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Superconductivity of topological insulator Bi_2Se_3

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The present paper deals with investigation of magnetoresistance and temperature dependencies of resistance for Pd-doped Bi_2Se_3 whiskers. The samples with palladium doping concentration of $(1 \div 2) \times 10^{19}$ cm^{-3} were studied in the temperature range of $1.5 \div 77$ K and magnetic field induction up to 1.5 T. A sharp drop in the whisker resistance was found at the temperature of 5.3 K and 2.2 K. This effect can be explained as a contribution of superconductivity at temperatures under 5.3 K. Low temperatures magnetoresistance investigations allow to obtain critical magnetic field for the superconductivity of about 1.5 T.

Keywords: nematicity, Bi_2Se_3, whiskers, superconductivity, magnetoresistance, critical fields.

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Introduction

Extraordinary kinetic effects such as the manifestation of superconductivity at high temperatures [1], weak anti-localization model [2, 3] and Shubnikov–de Haas oscillations [4, 5], the Kondo effect [6], Berry phase appearance [5], giant and/or negative magnetoresistance [7-9] were studied in functional 1D and 2D structures. They allow creating a new class of devices based on topological insulators [10-12].

Whiskers are ideal objects for observing quantum-dimensional effects, in particular, the shift of energy levels and the reduction of lattice parameters, as well as the appearance of luminescence in visible range and the size dependence of magnetic susceptibility [13].

The studies of magneto-transport properties of Bi_2Se_3 whiskers are interesting from a fundamental point of view. Previous low temperature investigations [2, 14, 15] in heavily doped Bi2Se3 whiskers revealed a number of interesting effects, in particular, the behaviour of their magnetoresistance in weak magnetic fields can be described by a two-dimensional model of weak antilocalization caused by electron-phonon, electron-electron and strong spin-orbital interactions.

The current study is devoted to the investigation of the magnetoresistance of Bi_2Se_3 whiskers in the range of low temperatures and a strong magnetic field. Low-temperature superconductivity with a critical temperature Tc near 5.3 K was found in the heavily doped whiskers, as well as an anomalous increase in magnetoresistance, probably due to the two-dimensional states of whisker surface. In addition, it was established that the minimum in the temperature dependence of whisker resistance at temperature 30 K occurs due to the Kondo effect.

Many works describe the competition of superconductivity and Kondo effect [16, 17]. Our previous study in Bi_2Se_3 whiskers doped to concentrations corresponding to the metal-insulator transition showed the possibility of the coexistence of partial superconductivity and the Kondo interaction [6].

I. Experiment

$Pd_xBi_2Se_3$ whisker growth has been performed according to vapour deposition method in a closed tube. Bromine was used as a transport agent. Precursors bismuth and selenium were loaded in the appropriate ratio to obtain the Bi_2Se_3 composite. Palladium was introduced into the quartz tube to produce n-type conductivity Bi_2Se_3 whiskers.

After evaporation high vacuum has been obtained in the closed system. According to vapor-liquid–crystal mechanism, we used palladium to initiate whisker growth. A sealed quartz tube has been situated into a horizontal furnace, in which a gradient of temperatures between "hot" (800 °C) and "cooled" (480 °C) part was created.

In the end, mirror-like surfaces Bi_2Se_3 whiskers have been grown. The obtained crystals had diameters from 20 to 30 nm and lengths of about 1 to 2 mm. Palladium doping concentration was measured using a microprobe X-ray analyser (CAMEBAX). In the grown Bi_2Se_3 whiskers obtained concentration vary between $(1 \div 2) \times 10^{19}$ cm^{-3}. No other impurities have been detected in the resulting crystals. 10 nm diameter platinum microwires were used as electrical contacts to the Bi_2Se_3 whiskers through a welding method [18, 19]. Therefore, n-type Bi_2Se_3 whiskers doped with palladium concentrations of $(1 \div 2) \times 10^{19}$ cm^{-3}, corresponding to the metallic side of the metal–insulator transition, were prepared and used to study their magnetic properties.

Measurements of the Bi_2Se_3 whisker's low-temperature conductivity was carried out at temperatures down to 1.5 K. Initially, using a helium cryostat samples were cooled to 4.2 K, and further reduction of temperature below 4.2 K achieved by evacuating the cryostat. In order to investigate magnetoresistance behaviour of n-type Bi_2Se_3 whiskers, alternating magnetic inductions from 0 to 1.5 T were applied using a Bitter magnet, scanning at a rate of 1.75 T per minute over a temperature range of 1.5 to 77 K.

II. Experimental results

2.1. Temperature dependence of resistance in Bi2Se3 whiskers

Bi_2Se_3 whiskers with doping concentration $(1 \div 2) \times 10^{19}$ cm^{-3} have been investigated at strong magnetic fields up to 10 T and a temperature range from 1.5 to 77 K. The temperature dependence of resistance at zero magnetic field is presented in Fig. 1.

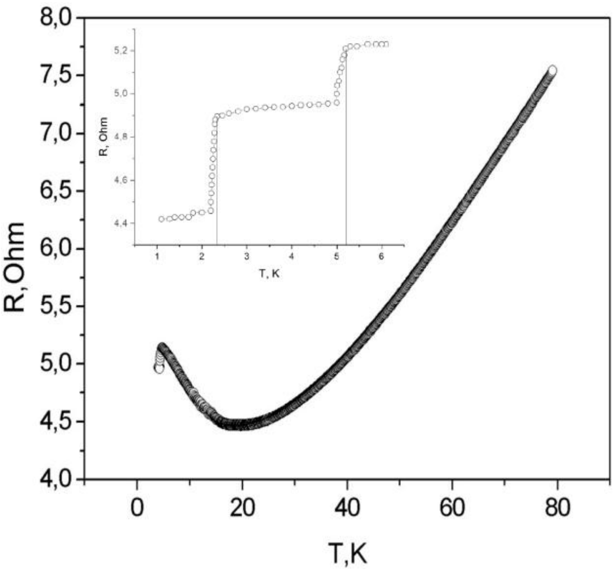

Fig. 1. Temperature dependence of Bi_2Se_3 whiskers at zero magnetic field.

A wide resistance minimum is seen at temperature between 20 and 25 K appeared from the impact of Kondo effect which significantly influences the whiskers resistance. A sharp drop of whiskers resistance occurred at temperature below 5.3 K which indicates in a possible partial superconductivity in the whiskers.

The electrical contacts to Bi_2Se_3 crystals are made from Pt microwires and were connected using the welding method. $PtBi_2$ is only known to be a superconductor at Tc = 1 K [20]. Studies of $PtBi_2$ crystal magnetoresistance up to the temperatures of Tc = 2 K have not shown any superconductivity characteristics [21].

Despite the fact that there is no information about the superconductivity of Pt-Se, we discard possible influence of electrical contacts to observed sharp drop of the whisker's resistance. Such conclusion is made based on the investigations of I–V characteristics in the range of temperatures from 1.5 to 77 K which hasn't provide any differences from Ohm law, which could have evidenced the opposite. Bi_2Se_3 crystals are known to be superconductive being doped with different impurities. For example, $Sr_xBi_2Se_3$ compounds enter superconductivity state at Tc = 2.7 K [22]. $Cu_xBi_2Se_3$ whiskers appeared to have superconductivity up to Tc = 3.8 K. Bi_2Se_3 whiskers doped with Nb [23] or Tl [24] have superconductive states at Tc of about 3 K. In this experiment, whiskers superconductivity is explained by the presence of Pd impurities since a sharp drop of the resistivity occurred at the temperature below 5.3 K, a temperature that does not align with the Curie temperatures.

2.2. Temperature dependence of resistance in Bi2Se3 whiskers

Magnetoresistance properties at different temperatures of Pd doped Bi_2Se_3 whiskers have been studied at magnetic field range from 0 to 1.5 T. Doping concentration of $Pd_xBi_2Se_3$ whiskers is $(1 \div 2) \times 10^{19}$cm^{-3} which corresponds to the metal side of MIT. Results of the investigation are presented in Fig. 2. The investigation hasn't shown any oscillations of Bi_2Se_3 whiskers in contrast to InSb [4] and GaSb [5]. Surface of the whiskers is in good arrange according to observed mirror-like faces using optical microscope. No amorphous phase detected with X-ray diffractogram (XRD) studies, so structure defects cannot be the reason of oscillations absence. We

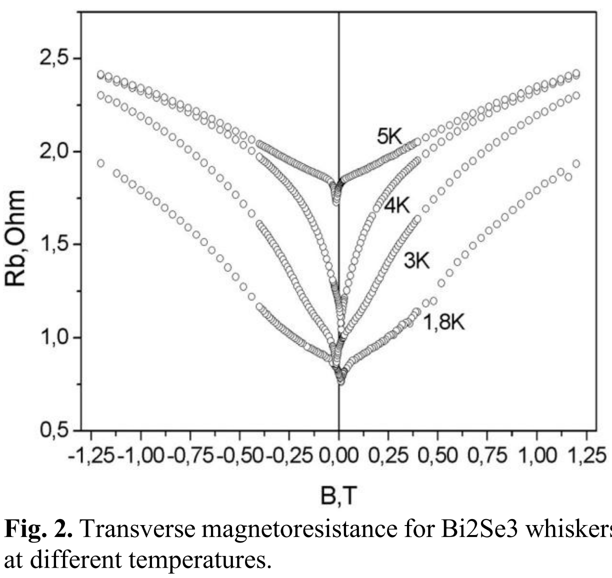

Fig. 2. Transverse magnetoresistance for Bi2Se3 whiskers at different temperatures.

assume that the rootcause of oscillations absence is big doping concentration of about $(1 \div 2) \times 10^{19}$ cm^{-3}. Two interesting features of whiskers are obtained. Anomalous upturn of magnetoresistance at 5.3 K due to low magnetic field (see Fig. 2). The upturn vanishes within the temperature rise (see Fig. 2).

According to findings in paper [25], similar cuprates resistivity behaviour is explained by charge carrier scattering that occurs to interact with magnetic impurity spins. Based on this finding, the magnetoresistance upturn can be linked to derivation of a superconductive state on whiskers.

III. Discussion

We have observed three characteristic peculiarities in the dependency R(T) (see Fig.1). First of all, a large minimum of resistance was observed which corresponds to temperature about 25 K. Next futures that obviously viewed at inset to Fig.1, are two fall down of the resistance at temperatures 5.3 K and of about 2.2 K. The first peculiarity was attributed to presence of Kondo effect in the whiskers that is connected with interaction of electron states of impurity with conductive electrons. The first fall drop of the resistance at 5.3 K was interpreted in the framework of model of unconventional superconductivity. The next future of the Fig.1, i.e., next fall down of the resistance near 2 K was surprise. The phenomenon has not unambiguous explanation. One can suppose a few explanations: (a) presence of nematicity in the whiskers due to our recent findings [15]; (b) presence in the whisker $PtBi_2$ complex due to use of Pt as initiator of the whisker growth. Taking into account our findings [15] in Pd doped Bi_2Se_3 wires a slow nematicity was observed, i.e., temperature of transition in superconductive state varied from 5.5 K to 4.9 K. So, it is impossible interpret the superconductivity at 2.2 K with nematicity existing. The nature of the above superconductivity is likely connected with presence of Pt impurity of the whisker surface and possible $PtBi_2$ complex forming. To check the nature in detail the next structural investigations of the whisker surface are need.

Since a resistance change is quite small, it's worth to assume that superconductivity state appears only in thin subsurface layer, so the observed phenomena is actually a partial superconductivity. As it's shown in experimental data, the doping concentration significantly affects the transition to superconductivity. Increased doping levels affect the balance between Kondo interactions and Cooper pairing. For example, Bi_2Se_3 crystals with a resistivity of ρ_{300K} = 0.004 Ohm × cm exhibit a significant range of carriers localized on impurities. This leads to Kondo interactions due to their interaction with free charge carriers. These interactions, along with thermal effects, disrupt Cooper pairs and impact the superconductivity of the whisker at 5.3 K. The data in Fig. 2 enables the determination of the upper critical magnetic field at which superconductivity vanishes.

Bc_2 can be obtained using the Ginzburg-Landau equation:

$$Bc_2(T) = Bc_2(0)(1 - t^2)/(1 - t^2), \quad (1)$$

where $t = T/T_c$. $Bc_2(T)$ conforms temperature T, where there is full suppression of superconductivity. After linear approximation we can also receive the upper critical field $Bc_2(0)$ using this equation and for whiskers of Bi_2Se_3 and it is about 1.5 T.

Partial superconductivity could be determined using following equation:

$$Bc_2 = \Phi_0/(2\pi\xi(0)^2), \quad (2)$$

where Φ_0 stands for the flux quantum equal to 2.07×10^{-15} T × m^2, ξ (0) is superconductor coherence length. Obtained superconductor coherence length ξ (0) = 18 nm for Bi_2Se_3 crystals. This value is much less comparing with 200 nm for $Cu_xBi_2Se_3$ crystals [26]. The Cooper pairs in Bi_2Se_3 whiskers have a coherence length of 18 nm, which is comparable to the 15 nm coherence length observed in $Sr_xBi_2Se_3$ whiskers [27]. This similarity to high-Tc superconductors suggests the potential for unique phenomena that differ from those typically seen in low-Tc materials [28]. The superconductivity gap could be determined by using this equation [26]:

$$\Delta = \frac{3.5K_BT_c}{2}, \quad (3)$$

With substitution of T_c = 5.3 K and Boltzmann constant K_B to the equation (3), we obtain the superconductive gap that is 0.8 meV. This value matches with the theoretical gap of 0.6 meV [26]. As previously mentioned, the likely cause of superconductivity in the crystals is the increased palladium doping concentration, which serves as the foundation for whisker growth. Experimental data [20] indicates the onset of superconductivity at T_c = 5.5 K in $Pd_xBi_2Te_3$ whiskers. Similarly, β-$PdBi_2$ whiskers exhibit superconductivity at T_c = 5.3 K [28], aligning with our experimental findings. The coherence length of β-$PdBi_2$ crystals is approximately 20 nm [28], which is also consistent with our results. These observations suggest that the superconductivity in Bi_2Se_3 crystals is associated with palladium doping. Furthermore, the resistivity does not drop to zero, indicating a low palladium concentration due to the challenges of implantation in whiskers.

Conclusion

For Bi_2Se_3 wires a temperature dependence of a resistance was investigated in the temperature fields from 1.5 to 77 K. The transition in the superconductive state of a part of the whisker was declared. The partial superconductivity preferably on the whisker surface was supposed due to a resistance didn't diminish to zero. The next step of our investigation was analysis of behavior of the wires in slow magnetic fields. For this purpose, the fields with magnetic field induction up to 1.5 T were used. Anomalous upturn of magnetoresistance at 5.3 K due to low magnetic field was shown. Due to analysis of magnetoresistance a set of superconductivity parameters like that of superconductive gap of 0.8 meV, superconductor coherence length ξ (0) = 18 nm were obtained. All of them indicate that a nature of the superconductivity has unconventional character, in particular a high Curie temperature. Experimental data indicates that superconductivity at Tc = 5.5 K in $Pd_xBi_2Se_3$ whiskers is similar with β-PdBi2 complex in the whiskers which exhibit superconductivity at Tc = 5.3 K aligning with our experimental findings. The coherence length of β-$PdBi_2$ crystals is approximately 20 nm, which is also consistent with our results. These observations suggest that the superconductivity in Bi_2Se_3 crystals is associated with palladium doping. Nature of next fall down of the resistance at 2.2 K is likely connected with presence in the whiskers of $PtBi_2$ complex with characteristic Curie temperatures of Tc = 2 K. Pt impurity was used as initiator of the whisker growth and due to whisker annealing localize at the crystal surface and in such a way could be responsible for partial superconductivity at low temperatures. The nature of this superconductivity requires further investigation of the whisker surface, particularly through Auger electron spectroscopy and ARPES analysis.

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Надпровідність топологічного ізолятора Bi_2Se_3

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У даній роботі досліджуються магнітоопір і температурні залежності опору ниткоподібних кристалів Bi_2Se_3, легованих Pd. Зразки з концентрацією домішок Pd $(1 \div 2) \times 10^{19}$ см$^{-3}$ були вивчені в діапазоні температур $1,5 \div 77$ К та при магнітній індукції до 1,5 Т. Було виявлено різке падіння опору ниткоподібних кристалів при температурах 5,3 К і 2,2 К. Цей ефект можна пояснити внеском надпровідності при температурах нижче 5,3 К. Дослідження магнітоопору при низьких температурах дозволяють визначити критичне магнітне поле для надпровідності, яке становить приблизно 1,5 Т.

Ключові слова: нематичність, ниткоподібні кристали Bi_2Se_3, надпровідність, магнетоопір, критичні поля.