

Superconductivity and abnormal pressure effect in $\text{Sr}_{0.5}\text{La}_{0.5}\text{FBiSe}_2$ superconductor

Lin Li¹, Yongliang Xiang¹, Yihong Chen¹, Wenhe Jiao²,
Chuhang Zhang², Li Zhang³, Jianhui Dai¹, Yuke Li^{1†}

¹Department of Physics and Hangzhou Key Laboratory of Quantum Matter,
Hangzhou Normal University, Hangzhou 310036, China

²Department of Physics, Zhejiang University of Science and technology Hangzhou
310023, China

³Department of Physics, China Jiliang University, Hangzhou 310018, China

Abstract.

Through the solid state reaction method, we synthesized a new BiSe_2 -based superconductor $\text{Sr}_{0.5}\text{La}_{0.5}\text{FBiSe}_2$ with superconducting transition temperature $T_c \approx 3.8$ K. A strong diamagnetic signal below T_c in susceptibility $\chi(T)$ is observed indicating the bulk nature of superconductivity. Different to most BiS_2 -based compounds where superconductivity develops from a semiconducting-like normal state, the present compound exhibits a metallic behavior down to T_c . Under weak magnetic field or pressure, however, a remarkable crossover from metallic to insulating behaviors takes place around T_{min} where the resistivity picks up a local minimum. With increasing pressure, T_c decreases monotonously and T_{min} shifts to high temperatures, while the absolute value of the normal state resistivity at low temperatures first decreases and then increases with pressure up to 2.5 GPa. These results imply that the electronic structure of $\text{Sr}_{0.5}\text{La}_{0.5}\text{FBiSe}_2$ may be different to those in the other BiS_2 -based systems.

PACS numbers: 74.70.Dd, 74.25.F-, 74.62.Fj, 74.25.Dw

† Electronic address: yklee@hznu.edu.cn

1. Introduction

Exotic superconductivity has been discovered in materials with layered crystal structures, such as the high- T_c cuprates[1] and the Fe-based superconductors[2] where the high- T_c or unconventional superconductivity is believed to be caused by the reduced dimensionality and electronic correlations. Recently, a new layered compound $Bi_4O_4S_3$ with $T_c \approx 8.6$ K[3, 4] has triggered intensive research interests, leading to a class of BiS_2 -based superconductors including $LnO_{1-x}F_xBiS_2$ ($Ln=La, Ce, Pr, Nd$) with T_c up to 10 K[5, 6, 7, 8, 9, 10]. Similar to the CuO_2 plane in cuprates and the Fe_2An_2 ($An = P, As, Se$) layers in pnictides, the common BiS_2 layer in the BiS_2 -based compounds is expected to play a key role in search for new superconductors by intercalating various block layers, for example, the $Bi_4O_4(SO_4)_{1-x}$ or $[Ln_2O_2]^{2-}$ layers. Following this idea, through the replacement of the LaO layer by the SrF block, a new class of BiS_2 -based superconductors $Sr_{1-x}Ln_xFBiS_2$ ($Ln=La, Ce$) with $T_c \approx 2.8$ K has been studied[11, 12, 13]. By first principle calculations the parent compounds $SrF(LnO)BiS_2$ are found to be band insulators without detectable antiferromagnetic transition or structure phase transition[14]. Superconductivity can be induced by electron doping into lattice[5] and enhanced by pressure[15].

To obtain higher T_c in these materials, various chemical substitutions have been attempted to alter the structural instability[5, 11, 16]. Among these, the isovalent substitution is a clean method to supply chemical pressure. Very recently, an isostructural $LaO_{1-x}F_xBiSe_2$ compound has been reported to exhibit enhanced-superconductivity with T_c of 3.5 K[17, 18] compared to the low- T_c phase in $LaO_{1-x}F_xBiS_2$ [5, 15]. Although the ARPES experiments[19] have suggested that the electronic structure and Fermi surface are quite similar in both compounds, the normal state of $LaO_{1-x}F_xBiSe_2$ shows the metallic behavior[17] in contrast to the semiconducting behavior of $LaO_{1-x}F_xBiS_2$. On the other hand, the applied physical pressures in BiS_2 -based compounds always induce a structure phase transition from tetragonal to monoclinic [20], leading to an abrupt improvement from low- T_c to high- T_c [15]. For $LaO_{1-x}F_xBiSe_2$, the reported pressure effect is to suppress the low- T_c but enhance the high- T_c [21]. Up to now, most studies including electronic structure[14], superconducting transition temperature[15] and the pairing symmetry[22, 23, 24, 25, 26, 27] have been mainly focused on the BiS_2 -based system, but superconductivity seems to be still under debate.

In the Letter, we report the successful synthesis of a novel La-doped $Sr_{0.5}La_{0.5}FBiSe_2$ sample. The compound is iso-structural to $SrFBiS_2$ with the $P4/nmm$ space group as confirmed by the XRD pattern measurement. Both the sharp superconducting transition in $\rho(T)$ and strong diamagnetic signals in $\chi(T)$ confirm the bulk superconductivity. In contrast to most of the BiS_2 -based compounds where the normal state exhibits a semiconducting behavior, $Sr_{0.5}La_{0.5}FBiSe_2$ exhibits a metallic behavior down to T_c . Interestingly, even a weak magnetic field or a weak pressure can induce a crossover from metallic to insulating behaviors in the normal state. In particular, by increasing

pressure, superconductivity is quickly suppressed. Accompanied with the decrease of T_c , the normal state resistivity first decreases and then increases with pressure. In any cases, the resistivity has a local minimum at T_{min} where the crossover from metallic to insulating behaviors takes place. We find that T_{min} gradually shifts to high temperature with increasing pressure or field. All these observations imply that the superconducting mechanism of the present system may be distinct from that of the BiS_2 -based superconductors.

2. Experimental

The polycrystalline sample of $Sr_{0.5}La_{0.5}FBiSe_2$ used in this study was synthesized by the two-step solid state reaction method. La_2Se_3 was pre-synthesized by reacting stoichiometric Se powders and La pieces at 1273 K for 15 hours. The as-grown La_2Se_3 and the powders of SrSe, SrF_2 , Bi, and Se as starting materials were weighted according to their stoichiometric ratio and then fully ground in an agate mortar. The mixture of powders was then pressed into pellets, heated in an evacuated quartz tube at 1073 K for 10 hours and finally furnace-cooled to room temperature.

Crystal structure characterization was performed by powder X-ray diffraction (XRD) at room temperature using a D/Max-rA diffractometer with $Cu K\alpha$ radiation and a graphite monochromator. Lattice parameters were calculated from least-squares fitting routine using Rietveld fitting. The (magneto)resistivity under several magnetic fields was measured with a standard four-terminal method covering temperature range from 2 to 300 K in a commercial Quantum Design PPMS-9 system and Oxford He³-16T system. The temperature dependence of d.c. magnetization was measured on a Quantum Design SQUID-VSM-7T. Measurement of resistivity under pressure was performed up to 2.5GPa on PPMS-9T by using HPC-33 Piston type pressure cell with the Quantum Design DC resistivity and AC transport options. Hydrostatic pressures were generated by a BeCu/NiCrAl clamped piston-cylinder cell. The sample was immersed in a pressure transmitting medium (Daphne Oil) covered with a Teflon cell. Annealed Au wires were affixed to contact surfaces on each sample with silver epoxy in a standard four-wire configuration.

3. Results and Discussion

3.1. Superconductivity

Fig. 1 shows the powder XRD patterns and the Rietveld structural refinement of the $Sr_{0.5}La_{0.5}FBiSe_2$ sample. The main diffraction peaks can be well indexed based on a ZrCuSiAs-type crystal structure with the P4/nmm space group except for two impurity phases, the Bi_2Se_3 and a starting material Bi. The refined lattice parameters are extracted to be $a = 4.1697\text{\AA}$ and $c = 13.9422\text{\AA}$, which are larger than those of $Sr_{0.5}La_{0.5}FBiS_2$ with $a = 4.0820 \text{ \AA}$ and $c = 13.8025 \text{ \AA}$, respectively[5].

Temperature dependence of resistivity (ρ) for $\text{Sr}_{0.5}\text{La}_{0.5}\text{FBiSe}_2$ under ambient pressure is plotted in Fig. 2. The inset of figure 2 shows the magnetic susceptibility under ZFC(Zero-Field cooling) and FC(Field cooling) modes with a magnetic field of 5 Oe. The strong diamagnetic signals are observed below 3.5 K. The estimated volume fraction of magnetic shielding from ZFC data is over 90%, bearing out the bulk superconductivity in our sample. The resistivity displays a metallic behavior in the whole temperature region above T_c , and, a linear temperature-dependence above 100 K. Such feature is in contrast to the semiconducting feature observed in $\text{Sr}_{0.5}\text{La}_{0.5}\text{FBiS}_2$ [11] and $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ [5]. Noted that the single crystal $\text{NdO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ [28] also exhibits the metallic behavior above T_c . This result seems to be a tendency of the metallic normal state in the BiS_2 - and BiSe_2 -based superconductors. Upon further cooling, a sharp superconducting transition with T_c of 3.8 K, which is sizably higher than that of $\text{Sr}_{0.5}\text{La}_{0.5}\text{FBiS}_2$ with $T_c \sim 2.8$ K, can be clearly seen. Considering the relatively larger radius of Se ion than that of S ion, the result seems to imply that the negative chemical pressure effect may enhance the superconductivity in the $\text{Sr}_{0.5}\text{La}_{0.5}\text{FBiSe}_2$ system.

Fig. 3(a) shows the low-temperature magnetoresistivity under various magnetic fields below 6 K for the $\text{Sr}_{0.5}\text{La}_{0.5}\text{FBiSe}_2$ sample. The sharp superconducting transition with fully vanished resistivity at about 3.5 K is clearly seen at zero-magnetic field, suggesting the good quality of the poly-crystalline sample. A relatively weak H (~ 0.8 T) suppresses T_c drastically, and induces an non-zero resistivity above 2 K, implying a low Meissner field due to the pinning of flux. The inset shows the temperature dependence of the upper critical field $\mu_0 H_{c2}(T)$, determined by using the 90% normal state resistivity criterion. The H_{c2} at zero temperature estimated by using the Werthamer-Helfand-Hohenberg(WHH) formula $H_{c2}(T) = -0.69T_c|\frac{\partial H_{c2}}{\partial T}|_{T_c}$ is about 5.5 T for T_c^{onset} . This value is rather large compared to that of the $\text{Sr}_{0.5}\text{La}_{0.5}\text{FBiS}_2$ system[11].

A logarithmic plot of the magnetoresistivity vs. temperature below 50 K with the applied magnetic field up to 9 T is shown in Fig. 3(b). Clearly, the resistivity shows a metallic behavior under zero field. Small magnetic fields cause a slight upturn above T_c and broaden the superconducting transition. With increasing magnetic field T_c shifts to lower temperature, while the value of resistivity gradually increases so that the upturn feature becomes more prominent. At higher field up to 9 T, superconductivity almost vanishes, instead, the $\rho(T)$ curves show a metal to semiconductor crossover around T_{min} , followed by a near $\log T$ -dependent feature at lower temperatures. The similar behavior was also observed in the $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiSe}_2$ crystal at 2.0 GPa[21]. As a result, the phase diagram in terms of magnetic field and temperature is mapped in Fig. 4.

3.2. Pressure effect

It is known that pressure is an effective method to tune the lattice structures and the corresponding electronic states without introducing more disorders. We performed the resistivity measurement for several different pressures, shown in Fig. 5. The inset shows the close view of resistivity transition below T_c at various pressures. A relatively

weak pressure can sizably reduce T_c but only slightly broaden the superconducting transition. Further increasing pressures, T_c shifts to lower temperatures quickly while the superconducting transition remains rather sharp. At higher pressures up to 2.5 GPa, a slight drop due to superconducting transition can be distinguished below 2.2 K. The fact that T_c decreases monotonously with pressure in the present $Sr_{0.5}La_{0.5}FBiSe_2$ sample is in contrast to other BiS_2 -based superconductors such $LnO_{1-x}F_xBiS_2$ and $Sr_{1-x}Ln_xFBiS_2$ systems[29, 30], where the T_c is enhanced to 10 K by pressure. In the $LaO_{1-x}F_xBiSe_2$ and $Eu_3F_4Bi_2S_4$ systems[21, 31, 32], while the superconducting phase with low- T_c is relatively unchanged, the one with a high- T_c is enhanced with $T_c \approx 10$ K up to 2.5 GPa.

Fig. 6 displays a close view of temperature dependence of resistivity at several representative pressures. Starting from 0.9 GPa, a resistivity upturn above T_c is induced by pressure. The upturn feature becomes more pronounced with increasing pressures, resulting in a clear crossover from metallic to semiconducting behaviors around T_{min} where the resistivity takes a local minimum. Apparently, T_{min} shifts toward higher temperatures with pressures. It is noted that the value of ρ_{300K} decreases with pressure, while ρ_{10K} first decreases below 1.3 GPa and then increases above 1.5 GPa. Consequently, while superconductivity is suppressed by pressure, the $\log(T)$ -dependence of resistivity in the normal state emerges. The region with this insulating feature increases quickly with pressure. Therefore compared with the pressure effect on other mentioned materials the pressure effect in the $Sr_{0.5}La_{0.5}FBiSe_2$ compound is abnormal. The measurement under further higher pressures should be highly desirable in the future in order to clarify whether the superconductivity in $Sr_{0.5}La_{0.5}FBiSe_2$ could be completely killed by pressure.

The phase diagram of pressure vs. temperature is summarized in Fig. 7. In the superconducting state, T_c in the present system decreases monotonously with pressure up to 2.5 GPa, in contrast to the universal features in other BiS_2 -based superconductors. In the normal state, the sample shows a highly metallic character in the whole temperature at ambient pressure, but undergoes a crossover from metallic to insulating behaviors when the physical pressure is beyond 0.9 GPa. With pressure up to 2.5 GPa, the superconductivity is suppressed and the sample becomes more insulating at low temperatures. Recall that T_c is enhanced in most BiS_2 - or $BiSe_2$ -based compounds as typically in $LaO_{1-x}F_xBiSe_2$ where T_c is enhanced to 6.5 K at 2.37 GPa [21]. The opposite pressure effect in our measured sample though with the similar BiS_2 layered structure may suggest a rather different electronic band structure.

4. Conclusion

In summary, we synthesized the $Sr_{0.5}La_{0.5}FBiSe_2$ polycrystalline sample. The resistivity vanishes below 3.8 K, which together with strong diamagnetic signals in magnetization data, confirming the bulk superconductivity. In contrast to most of the BiS_2 -based compounds where superconductivity is developed from the background of a semiconducting-like normal state, the normal state of $Sr_{0.5}La_{0.5}FBiSe_2$ exhibits a

metallic behavior down to T_c . Under magnetic field or pressure, a crossover from metallic to semiconducting behaviors is induced, and the superconductivity is suppressed accordingly. While the T_c decreases with increasing monotonously, the absolute value of the normal state resistivity first decreases and then increases with pressure. All these features are in contrast to the previously known BiS_2 -based superconductors.

While the semiconducting behavior in the normal state of most BiS_2 and $BiSe_2$ remains one of the puzzling issue in connection with the unconventional superconductivity, the opposite situation in the present compound, namely, the crossover from the metallic to semiconducting behaviors in the normal in the presence of magnetic field or pressure is rather unusual, pointing to a possible different mechanism of superconductivity in this family of materials. Such feature reminds us of a related single crystal compound $Nd(O,F)BiS_2$ [33], where the normal state exhibits the field-induced semiconducting behavior above T_c . This feature was attributed to the possible pseudo-gap phase extending to relatively higher temperatures as evidenced by the unusual superconducting fluctuations seen in the scanning tunneling spectroscopy (STS) experiment[33]. We thus expect that the superconducting mechanism of the present system may be also quite unique and deserve further investigations such as by ARPES, NMR or STS experiments in future.

Acknowledgments

Y. Li would like to thank Z. Xu and G. H. Cao for helpful discussions. This work is supported by the National Science Foundation of China (Grant No. 11274084 and 61376094) and National Training Programs of Innovation and Entrepreneurship for Undergraduates (201510346011).

References

- [1] Bednorz J G and Mller 1986 *Z. Physik B Condensed Matter.* **64**, 189
- [2] Kamihara Y, Watanabe T, Hirano M, and Hosono H 2008 *J. Am. Chem. Soc.* **130**, 3296
- [3] Mizuguchi Y, Fujihisa H, Gotoh Y, Suzuki K, Usui H, Kuroki K, Demura S, Takano Y, Izawa H, Miura O 2012 *Phys. Rev. B* **86**, 220510(R)
- [4] Singh S K, Kumar A, Gahtori B, Sharma G, Patnaik S, and Awana V P S 2012 *J. Am. Chem. Soc.* **134** 16504
- [5] Mizuguchi Y, Demura S, Deguchi K, Takano Y, Fujihisa H, Gotoh Y, Izawa H, Miura O 2012 *J. Phys. Soc. Jpn* **81** 114725
- [6] Demura S, Mizuguchi Y, Deguchi K, Okazaki H, Hara H, Watanabe T, Denholme S J, Fujioka M, Ozaki T, Fujihisa H, Gotoh Y, Miura O, Yamaguchi T, Takeya H, and Takano Y 2013 *J. Phys. Soc. Jpn* **82**, 033708
- [7] Jha R, Kumar A, Singh S K, and Awana V P S, 2013 *J. Appl. Phys.* **113**,
- [8] Awana V P S, Kumar A, Jha R, Kumar S, Kumar J, and Pal A, 2013 *Solid State Communications* **157**, 31
- [9] Xing J, Li S, Ding X, Yang H and Wen H H 2012 *Phys. Rev. B* **86**, 214518
- [10] Jha R, Singh S K, and Awana V P S 2013 *J. Sup. and Novel Mag* **26**, 499
- [11] Lin X, Ni X X, Chen B, Xu X F, Yang X X, Dai J H, Li Y K, Yang X J, Luo Y K, Tao Q, Cao G H, and Xu Z A 2013 *Phys. Rev. B* **87** 020504

- [12] Li L, Li Y K, Jin Y F, Huang H R, Chen B, Xu X F, Dai J H, Zhang L, Yang X, Zhai H F, Cao G, and Xu Z A 2015 *Phys. Rev. B* **91** 014508
- [13] Li Y K, Lin X, Li L, Zhou N, Xu X F, Cao C, Dai J H, Zhang L, Luo Y K, Jiao W H, Tao Q, Cao G H and Xu Z 2014 *Supercond. Sci. Technol.* **27** 035009
- [14] Li B, Xing Z W, and Huang G Q 2013 *Europhys. Lett.* **101**, 47002
- [15] Wolowiec C T, White B D, Jeon I, Yazici D, Huang K, and Maple M B 2013 *J. Phys.: Condens. Matter* **25**, 422201
- [16] Yazici D, Huang K, White B D, Jeon I, Burnett V W, Friedman A J, Lum I K, Nallaiyan M, Spagna S, and Maple M B 2013 *Phys. Rev. B* **87**, 174512
- [17] Maziopa A K, Guguchia Z, Pomjakushina E, Pomjakushin V, Khasanov R, Luetkens H, Biswas P K, Amato A, Keller H, and Conder K 2014 *J. Phys.: Condens. Matter* **26**, 215702
- [18] Tanaka M, Nagao M, Matsushita Y, Fujioka M, Denholme S J, Yamaguchi T, Takeya H, and Takano Y 2014 *J. Solid State Chem* **219** 168
- [19] Saini N L, Ootsuki D, Paris E, Joseph B, Barinov A, Tanaka M, Takano Y, and Mizokawa T 2014 *Phys. Rev. B* **90**, 214507
- [20] Tomita T, Ebata M, Soeda H, Takahashi H, Fujihisa H, Gotoh Y, Mizuguchi Y, Izawa H, Miura O, Demura S, Deguchi K, and Takano Y 2014 *J. Phys. Soc. Jpn* **83**, 063704
- [21] Liu J Z, Li S, Li Y F, Zhu X Y, Wen H H 2014 *Phys. Rev. B* **90**, 094507
- [22] Liang Y, Wu X, Tsai W F, and Hu J P 2014 *Front. Phys.* **9**, 194
- [23] Yildirim T 2013 *Phys. Rev. B* **87**, 020506(R)
- [24] Martins G B, Moreo A, and Dagotto E 2013 *Phys. Rev. B* **87**, 081102(R)
- [25] Lamura G, Shiroka T, Bonfa P, Sanna S, Renzi R De, Baines C, Luetkens H, Kajitani J, Mizuguchi Y, Miura O, Deguchi K, Demura S, Takano Y, and Putti M 2013 *Phys. Rev. B* **88**, 180509
- [26] Zeng L K, Wang X B, Ma J, Richard P, Nie S M, Weng H M, Wang N L, Wang Z, Qian T, and Ding H 2014 *Phys. Rev. B* **90**, 054512
- [27] Ye Z R, Yang H F, Shen D W, Jiang J, Niu X H , Feng D L, Du Y P, Wan X G, Liu J Z, Zhu X Y , Wen H H , and Jiang M H 2014 *Phys. Rev. B* **90**, 045116
- [28] Nagao M, Demura S, Deguchi K, Miura A, Watauchi S, Takei T, Takano Y, Kumada N, and Tanaka I, 2013 *J. Phys. Soc. Jpn* **82**, 113701
- [29] Wolowiec C T, White B D, Jeon I, Yazici D, Huang K, and Maple M B 2013 *J. Phys.: Condens. Matter* **25**, 422201
- [30] Rajveer J, Brajesh T, and Awana V P S 2015 *J. Appl. Phys* **117**, 013901
- [31] Jha R, Kishan H, and Awana V P S, 2015 *J. Sup. and Novel Mag.* **28**, L2229
- [32] Luo Y K, Zhai H F, Zhang P, Xu Z, Cao G H, and Thompson J D 2014 *Phys. Rev. B* **90**, 220510
- [33] Liu J Z, Fang D L, Wang Z Y, Xing J, Du Z Y, Zhu X Y, Yang H, and Wen H H 2014 *Europhys. Lett.* **106**, 67002

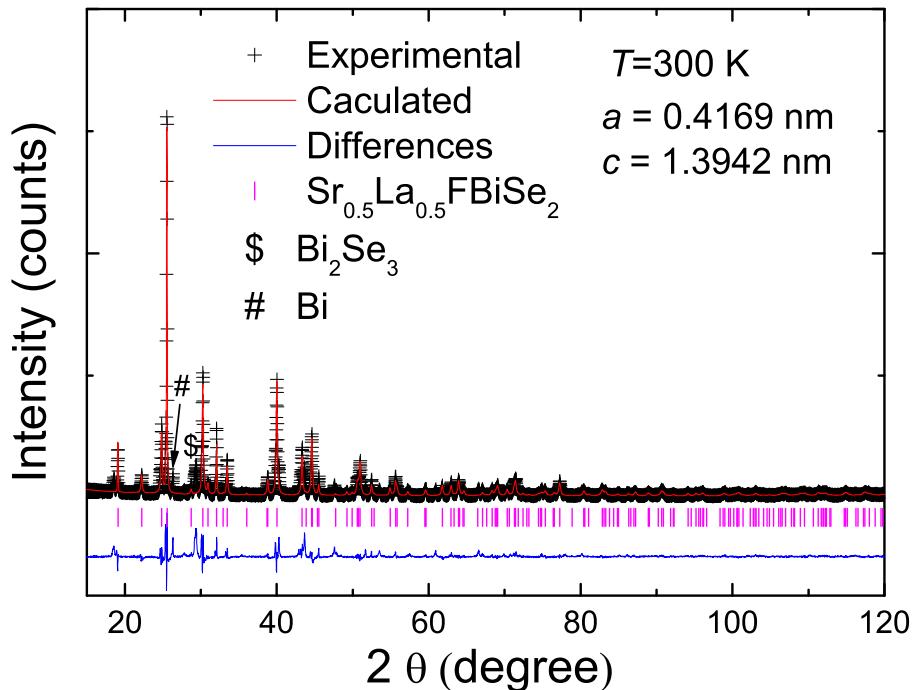


Figure 1. (color online). Powder X-ray diffraction patterns and the Rietveld refinement profile for $Sr_{0.5}La_{0.5}FBiSe_2$ sample at room temperature. The $\$$ and $\#$ peak positions designate the impurity phases of Bi_2S_3 and Bi , respectively.

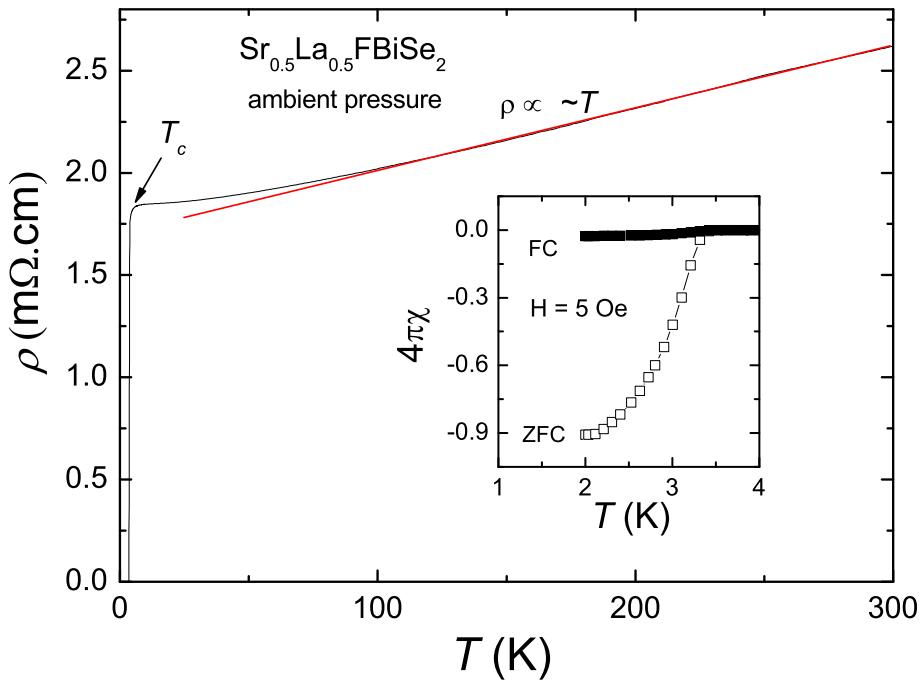


Figure 2. (a) Temperature dependence of resistivity for the polycrystalline $\text{Sr}_{0.5}\text{La}_{0.5}\text{FBiSe}_2$ sample under ambient pressure. The inset shows the magnetic susceptibility of $\text{Sr}_{0.5}\text{La}_{0.5}\text{FBiSe}_2$ under both ZFC and FC modes.

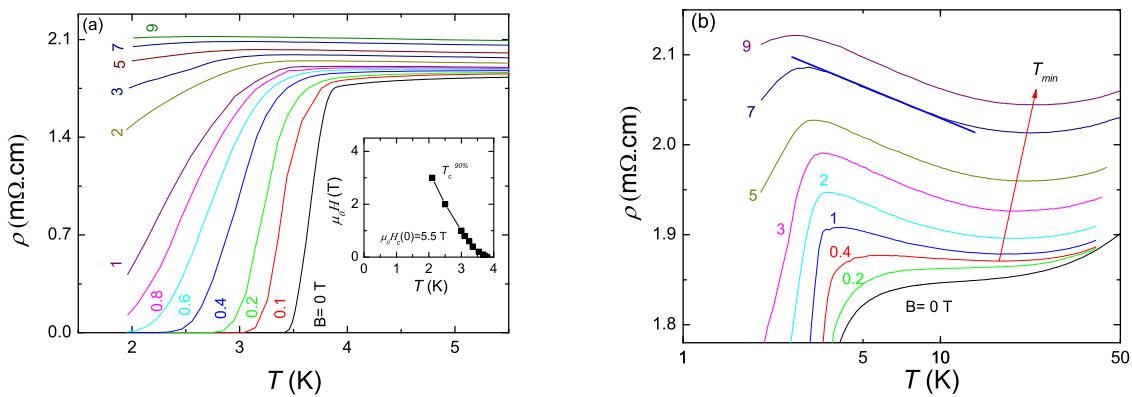


Figure 3. (a) Temperature dependence of resistivity (ρ) around T_c under magnetic fields up to 9 T for the $\text{Sr}_{0.5}\text{La}_{0.5}\text{FBiSe}_2$, the inset shows the H_{c2} data. (b) An enlarged plot of the temperature dependence of magnetoresistivity.

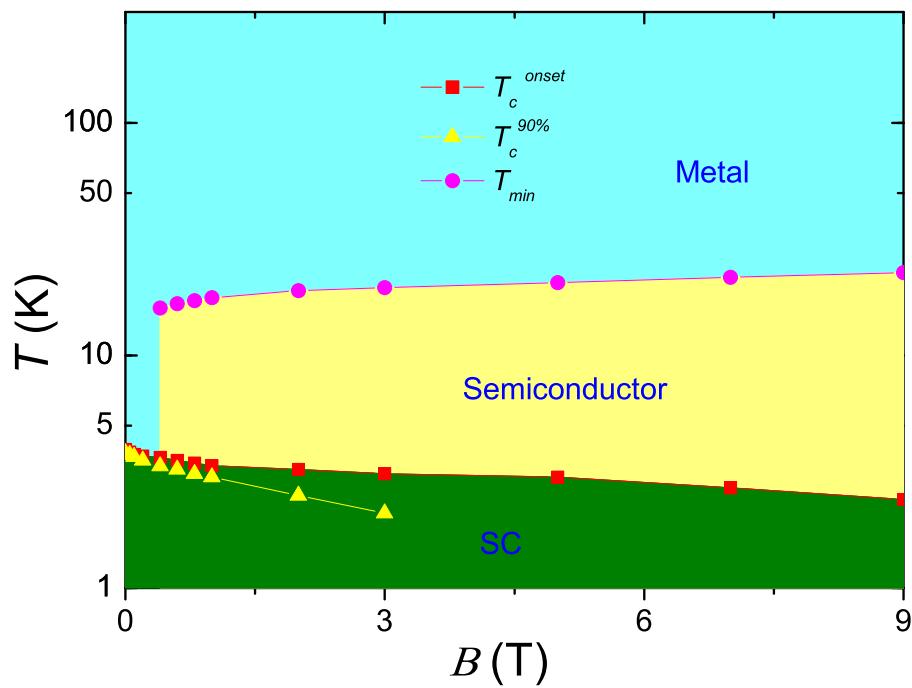


Figure 4. The phase diagram of temperature versus magnetic field for the $Sr_{0.5}La_{0.5}FBiSe_2$.

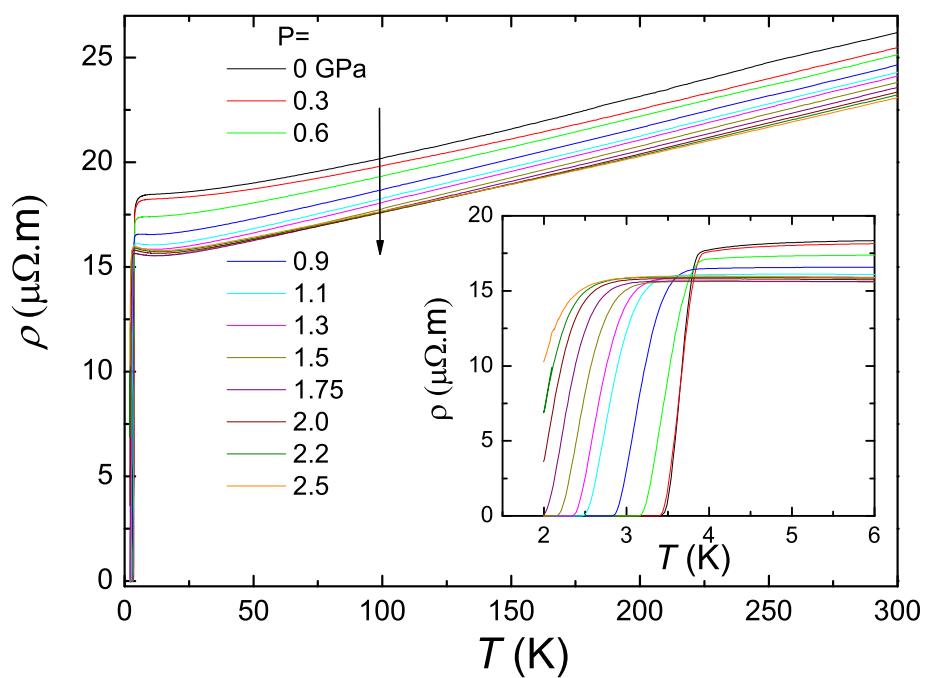


Figure 5. Temperature dependence of resistivity for $Sr_{0.5}La_{0.5}FBiSe_2$ sample at various pressures. The inset shows an enlarged view of resistivity below T_c .

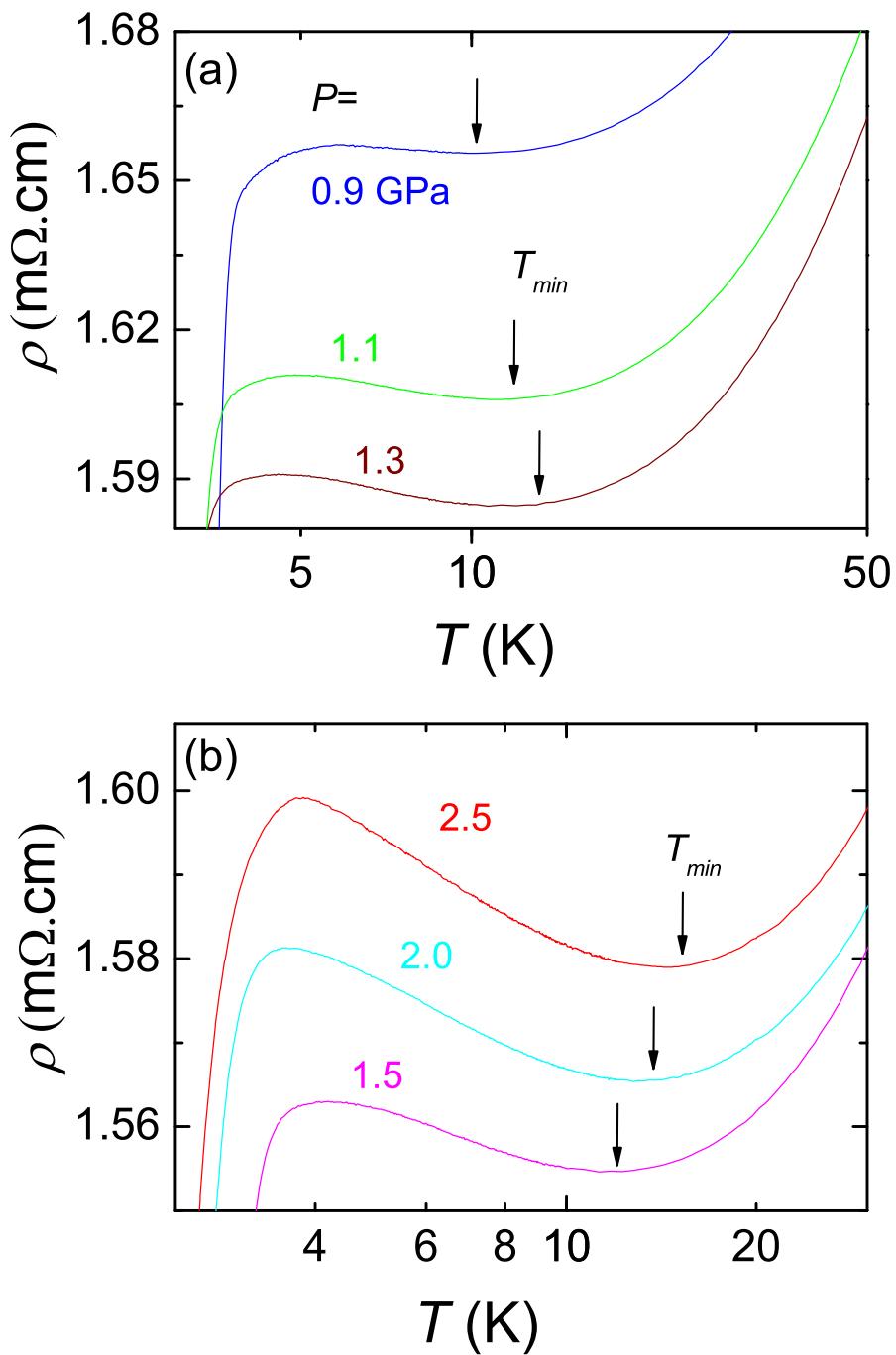


Figure 6. An enlarged view of temperature vs. resistivity at several representative pressures for the $Sr_{0.5}La_{0.5}FBiSe_2$ sample.

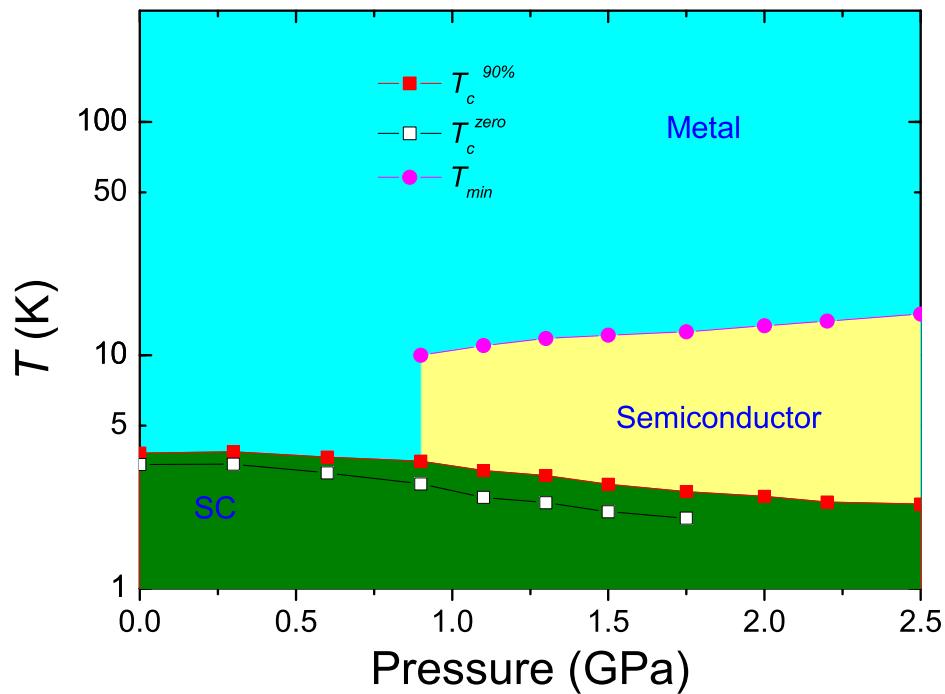


Figure 7. The phase diagram in terms of pressure and temperature for the $Sr_{0.5}La_{0.5}FBiSe_2$ sample.