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Unconventional superconductivity in PdxBi$_2$Se$_3$ whiskers

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In the paper, studies of the temperature dependence of the magnetoresistance of $Pd_xBi_2Se_3$ whiskers in the temperature range of 1.6-77K in a magnetic field up to 10 T were carried out. Crystals were grown by the method of chemical transport reactions in a closed bromide system. The source and crystallization zone temperatures were 1100 K and 780 K, respectively. Doping of the crystals was carried out during the growth process with a palladium impurity to concentrations of $(1 – 2) \times 10^{19}$ cm^{-3}. In the low-temperature region beginning at a temperature of 5 K and reaching a temperature 3.5 K, a sharp decrease in resistance was observed, which is associated with the transition of crystals to a superconducting state. Based on the analysis of the temperature dependence of the resistance at fixed magnetic fields from 0.01 to 0.5 T, the Curie temperature Tc_1=5.3 K and Tc_2=3.5 K as well as the upper critical magnetic field Bc_2=1.45 T and 0.25 T, respectively, were determined. The established parameters allow us to state that this is superconductor of a type II with unusual superconductivity. This is indicated by the ratio $\Delta_0/k_BT_c = 2.0$, which exceeds the standard BCS limit of 1.76 and indicates a relatively large value of the superconducting gap Δ_0=0.8 meV. The determined ratio A/γ^2, which establishes the relationship between the electron-electron and electron-phonon interaction, is about of $2a_o$, which indicates a strong fermionic interaction in the $Pd_xBi_2Se_3$ superconductor due to the interaction of Cooper pairs with phonons. The estimated value of the ratio of the Curie temperature to the effective Fermi temperature equal to 0.04 also falls within the range of $0.01 \leqslant T_c/T_F \leqslant 0.1$, which confirms the unconventional superconductivity in the investigated whiskers.

Keywords: whiskers, superconductivity, bismuth selenium, Curie temperature.

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Introduction

Intercalation of metal in Bi_2Se_3 compound gives a large impact on change of their electronic properties. In particular, it leads to arising of superconductivity. The superconductivity was observed in Sr, Cu, Pd and Nb doped matrix. The values of Curie temperatures are different for every structure, but they are defined as high temperature superconductors. The mechanisms of high temperature superconductivity regarding the relatively low-carrier density are still not found. Nevertheless, there are a numerous experimental data which confirmed the influence of SOI on the value of superconductivity. First of all, a transition from Ising atom orbital to Rashba (or Zeeman) spin-orbit interaction takes place in the compounds [1]. The latter SOI could break time-reversal symmetry of topological insulator surface leading to change of conditions for Cooper pairing creation [2]. Such is a common explanation of unconventional character of superconductivity which consists in rather high temperature of superconductivity. For example, in $Cu_xBi_{2-x}Se_3$ Curie temperature T_c is 3.4 K [3-6], for $Sr_xBi_{2-x}Se_3$ T_c is 3.5 K [7-10], for $Nb_xBi_{2-x}Se_3$ T_c is 2.5 K [11-16], while for $Pd_xBi_{2-x}Se_3$ T_c is 5.3 K [17-18]. In recent paper we also observed the transition to superconductive state for $Pd_xBi_2Se_3$ wires, which shown to be at 5.3 K [19-21]. Besides, the investigation of superconductivity in Bi_2Se_3 and Bi_2Te_3 compounds are very promising considering possible application in the high temperature superconductive device. A proximity of such topological semiconductors to $Bi_2Sr_2CaCu_2O_{8+\delta}$, allow to access higher temperature superconductivity – up to 80 K with rather large superconductive gap – up to 10 meV [22].

The aim of the present work is to establish the main parameters, which underline the unconventional character of the observed superconductivity in $Pd_xBi_{2-x}Se_3$ wires.

I. Method and object research

Bi$_2$Se$_3$ whiskers were grown by gas transport reactions method in a closed halogenide 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 from 1100 K to 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$_2$Se$_3$ whiskers. The samples of n-type conductivity Bi$_2$Se$_3$ whiskers with palladium doping concentration $(1 – 2) \times 10^{19}$ cm^{-3} that correspond to the metal side of the metal-insulator transition have been used for studying their magneto-transport properties. Thus, the doping of Bi$_2$Se$_3$ 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 volt-ampere characteristics were performed to check the electrophysical parameters of the metal-semiconductor contact.

The low-temperature conductivity of the Bi$_2$Se$_3$ whiskers have 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$_2$Se$_3$ 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$_2$Se$_3$ 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.

II. Experimental results

Investigation of electrical conductivity of Bi$_2$Se$_3$ whiskers doped to concentrations in the vicinity to MIT from metal side of the transition 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 Tc, or critical value of the magnetic field B$_c$. The temperature dependence of resistance (Fig. 1) is shown for Bi$_2$Se$_3$ whiskers. As shown from the Fig.1, in the low-temperature region beginning at a temperature of 5 K and reaching a temperature 3.5 K, a sharp decrease in resistance was observed, which is associated with the transition of crystals to a superconducting state. 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$_2$Se$_3$ whiskers. A possible mechanism of superconductivity emergence is the partial superconductivity on the surface of Bi$_2$Se$_3$ whiskers.

Particular attention was drawn to the study of magnetoresistance in the field of helium temperatures up to 1 T. Superconductivity suppression due to a magnetic field influences are informative for the determining its nature. Therefore, we conducted series of the experiments on the influence of the magnetic field on the behavior of whisker superconductivity (Fig. 2) that allows determining the critical magnetic field Bc$_2$ inasmuch the Ginzburg-Landau equations:

$$B_{c2}(T) = \frac{B_{c2}(0)(1-t_2)}{(1+t_2)}, \quad (1)$$

where t$_2$= T/Tc. According to expression (1), the dependence Bc$_2$(t) was constructed (Fig. 2, inset).

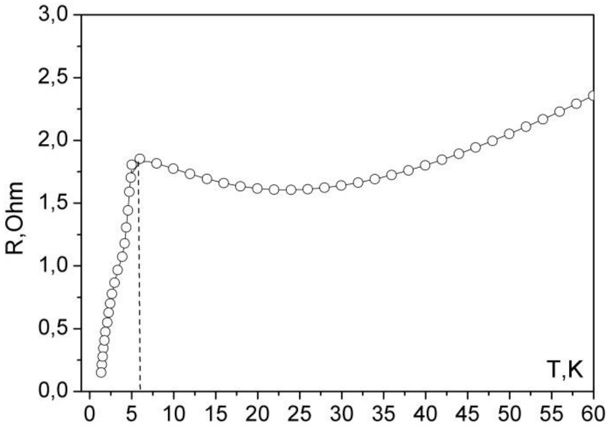

Fig. 1. Temperature dependency of resistance for Bi$_2$Se$_3$ whiskers at 4.2 – 60 K with doping concentration 10^{19} cm^{-3}.

Value of the critical field Bc$_2$(T) corresponds to the temperature T, for which there is a complete suppression of superconductivity. Then equation (1) permits us to determine upper critical magnetic field Bc$_2$(0) for the Bi$_2$Se$_3$ whiskers. Experimental data linear approximation gives a values of approximately Bc$_2$(0) equal to 0.25 T and 1.45 T (Fig. 2, inset), respectively. A crossover of line approximation with T/Tc axis (Fig. 2, inset) gives a temperature 3.5 K, that indicates in two step transition in superconductive state. The nature of the transition will be considered elsewhere. Using the expression:

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

where Φ_0 is quantum flux, that equal to 2.07×10^{-15} T×m^2, the coherence length of the superconductor $\xi(0)$=15 nm was obtained for Bi_2Se_3 whiskers. The coherence length value, which obtained for $Cu_xBi_2Se_3$ crystals, is substantially less than value of 200 nm [23]. The Cooper pair coherence length consists of 18 nm, that comparable to that $\xi(0)$ = 15 nm for $Sr_xBi_2Se_3$ [24], just like for high-Tc superconductors, can lead to variety of exciting phenomena in contradistinction to materials with low levels of Tc. Value of the superconducting gap can be determined due to expression [23]:

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

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 [23].

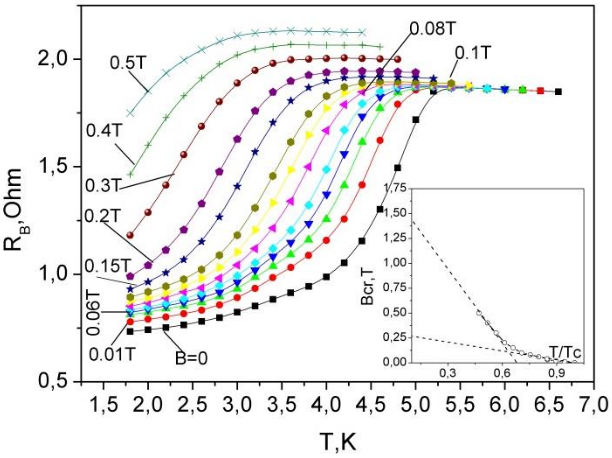

Fig. 2. Temperature dependences of resistance for Bi_2Se_3 whisker in the temperature range 1.6 – 7 K at fixed magnetic fields. Inset: Critical magnetic field induction for superconductivity in Bi_2Se_3 whiskers.

III. Discussion

The task of the chapter is to distinguish the main characteristic parameters which determine an unconventional superconductivity in the investigated structures. Thus, let us consider below the parameters for $Pd_xBi_2Se_3$ whiskers. Taking into account the obtained data, i.e. a value of superconductive gap Δ~ 0.8 meV, the ratio of energy gap Δ to k_BTc Δ_0/k_BT_c was estimated to be 2.0. The obtained value exceeds the standard BCS (Bardeen–Cooper–Schrieffer) value 1.764, confirming that $Pd_xBi_2Se_3$ is a strong-coupling superconductor. The similar parameter was observed in $Cu_x Bi_2Se_3$ structures, which consists of 2.046 [25]. Therefore, one can suppose, that the Δ_0/k_BT_c value exceeds BCS one for the all Bi_2Se_3 family and it could be used as a marker of unconventional superconductivity in such crystals.

As shown from Uemura's scaling rule [26], the maximum T_c in unconventional superconductors is in orders of magnitude greater than Tc for conventional ones and lie in proximity to T_B. The effective parameter for classification is a ratio of Curie temperature to effective Fermi temperature T_C/T_F. For conventional BCS superconductors T_C/T_F<1/1000. As shown from the Figure 3, the parameter T_C/T_F for various unconventional superconductors including compounds Bi_2Se_3 ranges from 0.01 to 0.1. Since the Curie temperature correlates with superfluid density n_s and is reciprocal to effective mass m* of charge carriers, unconventional superconductors have rather high density of state at Fermi energy. The reason of such enhancement of density of state is likely to result from electron-phonon interaction.

The superconductivity of this new phase fully satisfied the adiabatic Born–Oppenheimer approximation $\omega/E_F \ll 1$, according to the theory of acoustic phonon-mediated superconductivity [27]. To verify this, we calculated the Fermi energy E_F, which shown to be 7.7 eV, assuming a free electron gas approximation. This results in $\omega/E_F = 3.63\times10^{-3}$ by taking the highest frequencies of the A_{1g} mode. According to BCS theory the T_c is given by an equation
$T = 1.14\theta_D exp[-1/N(E_F)V_0]$ for a phonon-mediated superconductor in weak coupling limit with Debay temperature θ_D and $(E_F)V_0 = \delta - \mu$, where V_0 is effective electron–electron interaction potential containing an attractive part from electron-phonon interaction δ and a repulsive electron–electron contribution μ.

The electron–electron (e–e) scattering dominates over the e–p scattering at low temperatures for $M_xBi_2Se_3$ (M = Cu, Sr, Nb, Pd). For further estimation of the Kadowaki–Woods ratio A/γ^2, which measure a level of electron-electron correlation, one can fit $\rho(T)$ the data using the simple formula $\rho = \rho_0 + A\cdot T^2$. The results of Figure 1 allow to obtain the fitting parameters ρ_0 = 133.4 μΩ cm and A= 0.003 μΩ cm K^{-2}. For 2D conductance in metal, the coefficient A is given by

$$A = \left(\frac{8\pi^3 ack_{B}{}^{2}}{e^2h^3}\right)\left(\frac{m^{*2}}{kF^3}\right) \qquad (4)$$

Taking the values of a= 4.143 Å and c= 28.636 Å for Bi_2Se_3, m^* = 0.194m_e and k_F= 0.97 nm^{-1} [25], we obtain A = 0.006 μΩ cm K^{-2}. The received values of A from approximation of the data of Figure 1 and from the equation (4) give the good coincidence. This confirms that 2D conduction takes place in $Pd_xBi_2Se_3$, as is resulted from the layered whisker structure. Therefore, the 2D Fermi liquid conductance is dominant in the whiskers at low temperatures.

Then we estimate the electronic Sommerfield coefficient γ_s and the density of states at E_F by the relation [25]

$$\gamma_s = \frac{\mu_0 H_c{}^2(0)}{2\pi T_c{}^2} = \frac{1}{3}\pi^2 k_B{}^2 N(E_F) \qquad (5)$$

By use the above calculated parameters, we obtain γ_s = 0.8 mJ mol^{-1} K^{-2}and $N(E_F)$ = 1.3 states/eV atoms spin^{-1} per f.u. Taking into the calculated data, one can estimate A/γ^2 ratio, which consists of 2a_o, that is consistent with ones for heavily-fermion superconductors and approximates to most of cuprates, as well as rather exceeds the values for transition metals. The high values for A/γ^2 ratio is the next parameter, which evidences the unconventional superconductivity in the investigated crystals.

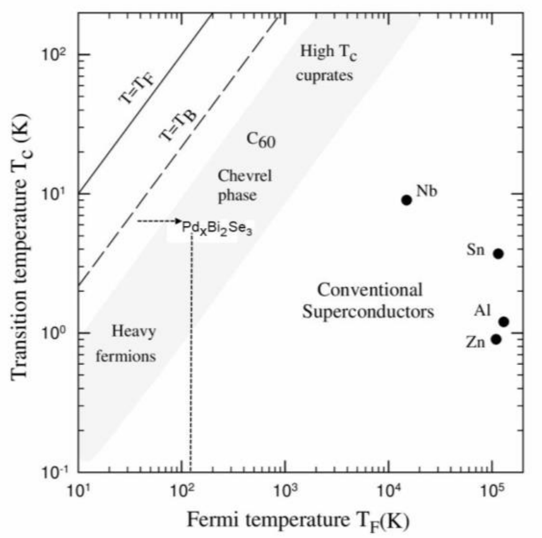

Fig. 3. Curie temperature versus effective Fermi temperatures for wide classes of superconductors.

One can calculate effective Fermi temperature T_F taking into account clean limit for 3D superconducting systems [28]:

$$k_B T_F = \frac{h^2}{2}\frac{(3\pi^2 n)^{2/3}}{m*} \quad (6)$$

Converting 3D system in 2D plane for topological surface carrier density $n^{2D}=n\cdot d_{int}$ (d_{int} is the interatomic distance) , one can obtain the equation for 2D electron gas

$$k_B T_F^{2D} = \frac{h^2 \pi n^{2D}}{m*} \quad (7)$$

By use of obtained values of n and m^* [29], we calculate the T_F^{2D} = 120 K, resulting in T_c/T_F^{2D} = 0.04, falling into the range of $0.01 \leqslant T_c/T_F \leqslant 0.1$ for unconventional superconductors. Thus, it is the next confirmation of unconventional superconductivity in $Pd_xBi_2Se_3$ whiskers.

Thus, the high Tc in Bi_2Se_3 compounds is connected with an increase of state density at Fermi energy as well as the strong electron-phonon coupling of charge carriers.

Conclusions

The investigations of temperature dependencies of resistance as well as magnetoresistance in PdxBi$_2$Se$_3$ whiskers in magnetic fields up to 10 T were fulfilled. The x content in the whiskers was of about 0.1, which gives the n-type conductance with carrier concentration exceeds 10^{19} cm^{-3}. The investigations were conducted in a wide temperature region from 1.6 K to liquid nitrogen temperatures. The resistance dependence on temperature has abruptly fall down below the temperature 5.3 K, which was shown to be a transition in superconductive state. This was confirmed by the temperature dependencies of magnetoresistance at fixed magnetic fields that allows to determine the upper magnetic field 1.5 T of superconductivity existing in the whiskers. The approximative estimation conducted in the paper for parameters underlining an unconventional character of superconductivity in the crystals of Bi_2Se_3 family. The first of such parameter is a ratio of superconductive gap Δ_0 to $k_B T_c$, which was shown to be of about 2.0. The value exceeds BCS one and is a marker of unconventional superconductivity in the crystals. The next parameter was the Kadowaki–Woods ratio A/γ^2, that characterized a level between electron-electron and electron-phonon interaction in the crystals. The ratio in unconventional superconductors exceeds the parameter of crystalline lattice, while for transition metals it still lies in the approximation to 0.01 a_0. For $Pd_xBi_2Se_3$ whiskers A/γ^2 exceeds 2 a_0, that evidence in unconventional superconductivity in them. The ratio of Curie temperature Tc and effective Fermi temperature T_F is the last characteristic parameter, which was determined in the paper and consists of 0.04 for PdxBi$_2$Se$_3$ whiskers indicating an approximation to temperature T_B in BCS theory. A proximity of T_C/T_F to clean limit also indicates in unconventional character of superconductivity.

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[1] H.Yi, L.H. Hu, Y. Wang, *et al. Crossover from Ising- to Rashba-type superconductivity in epitaxial* Bi_2Se_3*/monolayer* $NbSe_2$ *heterostructures*, Nat. Mater., 21, 1366 (2022); https://doi.org/10.1038/s41563-022-01386-z.

[2] C Z. Chang, P.Wei, & J.S. Moodera, *Breaking time reversal symmetry in topological insulators*, Mrs Bulletin, 39(10), 867 (2014); https://doi.org/10.1557/mrs.2014.195.

[3] M. Kriener, K. Segawa, Zhi Ren, S. Sasaki, Y. Ando, *Bulk Superconducting Phase with a Full Energy Gap in the Doped Topological Insulator CuxBi*$_2$*Se*$_3$, Phys. Rev. Lett. 106, 127004 (2011); https://doi.org/10.1103/PhysRevLett.106.127004.

[4] T. Kawai, C. Wang, Y. Kandori, Y. Honoki, K.Matano, T. Kambe, G.-Q.Zheng, *Direction and symmetry transition of the vector order parameter in topological superconductors CuxBi*$_2$*Se*$_3$, Nat Commun, 11(1), 1 (2020); https://doi.org/10.1038/s41467-019-14126-w.

[5] Y.S. Hor, A.J. Williams, J.G. Checkelsky, P. Roushan, J. Seo, Q.Xu, H.W.Zandbergen, A.Yazdani, N.P. Ong, R.J. Cava, *Superconductivity in* $CuxBi_2Se_3$ *and its implications for pairing in the undoped topological insulator*. Phys Rev Lett, 104(5), 057001 (2010); https://doi.org/10.1103/PhysRevLett.104.057001

[6] K. Matano, M. Kriener, K. Segawa, Y. Ando, G.-Q. Zheng, *Spin-rotation symmetry breaking in the superconducting state of* $CuxBi_2Se_3$. Nat Phys 12(9), 852 (2016); https://doi.org/10.48550/arXiv.1512.07086

[7] Z. Liu, X. Yao, J. Shao, M. Zuo, L. Pi, S. Tan, C. Zhang, Y. Zhang, *Superconductivity with Topological Surface State in* $Sr_xBi_2Se_3$, J. Am. Chem. Soc., 137, 10512 (2015); https://doi.org/10.1021/jacs.5b06815

[8] Z. Li, M. Wang, D. Zhang, N. Feng, W. Jiang, C. Han, W. Chen, M. Ye, C. Gao, J. Jia, et al., *Possible structural origin of superconductivity in Sr-doped* Bi_2Se_3. Phys Rev Materials, 2(1), 014201 (2018); https://doi.org/10.1103/PhysRevMaterials.2.014201

[9] Y. Pan, A. Nikitin, G. Araizi, Y. Huang, Y. Matsushita, T. Naka, A. De Visser, *Rotational symmetry breaking in the topological superconductor* $SrxBi_2Se_3$ *probed by upper-critical field experiments*. Sci Rep, 6(1), 1 (2016); https://doi.org 10.1038/srep28632.

[10] Jiayuan Hu, Wenxiang Jiang, Qi Lu, Chenhang Xu, Jiangtao Wu, Jinlong Jiao, Guohua Wang, Jie Ma, Dong Qian, *Manipulating the magneto-resistance of* Bi_2Se_3 *thin films by strontium doping*. Journal of Applied Physics, 132 (9): 095302 (2022); https://doi.org/10.1063/5.0092075.

[11] M. M. Sharma, P. Rani, L. Sang, X. L.Wang, & V. P. S. Awana, *Superconductivity below 2.5 K in* $Nb_{0.25}Bi_2Se_3$ *topological insulator single crystal*, Journal of Superconductivity and Novel Magnetism, *33*, 565 (2020); https://doi.org/10.48550/arXiv.1911.08108.

[12] B. Lawson, P. Corbae, G. Li, F. Yu, T. Asaba, C. Tinsman, Y.Qiu, J.E. Medvedeva, Y.S. Hor, L. Li, *Multiple fermi surfaces in superconducting Nb-doped* Bi_2Se_3. Phys Rev B **94**(4), 041114 (2016); https://doi.org/10.1103/PhysRevB.94.041114.

[13] T. Asaba, B. Lawson, C.Tinsman, L. Chen, P. Corbae, G. Li, Y. Qiu, Y.S. Hor, L. Fu, L. Li, *Rotational symmetry breaking in a trigonal superconductor Nb-doped* Bi_2Se_3, Phys Rev X, **7**(1), 011009 (2017); https://doi.org/10.1103/PhysRevX.7.011009.

[14] K. Kobayashi, T.Ueno, H. Fujiwara, T.Yokoya, J. Akimitsu, *Unusual upper critical field behavior in Nb-doped bismuth selenides*, Phys Rev B, **95**(18), 180503 (2017); https://doi.org/10.1103/PhysRevB.95.180503.

[15] J. Wang, F.Jiao, D. Zhang, M. Chang, L. Cai, Y. Li, C.Wang, S. Tan, Q. Jing, B. Liu, et al., Investigate the Nb doping position and its relationship with bulk topological superconductivity in $NbxBi_2Se_3$ by X-ray photoelectron spectra, J Phys Chem Solids, 137, 109208 (2020); https://doi.org/10.1016/j.jpcs.2019.109208.

[16] S.M. Kevy, H.E. Lund, L.Wollesen, K.J. Dalgaard, Y.-T. Hsu, S.Wiedmann, M. Bianchi, A.J.U. Holt, D. Curcio, D. Biswas, et al., *Structural and electronic inhomogeneity of superconducting Nb-doped* Bi_2Se_3, Phys Rev B, 103(8), 085107 (2021); https://doi.org/10.1103/PhysRevB.103.085107.

[17] Z Sharma, M., Sang, L., Rani, P., Wang, X., Awana, V. *Bulk superconductivity below 6 k in* $PdBi_2Te_3$ *topological single crystal*, J Supercond Nov Magn 1 (2020); https://doi.org/10.48550/arXiv.1912.09647.

[18] A. Vashist, Y. Singh, *The ht and pt phase diagram of the superconducting phase in Pd:* Bi_2Te_3, J Supercond Nov Magn **29**(8), 1975–1979 (2016); https://doi.org/10.1007/s10948-016-3499-x.

[19] N.S. Liakh-Kaguy, A.A. Druzhinin, I.P. Ostrovskii, Yu.N. Khoverko, *Magnetoresistance of* Bi_2Se_3 *Whiskers at Low Temperatures*, Physics and Chemistry of Solid State, 16 (2), 194, (2017); https://doi.org/10.15330/pcss.18.2.194-197.

[20] A. Druzhinin, I. Ostrovskii, Y. Khoverko, N. Liakh-Kaguy, & V.Troshina, *Magneto-transport properties of* Bi_2Se_3 *whiskers: superconductivity and weak localization*, Molecular Crystals and Liquid Crystals, 701(1), 82 (2020); https://doi.org/10.1080/15421406.2020.1732565.

[21] A.A. Druzhinin, N.S. Liakh-Kaguy, I.P. Ostrovskii, Y.M. Khoverko, & K. Rogacki, *Superconductivity and Kondo effect of* $PdxBi_2Se_3$ *whiskers at low temperatures*, Journal of Nano- and Electronic Physics, 9(5), 5013-1 (2017); https://doi.org/10.21272/jnep.9(5).05013.

[22] P. Zareapour, A.Hayat, S. Zhao, *et al.*, *Proximity-induced high-temperature superconductivity in the topological insulators* Bi_2Se_3 *and* Bi_2Te_3, Nat Commun , 3, 1056 (2012); https://doi.org/10.1038/ncomms2042.

[23] L. Wray, S.Y. Xu, Y. Xia, et al. *Observation of topological order in a superconducting doped topological insulator*, Nature Phys., 6, 855 (2010); https://doi.org/10.1038/nphys1762

[24] Mingtao Li, Yifei Fang, Curtis Kenney-Benson, and Lin Wang, *Superconductivity and electron–phonon interaction in* $SrxBi_2Se_3$ *under pressure*, New Journal of Physics, 23, 083011(2021); 1 https://doi.org/0.1088/1367-2630/ac14cf.

[25] Y. Fang, W. L.You, & M. Li, *Unconventional superconductivity in* $CuxBi_2Se_3$ *from magnetic susceptibility and electrical transport*, New Journal of Physics, *22*(5), 053026 (2020); https://doi.org/10.1088/1367-2630/ab7fca.

[26] Adrian Hillier, Robert Cywinski, *The classification of superconductors using muon spin rotation*, Applied Magnetic Resonance, 13(1) (1997); https://doi.org/10.1007/BF03161973.

[27] Uemura, Y. J. *Classifying superconductors in a plot of Tc versus Fermi temperature* T_F, Physica C: Superconductivity, 185, 733 (1991); https://doi.org/10.1016/0921-4534(91)91590-Z.

[28] J.Wang, K.Ran, S. Li, *et al.*, *Evidence for singular-phonon-induced nematic superconductivity in a topological superconductor candidate* $Sr_{0.1}Bi_2Se_3$. Nat Commun , 10, 2802 (2019); https://doi.org/10.1038/s41467-019-10942-2.

[29] M. T. Li, Y. F. Fang, J. C. Zhang, H. M. Yi, X. J. Zhou, & C. T. Lin, *Magnetotransport study of topological superconductor Cu0.10Bi2Se3 single crystal*. Journal of Physics: Condensed Matter, 30(12), 125702, (2018); https://doi.org/10.1088/1361-648X/aaaca1.

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Незвичайна надпровідність в ниткоподібних кристалах PdxBi$_2$Se$_3$

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У роботі проведені дослідження температурної залежності магнітоопору ниткоподібних кристалів Pd$_x$Bi$_2$Se$_3$ в температурній області 1,6-77К в магнітному полі до 10 Тл. Кристали вирощувалися методом хімічних транспортних реакцій в закритій бромідній системі. Температури зони джерела та кристалізації становили 1100 К та 780К, відповідно. Легування кристалів здійснювалося в процесі росту домішкою паладію до концентрацій $(1 – 2) \times 10^{19}$ см$^{-3}$. В низькотемпературній області, починаючи з температури 5 К і досягаючи температури 3,5 К, спостерігалося різке зменшення опору, яке пов’язано з переходом кристалів в надпровідний стан. На основі аналізу температурних залежностей опору при фіксованих магнітних полях від 0,01 до 0,5 Тл визначено температуру Кюрі T_{c1}=5,3 К і T_{c2}=3,5 К та верхнє критичне магнітне поле Bc2=1,45 Тл та 0,25 Тл, відповідно. Встановлені параметри дозволяють стверджувати, що це надпровідник ІІ-го роду з незвичайним характером надпровідності. На це вказує відношення Δ_0/k_BT_c = 2,0, яке перевищує стандартний БКШ ліміт 1,76 і свідчить про відносно велике значення надпровідної щілини Δ_0=0,8 меВ. Визначене відношення A/γ^2, яке встановлює взаємозв’язок електрон-електронної та електрон-фононної взаємодії, становить $2a_0$, що свідчить про сильну ферміонну взаємодію в надпровіднику Pd$_x$Bi$_2$Se$_3$, зумовлену взаємодією куперівських пар з фононами. Оцінена величина відношення температури Кюрі до ефективної температури Фермі T_c/T_F^{2D}= 0,04 також попадає в область $0,01 \leqslant T_c/T_F \leqslant 0,1$, що підтверджує незвичайний характер надпровідності у досліджуваних ниткоподібних кристалах.

Ключові слова: ниткоподібні кристали, надпровідність, вісмут селен, температура Кюрі.