JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. 9 No 5, 05013(5pp) (2017)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том 9 № 5, 05013(5cc) (2017)

Superconductivity and Kondo Effect of $Pd_xBi_2Se_3$ Whiskers at Low Temperatures

A.A. Druzhinin[1,2*], N.S. Liakh-Kaguy[1†], I.P. Ostrovskii [1,2], Yu.M. Khoverko[1,2], K. Rogacki[2]

[1] *Ukraine Lviv Polytechnic National University, 12, S. Bander str., 79013 Lviv, Ukraine*
[2] *International Laboratory of High Magnetic Fields and Low Temperatures Wroclaw, Poland*

(Received 20 May 2017; revised manuscript received 08 September 2017; published online 16 October 2017)

Temperature dependencies of Bi_2Se_3 whiskers' resistance with Pd doping concentration of $(1\text{-}2) \times 10^{19}\,cm^{-3}$ where measured in temperature range 1.5-77 K. At temperature 5.3 K a sharp drop in the whisker resistance was found. The effect observed is likely resulted from the whiskers partial transition in superconducting state at temperature 5.3 K, which is likely connected with β-$PdBi_2$ inclusions in the whiskers. Transverse magnetoresistance in n-type Bi_2Se_3 whiskers with different doping concentration in the vicinity to the metal-insulator transition from metal side of the transition was studied in magnetic field 0-10 T. The magnetic field suppression of superconductivity allows to determine the main parameters: upper critical magnetic field $B_{c2} = 1.5$ T, superconductor coherence length $\xi(0) = 15$ nm, superconductive gap $\Delta \sim 0.8$ meV. Besides on the temperature dependence of the whisker resistance and magnetoresistance a minimum was observed in the temperature range 20-25 K that is connected with appearance of Kondo effect.

Keywords: Bi_2Se_3 whiskers, Transverse magnetoresistance, Effect Kondo, Superconductivity.

DOI: 10.21272/jnep.9(5).05013 PACS numbers: 73.43.Qt, 71.30.+h

1. INTRODUCTION

Studies of topological materials (TM) are very promising for revealing various extraordinary effects such as superconductivity [1], Kondo effect [2], presence of Majorana fermions [3] etc. Some works concern to investigation of interaction of the above effects, e.g. in [4] a possible influence of Majorana fermions on Kondo behavior in TM is comprehensively studied. On the other hand, there are many works describing a competition of Kondo effect and superconductivity [5-7]. Our previous investigation have indicated in a possibility of co-existing Kondo effect and partial superconductivity in GaSb whiskers heavily doped to concentrations corresponding to MIT [8]. Magnetotransport properties of various heavily doped semiconductor whiskers such as Ge, InSb, GaSb at low temperatures [9-12] allowed us to establish SdH oscillations, week antilocalization as well as strong spin-orbital interaction. The current study concerns to investigation of Bi_2Se_3 whisker magnetoresistance in low temperature range (1.5-77 K) and high magnetic field up to 10 T. Low temperature superconductivity with critical temperature Tc near 5.3 K as well as anomalous magnetoresistance upturn is revealed in the whiskers and likely connected with 2*D* states of the whisker surface. Besides minimum on the temperature dependence of the whisker resistance at 30 K is found to originate as a result of Kondo interaction.

2. EXPERIMENT

The whiskers of $Pd_xBi_2Se_3$ for $x = 0.001\text{-}0.002$ were prepared by chemical vapors deposition (CVD) method in closed quartz reactor. Bromine was used as transport agent. The precursors Bi and Se in corresponded ratio to obtain Bi_2Se_3 compound as well as Pd were load in quartz tube and evaporated to high vacuum. Pd impurity was used for initiation of the whiskers growth according to vapour-liquid-solid (VLS) mechanism. The reactor was situated in horizontal furnace with temperature gradient. The high temperature part of the tube has 800℃, while low temperature part of the tube, where the whiskers grow, has 480℃. As a result of growth process with duration of about 1 hour the whiskers with mirror faces were obtained. The whisker diameter ranges from 20 to 30 μm, their length approach to 1-2 mm. The investigation of the whisker by microprobe X-ray analizator (CAMEBAX) allows to determine the concentration of Pd in the whiskers of about $(1\text{-}2) \times 10^{19}\,cm^{-3}$. There are no any others impurities in the whiskers as shown by the method (up to the values of trace concentrations of the method of about $10^{18}\,cm^{-3}$). The electrical contacts for the whiskers were made by welding of Pt microwire with diameter of 10 μm. The type of the whisker conductance was checked on the sing of thermo-e.m.f. and was established to be *n*-type. Two groups of n-type Bi_2Se_3 whiskers with different doping concentration in the vicinity to MIT from metal side of the transition were selected to study their resistance and magnetoresistance:

Bi_2Se_3 whiskers with the impurity concentration $(1 \times 10^{19}\,cm^{-3})$ in the nearest approximation to MIT with resistivity $\rho_{300\,K} = 0.0053$ Ohm × cm;

Bi_2Se_3 whiskers with the greater impurity concentration $(2 \times 10^{19}\,cm^{-3})$ with resistivity $\rho_{300\,K} = 0.004$ Ohm × cm.

Low-temperature conductivity of Bi_2Se_3 whiskers was investigated in the temperature range 1.5-77 K. For these studies crystals were placed in the helium cryostat where they were cooled to temperature 4.2 K. The lower temperatures below 4.2 K were reached by pumping the cryostat (up to 1.5 K). The effect of magnetic field on the properties of the whiskers was studied using the Bitter magnet with the induction 10 T

* druzh@polynet.lviv.ua
† liakh76@gmail.com

and time scanning the field 1.75 T/min in the temperature range 1.5-77 K.

3. RESULTS AND DISCUSSION

3.1 Temperature dependence of Bi_2Se_3 whisker resistance

Bi_2Se_3 whisker resistance is investigated in wide temperature range (1.5-77 K) at magnetic field induction up to 10 T. The temperature dependence of resistance for the whiskers with different doping concentration at a zero magnetic field is shown in Fig. 1.

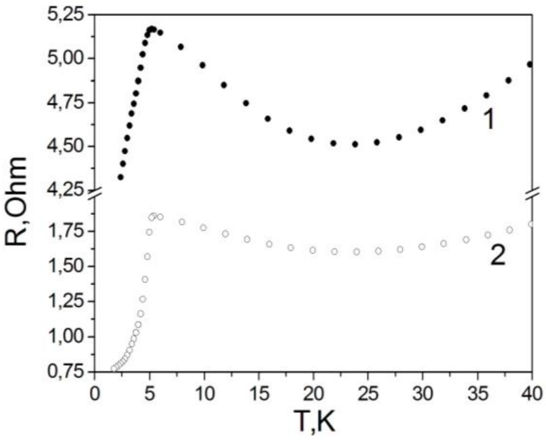

Fig. 1 – Temperature dependence of resistance for n-type Bi_2Se_3 whiskers with various resistivity: 1 – $\rho_{300\,K}$ = 0.0053 Ohm × cm; 2 – $\rho_{300\,K}$ = 0.004 Ohm × cm

There are the following peculiarities of the curves in the range of low temperatures (Fig. 1): a) a sharp drop of the whisker resistance at temperature below 5.3 K; b) a wide minimum of the whisker resistance in temperature range 20-25 K. Below let us consider the peculiarities more detail.

The possible reason of the obtained sharp drop of the whisker resistance could be an influence of electrical contacts to the whiskers or a partial superconductivity of the whiskers. Thus, material of electrical contact to the whiskers is known to appear the whisker superconductivity, e.g. superconductivity of Nb/InAs-nanowire junction [13], etc. The electrical contacts to Bi_2Se_3 whiskers were made by Pt microwire welding. A seria of investigation of I-V characterestics in the range 1.5-77 K does not show any deviations from Ohm law that indicates that electrical contacts could not be a reason of revealed sharp drop of the whisker resistance. A possible combination of Pt with Bi or Se gives such results. PtBi is known to be a superconductor with T_c = 1 K [14]. Comprehensive investigations of magnetoresistance of $PtBi_2$ crystals up to temperatures T_c = 2 K have no revealed any superconductivity of this compound [15]. There are no data about the superconductivity of Pt-Se compounds. The above results confirmed that revealed sharp drop of the whisker resistivity could not connect with electrical contacts.

Let us consider the special topic of superconductivity originated from Bi. Interfaces in pure as well as doped Bi bicrystals can show superconductivity up to T_c = 21 K [16], although Bi as bulk is not a superconductor (it has only very low T_c = 0.5 mK [17]). Besides Bi_2Se_3 doped with various impurities could be superconductive. For example, $Sr_xBi_2Se_3$ compounds revealed the superconductivity with T_c = 2.7K [18], while $Cu_xBi_2Se_3$ compounds demonstrate a superconductivity up to T_c = 3.8 K. Bi_2Se_3 compounds doped with Nb [19] or Tl [20] revealed the superconductive states with Tc of about 3 K. A sharp drop of the resistivity in our experiment corresponds to temperature below 5.3 K, which not coincides with Curie temperatures for the above compounds. Thus, a reason of the whisker superconductivity should be connected with Pd impurity, which will be discussed below.

The observed minimum on the temperature dependence of resistance for Bi_2Se_3 whiskers is likely to result from a contribution of Kondo effect. Kondo effect is usually revealed in materials doped with magnetic impurities [21, 22]. The dominant role plays exchange interaction between magnetic moments of intrinsic 3d electron localized on magnetic impurities and free charge carriers. One can assume that the similar anomalies of the temperature dependence of the resistance may occur in semiconductors doped with non-magnetic impurities to the concentration correspondent to MIT [23]. Then exchange interaction takes place between magnetic moments of twice occupied by charge carrier impurities and free charge carriers. Such Kondo effect was observed in heavily doped with boron Si-Ge whiskers that have no any magnetic impurities [24]. Besides we observed the similar effect in n-type conductivity GaSb whiskers with concentration near the MIT [8].

The resistivity of the material described by the equation [21]:

$$\rho_e \approx \rho_o\left[1-\frac{4J}{N}\zeta(E_F)\ln\frac{E_F}{kT}\right], \qquad (1)$$

where ρ_e – resistivity value due to exchange interaction, ρ_o – resistivity values calculated by Born approximation, $\zeta(E_F)$ – the density of states at the Fermi level, E_F – Fermi energy, N – impurity concentration, J – exchange interaction integral, k – Boltzmann constant, T – temperature.

The density of states at the Fermi level increases in crystals by applying of magnetic field. These could lead to appearance of anomalous magnetoresistance, which is positive or negative depending on the sign of the exchange interaction integral J, according to the model proposed in work [21]. As Kondo effect occurs as a result of the exchange process between localized on impurity atoms electron and free carriers, then the effect can be seen only at identified impurity concentration when it is possible the formation of sufficient number of elementary processes in interaction between free carriers and those localized. Energy dependence of the density of states in the system qualitatively changes due to the interaction carriers, which is reflected in the temperature dependences as a minimum resistance.

Our results showed that the maximum Kondo effect was observed for Bi_2Se_3 whiskers with resistivity $\rho_{300\,K}$ = 0.0053 Ohm × cm. Deep minimum of the resistance is visible on the curve 1 of Fig. 1 at temperature range to 20-25 K.

Increasing the impurity concentration increases the probability of overlapping of wave functions, resulting in increased value of direct exchange interaction, which can lead to a change in the sign of exchange interaction integral J.

Attenuation of Kondo effect observed with little change in doping impurity concentration, in particular in Bi_2Se_3 whiskers with resistivity $\rho_{300\ K} = 0.004$ Ohm × cm of the same diameter. So, minimum of the resistance is invisible in the temperature range 1.5-40 K (Fig. 1, curve 2).

3.2 Magnetoresistance of Bi_2Se_3 whiskers

The next investigation concerns the behavior of the whisker resistance at applying magnetic field. Transverse magnetoresistance in n-type Bi_2Se_3 whiskers with doping concentration (1-2) × 10^{19} cm^{-3} in the vicinity to the metal-insulator transition from metal side of the transition were studied in the temperature range 4.2-77 K and magnetic field 0-10 T (Fig. 2). There are no any oscillations of Bi_2Se_3 whisker magnetoresistance in contrast to behavior of magnetoresistance for InSb [12] or GaSb [11] whisker, where in wide range of impurity concentrations SdH oscillations occur. The absence of oscillations could be connected with imperfection of the whisker crystal structure or their heavily doping. The investigation of the whisker surface in optical microscope shows a mirror-like faces of the whiskers, which indicates in good arranged surface lattice. X-ray diffractogram (XRD) investigations does not show any amorphous phase in the whiskers. Therefore, the absence of magnetoresistance oscillations may be attributed to heavily doping of the whiskers to concentration of about (1-2) × 10^{19} cm^{-3}.

Nevertheless, there are two interesting features of the whisker magnetoresistance: c) the first one is anomalous upturn at low magnetic field at $T = 4.2$ K (see upper inset to Fig. 2); d) on the temperature dependency of the whisker magnetoresistance at $B = 10$ T a wide minimum is clearly obvious at the temperature range 25-30 K (see bottom inset to Fig. 2).

c) It is worthy to note that at temperature increase the above upturn disappears (see Fig. 2).

An anomalous upturn in the magnetoresistance could be explained by a few ways. The authors of [25] explained the analogical behavior of resistivity of cuprates by charge carrier scattering due to interplay with magnetic impurity spins. P. Fournier et al. [26] believed that anomalous resistance upturn is a result of two dimensional (2D) weak localization called by crystal disorder. In our previous work we have observed a coexisting weak antilocalization and superconductivity in GaSb whiskers [11]. Besides we have observed remarkable crossover from WAL to WL in GaSb whiskers at $T = 3$ K [8]. Here there are no reasons to assume the presence of any localization of electrons in Bi_2Se_3 whiskers. We believe that magnetoresistance upturn is called by superconductivity.

d) Wide minimum on the temperature dependency of the whisker magnetoresistance at $B = 10$ T (see bottom inset to Fig. 2) is clearly observed at temperature 25-30 K. This coincides with minimum on the temperature dependency of the whisker resistance in zero magnetic field (see Fig. 1). This fact could be the evidence of Kondo effect. Despite of high magnetic field of about 10 T Kondo interaction of conductance singlet electrons with localized by impurity electron is rather strong and independent on magnetic field intensity.

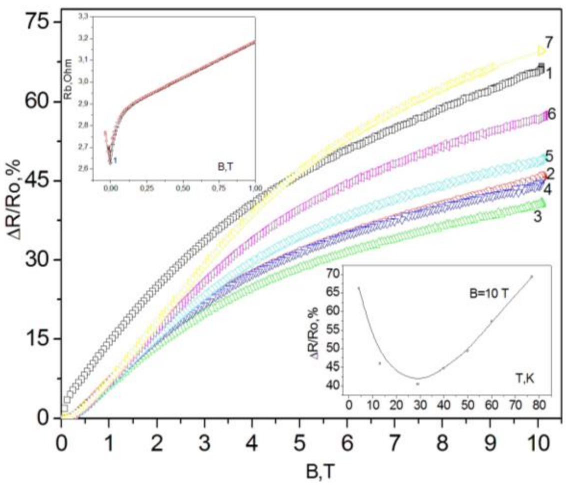

Fig. 2 – Magnetoresistance of n-type Bi_2Se_3 whisker at different temperatures: 1 – 4.2 K; 2 – 13 K; 3 – 29 K; 4 – 40 K; 5 – 50 K; 6 – 60 K; 7 – 77 K

The vicinity to MIT is known to substantially rise the temperature of material transition in superconductive state [27]. Taking this fact into account the observed sharp drops of Bi_2Se_3 whiskers resistance at temperatures below 5.3 K was assumed to connect with partial superconductivity of the whiskers. The value Tc of about 5.3 K was determined from experimental data (Fig. 1, curve 1,2). Another confirmation of transition to superconductive state is Fig. 2 (upper inset), where it is obviously seen a formation of cusp (at 4.2 K), which could be connected with superconductive state.

The main characteristics of the whiskers superconductivity is very small change in the whisker resistance. This fact indicates in existing of superconductive state only in thin subsurface layer of the whiskers. The possible mechanism of appearance of superconductivity is partial superconductivity of the whisker surface.

As is obvious from experimental data transition to superconductive state substantially depends on impurity concentration. Thus, in the whiskers with resistivity $\rho_{300\ K} = 0.0053$ Ohm × cm a competition of Kondo interaction and Cooper interaction is observed. The whiskers have metallic conductivity, but the impurity concentration is slightly larger than Nc for MIT in Bi_2Se_3 material. For such samples a part of carriers are localized on impurities and interact with free charge carriers resulting in Kondo interaction. This interaction as well as thermal interaction destroy Cooper pairs and correspondingly influence on the whisker superconductivity at 5.3 K (as compare curves 1 and 2 in Fig. 1 at temperatures below 5.3 K).

Suppression of superconductivity by magnetic field is informative for determination of its nature. Thus, we have carried out a series of experiments as for influence of magnetic field on superconductivity behaviour in the whiskers. These experiments allow us to determine of Bc_2 taking into account Ginzburg-Landau equation:

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

where $t = T/T_c$.

According to the equation (2) dependence of $B_{c2}(t)$ was built (Fig. 3).

The value $B_{c2}(T)$ corresponds to temperature T, for which a full suppression of the superconductivity takes place. Then, the equation (2) allows us to determine the upper critical field $B_{c2}(0)$ for Bi_2Se_3 whisker. The linear approximation of the experimental data gives the value of about $B_{c2}(0) = 1.5$ T (Fig. 3).

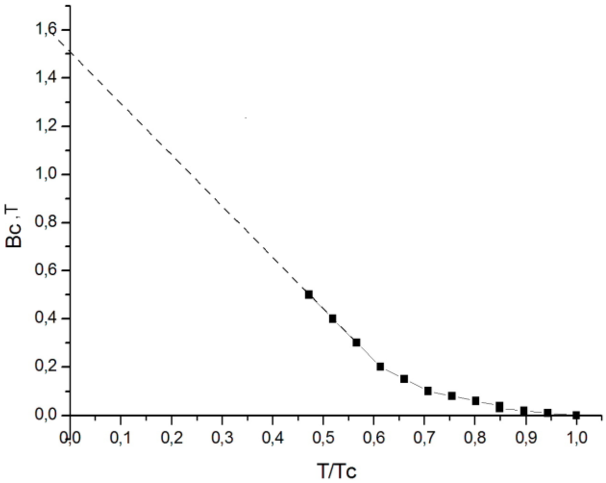

Fig. 3 – The critical field B_c(T) versus reduced transition temperature T/T_c for n-type Bi_2Se_3 whiskers. The dash line shows the Ginzburg-Landau fit to the experimental data

Using the equation:

$$B_{c2}(0) = \Phi_0/2\pi\xi(0)^2, \quad (3)$$

where Φ_0 is the flux quantum equal to 2.07×10^{-15} T×m², we obtained superconductor coherence length $\xi(0) = 15$ nm for Bi_2Se_3 whiskers.

The obtained value of coherence length is substantially less than the value 200 nm for $Cu_xBi_2Se_3$ crystals [28]. The short coherence length 18 nm of Cooper pairs, comparable with that for Sr_x Bi_2Se_3 ($\xi(0) = 15$ nm) [29] as well as for high-T_c superconductors, could lead to a variety of fascinating phenomena in contrast to low-T_C materials [30]. As a result we have observed Kondo effect together with superconductivity in the whiskers.

The value of superconducting gap could be determined from the equation [28]:

$$\Delta = 3.5\ K_B T_c/2. \quad (4)$$

Substituting $T_c = 5.3$ K and Botsmann constant K_B, we have obtained the superconductive gap of about 0.8 meV, which is in good agreement with literature data 0.6 meV [28].

Let us discussed a possible reason of Bi_2Se_3 whisker superconductivity. The most probable mechanism of superconductivity is intercalation of Pd impurity, which was used as initiator of the whisker growth. There are data [31] about an appearance of superconductivity with $T_c = 5.5$ K for $Pd_xBi_2Te_3$ crystals. Besides, β-$PdBi_2$ crystals are superconductive with $T_c = 5.3$ K [32], which coincides with data of our experiment. The coherence length for β-$PdBi_2$ crystals is about 20 nm [32] that is in good agreement with our results. The above data evidence the possible reason of superconductivity in Bi_2Se_3 whiskers with intercalation of Pd impurity. Partial superconductivity is in good coincidence with data [31] for $Pd_xBi_2Te_3$ crystals, where a resistivity also does not down to zero. It seems to be a consequence of rather low Pd concentration connected with hard intercalation in Bi_2Se_3 whiskers. For deepening the nature of the observed superconductivity further structure and ARPES investigations should be conducted.

4. CONCLUSIONS

Temperature dependences of the resistance in n-type $Pd_xBi_2Se_3$ whiskers with different impurity concentration in the vicinity to the MIT from metal side of the transition $(1\text{-}2) \times 10^{19}$ cm^{-3} were studied in the temperature range 1.5-77 K. The peculiarities of whisker resistance such as sharp drop at low temperature 5.3 K were observed for Bi_2Se_3 whiskers with various Pd concentration, that could be explained by partial superconductivity of the whiskers. Analysis of magnetic field influence on the whisker conductivity allows to determine the main superconductor parameters: upper critical magnetic field $B_{c2} = 1.5$ T, superconductor coherence length $\xi(0) = 15$ nm, superconductive gap $\Delta \sim 0.8$ meV. The obtained values indicate that a reason of observed superconductivity is likely resulted from a presence of β-$PdBi_2$ complex originated from Pd intercalation in the crystal during their growth by VLS mechanism.

The rather low values of superconductor coherence length like that as in cuprates indicate in a possibility to observe others exotic phenomena in the whiskers. For Bi_2Se_3 whiskers with resistivity $\rho_{300\,K} = 0.0053$ Ohm × cm a resistance minimum was observed at temperature about to 20-25 K, that may indicate in Kondo effect presence in the crystals. The effect is connected with exchange interaction between magnetic moments of singlet electron localized on impurities and free charge carriers and occurs only at certain impurity concentration at the vicinity to MIT.

REFERENCES

1. 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. *Phys Rev Lett.* **104**, 057001 (2010).
2. M. Dzero, K. Sun, V. Galitski, P. Coleman. *Phys. Rev. Lett.* **104**, 106408 (2010).
3. F. Wilczek, *Nature Phys.* **5**, 614 (2009).
4. M. Lee, J.S. Lim, R. López., *Phys. Rev. B* 87, 241402(R) (2013).
5. Y. Matsushita, H. Blum, T.H. Geballe, I.R.Fisher. *Phys. Rev. Lett.* **94**, 157002 (2005).
6. F. Steglich, S. Wirth. *Rep. Prog. Phys.* **79**, 084502 (2016)
7. M.B. Salamon, N. Cornell, M. Jaime, F.F. Balakirev, A. Zakhidov, J. Huang, H. Wang. *Sci. Rep.* **6**, 21469 (2016).
8. A. Druzhinin, I. Ostrovskii, Yu. Khoverko, N. Liakh-Kaguy. *Fizika Nizkikh Temperatur* **43**, 871 (2017).
9. A.A. Druzhinin, I.P. Ostrovskii, Yu.N. Khoverko, N.S. Liakh-Kaguy, A.M. Vuytsyk, *Functional Materials* **21**, 130 (2014).
10. A. Druzhinin, I. Ostrovskii, Yu. Khoverko, N. Liakh-Kaguy. *Fizika Nizkikh Temperatur* **42**, 581 (2016).
11. A. Druzhinin, I. Ostrovskii, Yu. Khoverko, N. Liakh-Kaguy, I. Khytruk, K. Rogacki. *Materials Research Bulletin* **72**, 324 (2015).
12. I. Khytruk, A. Druzhinin, I. Ostrovskii, Yu. Khoverko, N. Liakh-Kaguy, K. Rogacki, *Nanoscale Research Letters* **12**, 156 (2017).
13. H.Y. Günel, I.E. Batov, H. Hardtdegen, K. Sladek, A. Winden, K. Weis, G. Panaitov, D. Grutzmacher, Th. Schapers, *J. Appl. Phys.* **112**, 034316 (2012)
14. B.T. Matthias, *Phys. Rev.* **92**, 874 (1953).
15. C.Q. Xu, X.Z. Xing, X. Xu, L.Q. Che, B. Chen, X. Lu, J. Dai, Z.X. Shi, *Phys. Rev. B* **94**, 165119 (2016).
16. F.M. Muntyanu, A. Gilewski, K. Nenkov, A. Zaleski, V. Chistol. *Solid State Commun.* **147**, 183 (2008).
17. O. Prakash, A. Kumar, A. Thamizhavel, S. Ramakrishnan *Science* **355**, 52 (2017).
18. G. Du, Y. Li, J. Schneeloch, R.D. Zhong, G. Gu, H. Yang, H. Lin, H.-H. Wen, *Sci. China Phys. Mech. Astron.* **60**, 037411(2017).
19. B.J. Lawson, P. Corbae, G. Li, F. Yu, T. Asaba, C. Tinsman, Y. Qiu, J.E. Medvedeva, Y.S. Ho, L. Li, *Phys. Rev. B*, **94**, 041114 (2016).
20. Z. Wang, A.A. Taskin, T. Frolich, M. Braden, Y. Ando, *Chem. Mater.* **28**, 779 (2016).
21. L. Kouwebhoven, L. Glazman, *Physics World*, **253**, 33 (2001).
22. J.-H. Chen, L. Liang, *Nature Phys.* **7**, 535 (2011).
23. A.N. Ionov, *JETP Letters*, **29**,(1), 76 (1979).
24. A.A. Druzhinin, I. Ostrovskii, Yu.M. Khoverko, R.M. Koretskyy, *Sensors electronics and microsystem technology*, **3**, 50 (2012). (in Ukrainian).
25. Y. Dagan, A. Biswas, M.C. Barr, W.M. Fisher, R.L. Greene. *Phys. Rev. Lett.* **94**, 057005 (2005).
26. P. Fournier, J. Higgins, H. Balci, E. Maiser, C.J. Lobb, R.L. Greene, *Phys. Rev. B* **62**, R11993 (2000).
27. T. Klein, P. Achatz, J. Kacmarcik, C. Marcenat, F. Gustafsson, J. Marcus, E. Bustarret, J. Pernot, F. Omnes, B.E. Sernelius, C. Persson, A. Ferreira da Silva, C. Cytermann. *Phys.Rev. B* **75**, 165313 (2007).
28. L.A. Wray, S.-Y. Xu, Y. Xia, Y.S. Hor, D. Qian, A.V. Fedorov, H. Lin, A. Bansil, R.J. Cava, M.Z. Hasan. *Nat. Phys.* **6**, 855 (2010).
29. Shruti, V.K. Maurya, P. Srivastava, S. Patnaik. *AIP Conference Proceedings* **1731**, 130046 (2016).
30. M. Tinkham, *Introduction to Superconductivity*. (New York: McGraw-Hill, Inc.: 1996).
31. Y.S. Hor, J.G. Checkelsky, D. Qu, N.P. Ong, R.J. Cava. *J. Phys. Chem. Solids* **72**, 572 (2010).
32. M. Sakano, K. Okawa, M. Kanou, H. Sanjo, T. Okuda, T. Sasagawa, K.Ishizaka, *Nat. Commun.* **6**, 8595 (2015).