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Critical fields and features of electromagnetic transport of Bi_2Se_3 whiskers at low temperatures

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The temperature dependences of resistance of *n*-type conductivity Bi_2Se_3 whiskers with doping concentration (1–2)·10^{19} cm^{-3} were studied in the temperature range 1.6–300 K. The sharp drop of the resistance was detected that is a result of a partial transition to the superconductive state at the critical temperature T_c = 5.3 K and probably due to the inclusion of β-$PdBi_2$ phase in the studied samples. The transverse magnetoresistance of Bi_2Se_3 whiskers with various concentration of Pd doping impurity corresponding to the metal side of metal–insulator transition was studied in a magnetic field of 0–10 T. Superconductivity suppression effect by the magnetic field was found that permits to create the basic parameters such as the upper critical field B_{c2} = 1.5 T, the coherence length of the superconductor ξ (0) = 15 nm and the superconducting gap Δ ≈ 0.8 meV. Studies of the *n*-type conductivity Bi_2Se_3 whiskers allow to create on their basis magnetic field sensors with a sensitivity of about 3.5 %/T, capable in the temperature range of 4.2–77 K. The investigated crystals can also be used in the magnetic switch-control sensors magnetic switches due to the transition to the superconducting state at the critical temperature T_c, depending on a magnetic field induction.

Keywords: Bi_2Se_3 whiskers, transverse and longitudinal magnetoresistance, superconductivity, magnetic switch-control sensor.

1. Introduction

Numerous studies are focused on the functional 1D and 2D materials that are suitable for the creation of different devices, which work in difficult operating conditions [1, 2]. Moreover, unique effects such as high-temperature superconductivity [3], the Kondo effect [4], the occurrence of the Berry phase [5, 6], Shubnikov–de Haas oscillations (SdH) [6], giant (GMR) or negative (NMR) magnetoresistance [7–11] have been seen. All of them open the possibility of creating a new class of devices based on topological insulators [3], which by their properties can be attributed to specific devices [12].

Different structures on the InSb material base with narrow bandgap could be used in electronic device applications due to their high electron mobility, peak velocities, and small electron effective mass. The high velocities of antimonide based compound semiconductors were observed in the analog electronic devices with low power consumption at low electric fields [12–14].

On the other hand, filamentary crystals are ideal model objects with the possibility of the existence of quantum-dimensional effects. Among these effects are: a decrease in the lattice parameter, a shift in energy levels, the luminescence appearance in the visible range as the diameter is reduced to less than 1 μm, the appearance of a dimensional dependence of the magnetic susceptibility, which is different from the one observed in bulk samples [15].

In this case, the study of the magneto-transport properties of Bi_2Se_3 whiskers is interesting from both practical and fundamental point of view. Firstly, the magnetic response of this material determines the possibility of using whiskers in sensors of various physical quantities under the influence of an external magnetic field. Previous studies [16, 17] of Bi_2Se_3 whiskers at low temperatures have revealed a number of interesting effects. In work [16], the temperature dependence of resistance was measured in the temperature range 1.5–300 K and the sharp drop was found at a temperature below 5.3 K. At the same time, the magnetoresistance behavior of Bi_2Se_3 whiskers in weak magnetic fields could be described due to the two-dimensional weak antilocalization model that corresponded to the electron-electron, electron-phonon and spin-orbit interaction. As follows, the behavior of the temperature dependence of the resistance is covered to the contribution as the superconductivity and weak electron antilocalization. Using a sharp drop in electrical conductivity and magnetic resistance with certain values of the critical field (B_c) at low temperatures, it is possible to offer realization of this effect in switch-control sensors, which could be used in difficult operating conditions. The magnetoresistance behavior at high temperatures, where its growth with the temperature increase was previously investigated, seems interesting.

Thus, the aim of the work is to study the magnetic resistance of Bi_2Se_3 whiskers in the temperature range 1.6–300 K in strong magnetic fields with induction up to 10 T with their further application in sensors, which operate in difficult conditions.

2. Method and object research

Filamentous crystals of Bi_2Se_3 were grown by gas transport reactions in a closed ampoule type system. The transport agent bromine was used to transfer the material from the evaporation zone to the cooling zone, which serves as a zone of crystallization and growth of crystals. In order to ensure stable crystal growth, it was necessary to create a temperature gradient along the length of the ampoule, which was in the range 1100–780 K for the evaporation zone and the crystallization zone, respectively. An admixture of palladium was added in a closed ampoule to ensure the required level of doping with the impurity in Bi_2Se_3 whiskers. The samples of *n*-type conductivity Bi_2Se_3 whiskers with palladium doping concentration $(1–2)\cdot 10^{19}$ cm^{-3} that correspond to the metal side of the metal–insulator transition (MIT) have been used for studying their magneto-transport properties. Thus, the doping of Bi_2Se_3 whiskers was carried out during the growth of whiskers, which provides the flexibility of the method. The crystals were joined to platinum conductors by pulse welding. The creation of Pt–BiSe eutectic provides the mechanical strength and ohmic of the metal-semiconductor contact. Measurements were performed according to a four-contact scheme. The measurements of current-voltage characteristics were performed to check the electrophysical parameters of the metal-semiconductor contact (Fig. 1).

The low-temperature conductivity of the Bi_2Se_3 whiskers has been studied at temperatures down to 1.6 K. Ensuring such a low temperature allowed the design of a special insert and helium cryostat type Oxford. It helped to carry out the experiments within the framework of the agreement on scientific cooperation between Lviv Polytechnic National University, Lviv, Ukraine and the Institute of Low Temperature and Structure Research, Wroclaw, Poland. The design of a special insert for studying the electrophysical properties of Bi_2Se_3 whiskers gave the possibility of simultaneous pumping and injection of helium vapor into a closed space of the insert, in which a rarefied pressure of about 0.6 bar was previously maintained. Continuous pumping of helium vapor from the insert provided a decrease in the temperature study to 1.6 K. Temperature stabilization of the study process was maintained using a PID-temperature controller. Automatic registration, visualization and saving the data arrays into files have been used to measure the voltage at the potential contacts of samples. In addition, a preliminary assessment of the electrophysical parameters of Bi_2Se_3 whiskers was conducted with the help of a certified hardware and research complex PPMS (Physical Properties Measured System), which involves the study of galvanomagnetic effects (Hall potential) to assess the level of doping. Measurements were performed on both alternating and direct currents.

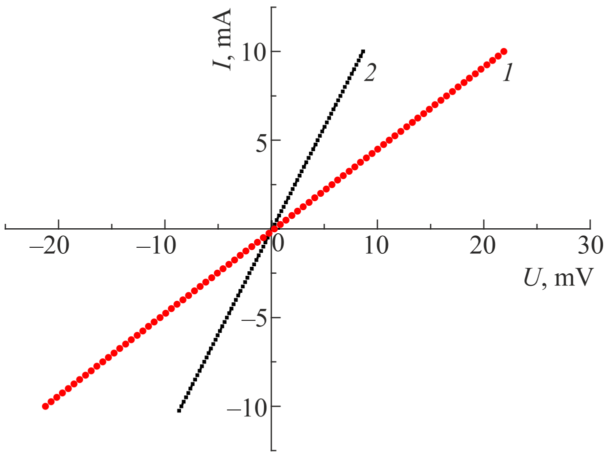

Fig. 1. The current-voltage characteristics of Bi_2Se_3 whiskers at temperatures, K: 4.2 (*1*), 77 (*2*).

3. Experimental results and discussion

Investigation of electrical conductivity of Bi_2Se_3 whiskers was carried out in the temperature range 4.2–300 K. Investigation of magnetoresistance of the whiskers was carried out in the temperature range 1.6–100 K. The properties of the whiskers were considered in the context of the superconductivity of the second type-II at ultra-low temperatures [16]. The resistance changes abruptly, only approaching zero, reaches residual values with a certain critical temperature T_c, or critical value of the magnetic field B_c. Particular attention was drawn to the study of magnetoresistance in the field of helium temperatures up to 1 T. The temperature dependence of resistance (Fig. 2) is shown for Bi_2Se_3 whiskers doped to concentrations in the vicinity to MIT from metal side of the transition. Main characteristics for whisker superconductivity are a very little change in their resistance that indicates the existence of a superconducting state exclusively in a thin subsurface layer of Bi_2Se_3 whiskers. A possible mechanism of superconductivity emergence is the partial superconductivity on the surface of Bi_2Se_3 whiskers.

Superconductivity suppression due to a magnetic field influences are informative for the determining its nature. We carried out series of the experiments on the influence of the magnetic field on the behavior of whisker superconductivity and determined the critical magnetic field B_{c2} from the Ginzburg–Landau equations:

$$B_{c2}(T) = \frac{B_{c2}(0)(1-t^2)}{1+t^2}, \tag{1}$$

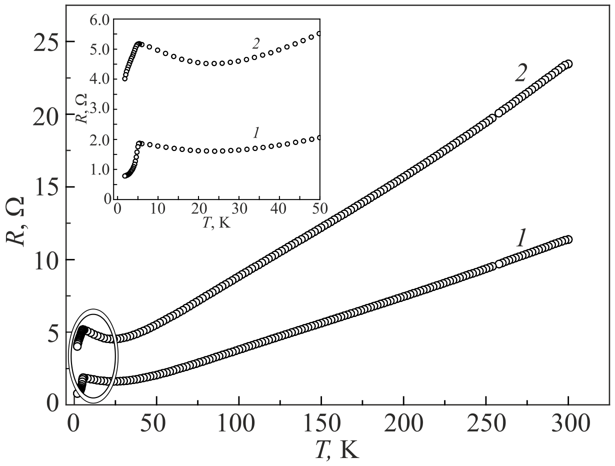

Fig. 2. Temperature dependences of resistance for Bi_2Se_3 whiskers at 4.2–300 K with different doping concentration, cm^{-3}: $1\cdot10^{19}$ (*1*), $2\cdot10^{19}$ (*2*). Inset: temperature dependence of resistance for Bi_2Se_3 whiskers in the temperature range 4.2–50 K.

where $t = T/T_c$. According to expression (1), the dependence $B_{c2}(T)$ was plotted (Fig. 3).

Value of the critical field $B_{c2}(T)$ corresponds to the temperature T, for which there is a complete suppression of superconductivity. Then Eq. (1) permits us to determine upper critical magnetic field $B_{c2}(0)$ for the Bi_2Se_3 whiskers. Experimental data linear approximation gives a value of approximately $B_{c2}(0)$ = 1.5 T (see Fig. 4, inset). One can find the superconducting coherence length ξ(0) from expression:

$$B_{c2}(0) = \frac{\Phi_0}{2\pi\xi(0)^2}, \quad (2)$$

where Φ_0 is quantum flux, that equal to $2.07\cdot10^{-15}$ $T\cdot m^2$. We obtained that ξ(0) = 15 nm for Bi_2Se_3 whiskers. The coherence length obtained for $Cu_xBi_2Se_3$ crystals are substantially less than value of 200 nm [18]. The Cooper pair

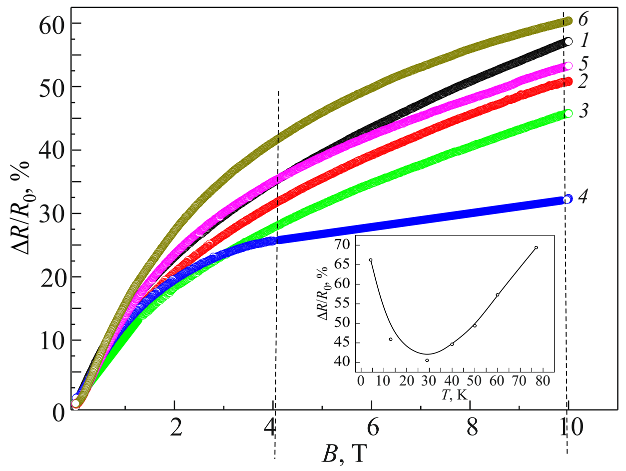

Fig. 3. Longitudinal magnetoresistance of Bi_2Se_3 whisker at different temperatures, K: 4.2 (*1*), 10 (*2*), 20 (*3*), 40 (*4*), 60 (*5*), 90 (6). Inset: temperature dependence of longitudinal magnetoresistance in Bi_2Se_3 whisker at magnetic field induction 10 T.

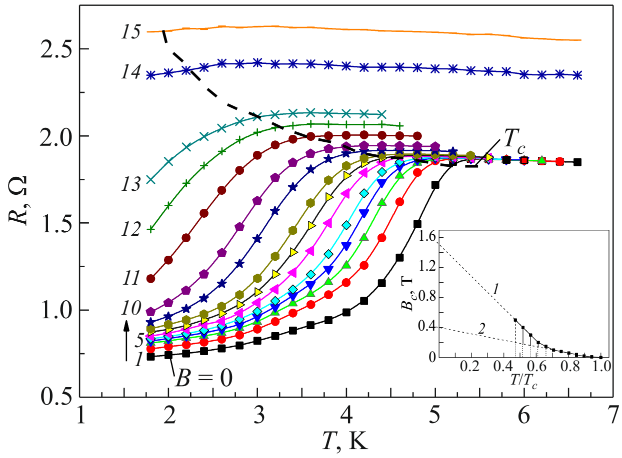

Fig. 4. Temperature dependences of resistance for Bi_2Se_3 whisker in the temperature range 1.6–7 K at fixed magnetic fields, T: 0 (*1*), 0.01 (*2*), 0.02 (*3*), 0.03 (*4*), 0.04 (*5*), 0.06 (*6*), 0.08 (*7*), 0.1 (*8*), 0.15 (*9*), 0.2 (*10*), 0.3 (*11*), 0.4 (*12*), 0.5 (*13*), 1.0 (*14*), 1.5 (*15*). Inset: Critical magnetic field induction for superconductivity (*1*) in Bi_2Se_3 whiskers [16] and weak localization (*2*).

coherence length consists of 18 nm, that comparable to that ξ(0) = 15 nm for $Sr_xBi_2Se_3$ [19], just like for high-T_c superconductors, can lead to variety of exciting phenomena in contradistinction to materials with low levels of T_c [20].

Value of the superconducting gap can be determined due to expression [18]:

$$\Delta = \frac{3.5 k_B T_c}{2}. \quad (3)$$

Substituting the value of T_c = 5.3 K and the Boltzmann's constant k_B, we obtained a superconducting gap of approximately 0.8 meV that agrees well with the literature data of 0.6 meV [18].

Let's discuss the possible cause of the superconductivity in the Bi_2Se_3 whiskers. The most possible mechanism of the whisker superconductivity is the intercalation of the Pd doping impurity that was used as an initiator of their growth. There are the literature data [21] on the superconductivity appearance with the critical temperature T_c = 5.5 K in the $Pd_xBi_2Te_3$ crystals. In addition, β-$PdBi_2$ crystals are superconducting with T_c = 5.3 K [22] that coincides with the data of our experiments. The superconductivity coherence length is approximately of 20 nm in β-$PdBi_2$ crystals [22], which agrees well to our results. These data indicate a possible cause of the superconductivity connected with the intercalation of Pd impurities in the Bi_2Se_3 whiskers. The partial superconductivity agrees well with the data [21] for the $Pd_xBi_2Te_3$ crystals, when the resistivity also does not fall to zero. This may be due to the rather low concentration of Pd dopants associated with rigid intercalation in the whiskers. To deepen the nature of the superconductivity observed in the whiskers, it is worth conducting further structure and research of ARPES.

The behavior of the magnetoresistance could be related to two probable causes: the weak localization and the electron-electron interaction or coexistence of these both effects. The weak localization effect occurs in the diffuse mode with electron relaxation time τ when $k_B T^{\tau}/h < 1$, whilst the electron-electron interaction predominates in the transient and the ballistic mode at $k_B T^{\tau}/h > 1$. In addition, it is worth noting that weak localization effect takes place in the weak magnetic fields, but the electron-electron interaction occurs in the strong fields [23].

Figure 3 shows that the magnetoresistance change of *n*-type conductivity Bi_2Se_3 in the field 4–10 T and at different temperatures acquires a linear character with a sensitivity to changes in the field 3.6 %/T. Such properties could be used in magnetic field sensors with the magnetoresistive principle of operation, which work at cryogenic temperatures in the range 4.2–77 K. However, must be taken into account the temperature change of the magnetoresistance in Bi_2Se_3 whiskers, at which the magnetoresistance falls in the range 4.2–30 K, and then it increases with increasing temperature (see Fig. 3, inset) by magnetic field induction 10 T. The alternating properties of the whisker magnetoresistance with critical temperature T_c = 30 K can be used for so-called switch-devices.

Figure 4 shows the dependence of the resistance of the Bi_2Se_3 whiskers with the concentration of charge carriers $1\cdot10^{19}$ cm^{-3} at ultra-low temperatures in the range 1.6–7 K at different fixed values of magnetic field induction in the range 0–1.5 T.

In *n*-type conductivity Bi_2Se_3 whiskers with the concentration of charge carriers $1\cdot10^{19}$ cm^{-3} there is a sharp drop in magnetoresistance in the temperature range 1.6–7 K with different value B_c transition to the superconducting state. This can be used in magnetic switch-control sensors. Figure 5 shows the temperature dependence of the transverse magnetoresistance with different values of the critical transition temperature T_c.

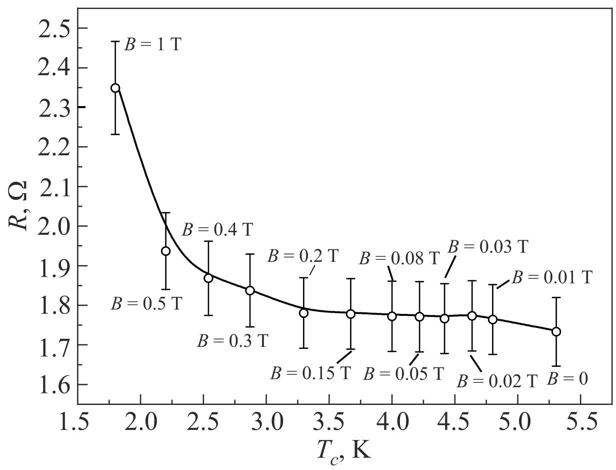

Fig. 5. Temperature dependences of transverse magnetoresistance in Bi_2Se_3 whiskers vs critical temperature of transition.

From Fig. 5 can be seen that the Bi_2Se_3 whiskers have a negative coefficient of resistance in magnetic fields with induction up to 1 T in the temperature range 1.5–5.5 K. Its value is approximately 7.3 %/K.

4. Conclusions

It was established, that *n*-type conductivity Bi_2Se_3 whiskers with Pd doping concentration level (1–2)$\cdot10^{19}$ cm^{-3} that corresponds to the metal side of the metal–insulator transition in the temperature range 1.6–300 K and magnetic fields with induction up to 10 T can be used in devices at ultra-low temperatures. It was shown, that Bi_2Se_3 whisker can be used in magnetic field sensors with the magnetoresistive principle of operation in the temperature range 4.2–77 K. Magnetoresistance of the whiskers is linear in the field 4–10 T with a sensitivity to changes in the field 3.6 %/T. In addition, the alternating properties of the magnetoresistance of the whiskers with critical temperature $T_c \approx 30$ K can be used in the magnetic field of 10 T and at cryogenic temperatures of 4.2–77 K in switch-devices.

Bi_2Se_3 whiskers with *n*-type conductivity, which were used at ultra-low temperatures (1.5–5.5 K), can employ in threshold devices that work in harsh operating conditions. Therefore, the magnetic switch-control sensors use transition to the superconducting state with its critical transition temperature T_c depending on the magnetic field, in which the crystal is located. The negative coefficient of resistance in such whiskers reaches near 7.3 %/K.

1. D. G. Hayes, C. P. Allford, G. V. Smith, C. McIndo, L. A. Hanks, A. M. Gilbertson, and P. D. Buckle, *Semicond. Sci. Technol.* **32**, 085002 (2017).
2. I. Fezai and S. Jazir, *Superlattice. Microst.* **59**, 60 (2013).
3. Y. Yan, Z. M. Liao, Y. B. Zhou, H. C. Wu, Y. Q. Bie, J. J. Chen, and D. P. Yu, *Sci. Rep.* **3**, 1264 (2013).
4. A. Druzhinin, I. Ostrovskii, Yu. Khoverko, and N. Liakh-Kaguy, *Fiz. Nizk. Temp.* **43**, 871 (2017) [*Low Temp. Phys.* **43**, 692 (2017)].
5. H. Murakawa, M. S. Bahramy, M. Tokunaga, Y. Kohama, C. Bell, Y. Kaneko, and Y. Tokura, *Science* **342**, 1490 (2013).
6. A. Druzhinin, I. Ostrovskii, Yu. Khoverko, N. Liakh-Kaguy, and K. Rogacki, *Fiz. Nizk. Temp.* **44**, 1521 (2018) [*Low Temp. Phys.* **44**, 1189 (2018)].
7. A. Husmann, J. Betts, G. B. Boebinger, A. Migliori, T. Rosenbaum, and M. L. Saboungi, *Nature* **417**, 421 (2002).
8. A. Druzhinin, I. Ostrovskii, Yu. Khoverko, and N. Liakh-Kaguy, *Fiz. Nizk. Temp.* **42**, 581 (2016) [*Low Temp. Phys.* **42**, 453 (2016)].
9. Y. A. Soh and G. Aeppli, *Nature* **417**, 392 (2002).
10. F. Y. Yang, K. Liu, K. Hong, D. H. Reich, P. C. Searson, and C. L. Chien, *Science* **284**, 1335 (1999).
11. S. A. Solin, T. Thio, D. R. Hines, and J. J. Heremans, *Science* **289**, 1530 (2000).

12. B. R. Bennett, R. Magno, J. B. Boos, W. Kruppa, and M. G. Ancona, *Solid State Electron.* **49**, 1875 (2005).
13. M. Edirisooriya, T. D. Mishima, C. K. Gaspe, K. Bottoms, R. J. Hauenstein, and M. B. Santos, *J. Cryst. Growth* **311**, 1972 (2009).
14. H. Peng, K. Lai, D. Kong, S. Meister, Y. Chen, X. L. Qi, and Y. Cui, *Nat. Mater.* **9**, 225 (2010).
15. A. Druzhinin, I. Ostrovskii, Y. Khoverko, N. Liakh-Kaguy, and A. Lukyanchenko, *Mol. Cryst. Liq. Cryst.* **674**, 1 (2018).
16. A. Druzhinin, I. Ostrovskii, Y. Khoverko, K. Rogacki, and N. Liakh-Kaguy, *Appl. Nanosci.* **8**, 877 (2018).
17. A. A. Druzhinin, N. S. Liakh-Kaguy, I. P. Ostrovskii, Yu. M. Khoverko, and K. Rogacki, *J. Nano- Electron. Phys.* **9**, 05013-1 (2017).
18. L. A. Wray, S. Y. Xu, Y. Xia, Y. San Hor, D. Qian, A. V. Fedorov, and M. Z. Hasan, *Nat. Phys.* **6**, 855 (2010).
19. Shruti, V. K. Maurya, P. Srivastava, and S. Patnaik, *Emergence of superconductivity in topological insulator* Bi_2Se_3 *by* Sr *intercalation*, in: AIP Conference Proceedings 1731(1), 130046 (2016).
20. M. Tinkham, *Introduction to Superconductivity*, McGraw-Hill. Inc., New York (1996), Ch. 3.
21. Y. S. Hor, J. G. Checkelsky, D. Qu, N. P. Ong, and R. J. Cava, *J. Phys. Chem. Solids* **72**, 572 (2011).
22. M. Sakano, K. Okawa, M. Kanou, H. Sanjo, T. Okuda, T. Sasagawa, and K. Ishizaka, *Nat. Commun.* **6**, 1 (2015).
23. D. R. Leadley, V. V. Andrievskii, I. B. Berkutov, Y. F. Komnik, T. Hackbarth, and O. A. Mironov, *J. Low Temp. Phys.* **159**, 230 (2010).

Критичні поля та особливості електромагнітотранспорту ниткоподібних кристалів Bi_2Se_3 при низьких температурах

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Досліджено температурні залежності опору ниткоподібних кристалів Bi_2Se_3 провідності *n*-типу з концентрацією легуючої домішки (1–2)·10^{19} см$^{-3}$ в інтервалі температур 1,6–300 К. Виявлено різке падіння опору, що є результатом часткового переходу в надпровідний стан за критичної температури T_c = = 5,3 К, ймовірно, пов’язане з включенням β-$PdBi_2$ фази у досліджуваних зразках. У магнітних полях з індукцією 0–10 Тл вивчено поперечний магнітоопір ниткоподібних кристалів Bi_2Se_3 із різною концентрацією легуючої домішки Pd, що відповідає металевій стороні переходу метал–діелектрик. Встановлено ефект пригнічення надпровідності магнітним полем, який дозволяє визначити такі основні параметри, як верхнє критичне поле B_{c2} = 1,5 Тл, довжину когерентності надпровідника ξ (0) = 15 нм та величину надпровідної щілини Δ ≈ 0,8 меВ. Проведені дослідження ниткоподібних кристалів Bi_2Se_3 провідності *n*-типу можуть бути використані для створення датчиків магнітного поля з чутливістю близько 3,5 % / Тл, які дієздатні в інтервалі температур 4,2–7 К. Досліджені кристали також можуть використовуватися в магнітних перемикачах за рахунок переходу в надпровідний стан за критичної температури T_c, залежної від індукції магнітного поля.

Ключові слова: ниткоподібні кристали Bi_2Se_3, поперечний і поздовжній магнітоопір, надпровідність, магнітний перемикач.