korolyshin. Ukrainian Phys. J., 31(6), 919 (1986).
[14] E.V. Oleshko, E.I. Veliyulin, V.N. Kozyrenko, S.Sh. Kahramanov. *Characteristics of changes in the electron structure of bismuth telluride due to self-intercalation with copper*. Sov.Phys. Semicond., 25(6), 647 (1991).
[15] V.V. Sologub, A.D. Goletskaya, R.V. Parfen'ev, *Some peculiarities of the Bi_2Te_3 valence band*. Sov. Phys. Solid State, 14 (1972) 783.
[16] V.A. Kul'bachinskii, A.Yu. Kaminskii, N. Miyajima, M. Sasaki, H. Negishi, M. Inoue, H. Kadomatsu. *Quantum Hall effect in the bulk semiconductors bismuth and antimony tellurides: Proof of the existence of a current-carrier reservoir*. Journal of Experimental and Theoretical Physics Letters, 70(11), 767 (1999); https://doi.org/10.1134/1.568260.
[17] Dong-Xia Qu, Y.S. Hor, Jun Xiong , R.J. Cava, N.P. Ong. *Quantum oscillations and hall anomaly of surface states in the topological insulator Bi_2Te_3.* Science, 329 (5993), 821 (2010); https://doi.org/10.1126/science.1189792.
[18] S.Sh. Gahramanov, Y.A. Abdullayev, H.V. Orujova, A.A. Badalov, N.A. Abdullayev. Low Dissipative State of Bi2Se3 and Bi2Te3 Surfaces. J. Surf. Investig. 18, 573–578 (2024). https://doi.org/10.1134/S1027451024700125.
[19] M.M. Otrokov, I.I. Klimovskikh, H. Bentmann, N.A. Abdullayev et al. Prediction and observation of an antiferromagnetic topological insulator. Nature 576, 416–422 (2019). https://doi.org/10.1038/s41586-019-1840-9.

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Розщеплення енергетичних зон із міжшаровим розширенням у Bi_2Te_3<Ni>

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В результаті розробленої технології в процесі самоорганізації на площині Bi_2Te_3<Ni> (0001) утворюється впорядкований масив нановістрівців. Проникаючі переважно в міжшаровий простір домішки створюють об'ємні періодичні надгратки, що складаються з масивів нановістрівців між пакетами шарів, які в результаті розсуваються. Симетрія кристала Bi_2Te_3 забороняє змішування станів $|s\rangle$ і $|d_z^\eta\rangle$ із $|p_x\rangle$ та $|p_y\rangle$, та $|d_z^\eta\rangle$ з іншими d-станами в точках високої симетрії зони Бріллюена, тоді як змішування всіх станів допускається в точках низької симетрії. У результаті, підвищення потенційного бар'єру за рахунок міжшарового розширення супроводжується зміщенням і розщепленням ($\Delta E \sim 20$ меВ) деяких зон та утворенням енергетичної щілини.

Ключові слова: енергетичні зони, самоорганізація, коливання магнітоопору.