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

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Received 29 December 2015, revised 26 January 2016
Accepted for publication 29 January 2016
Published 10 March 2016

Abstract

Through the solid state reaction method, we synthesized a new BiSe$_2$-based superconductor Sr$_{0.5}$La$_{0.5}$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 $T_{c\text{min}}$ where the resistivity picks up a local minimum. With increasing pressure, $T_c$ decreases monotonously and $T_{c\text{min}}$ 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 Sr$_{0.5}$La$_{0.5}$FBiSe$_2$ may be different to those in the other BiS$_2$-based systems.

Keywords: superconductivity, BiSe$_2$-based superconductor, pressure effect, phase diagram

(Some figures may appear in colour only in the online journal)

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$_4$O$_4$S$_3$ 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$_x$BiS$_2$ (Ln = La, Ce, Pr, Nd) with $T_c$ up to 10 K [5–10]. Similar to the CuO$_2$ plane in cuprates and the Fe$_2$AN$_2$ (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$_2$O$_2$(SO$_4$)$_{1-x}$ or [Ln$_2$O$_3$]$^{2-}$ 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$_x$FBiS$_2$ (Ln = La, Ce) with $T_c \approx 2.8$ K has been studied [11–13]. 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$_{x}$BiSe$_{2}$ 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$_{x}$BiSe$_{2}$ [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$_{x}$BiSe$_{2}$ shows the metallic behavior [17] in contrast to the semiconducting behavior of LaO$_{1-x}$F$_{x}$BiSe$_{2}$. 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$_{x}$BiSe$_{2}$, 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 [22-27] have been mainly focused on the Bi$_2$Se$_3$-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 isostructural to SrFBiSe$_2$ with the P4/nmm space group as confirmed by the x-ray diffraction (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 Bi$_2$Se$_3$-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 $T_{\text{min}}$ where the crossover from metallic to insulating behaviors takes place. We find that $T_{\text{min}}$ 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 Bi$_2$Se$_3$-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$_2$Se$_3$ was pre-synthesized by reacting stoichiometric Se powders and La pieces at 1273 K for 15 h. The as-grown La$_2$Se$_3$ 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 h and finally furnace-cooled to room temperature.

Crystal structure characterization was performed by powder XRD at room temperature using a D/Max-rA diffractometer with Cu $K_{α}$ 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 He$^3$-16 T system. The temperature dependence of DC magnetization was measured on a Quantum Design SQUID-VSM-7 T. Measurement of resistivity under pressure was performed up to 2.5 GPa on PPMS-9 T 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

Figure 1 shows the powder XRD patterns and the Rietveld refinement profile for Sr$_0.5$La$_0.5$FBiSe$_2$ sample at room temperature. The S and $#$ peak positions designate the impurity phases of Bi$_2$Se$_3$ and Bi, respectively.

![Figure 1. Powder x-ray diffraction patterns and the Rietveld refinement profile for Sr$_0.5$La$_0.5$FBiSe$_2$ sample at room temperature.](image-url)
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 Sr$_{0.5}$La$_{0.5}$FBS$_2$ [11] and LaO$_{0.5}$F$_{0.5}$BiS$_2$ [5]. Noted that the single crystal NdO$_{0.5}$F$_{0.5}$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 Sr$_{0.5}$La$_{0.5}$FBS$_2$ 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 Sr$_{0.5}$La$_{0.5}$FBS$_2$ system.

Figure 3(a) shows the low-temperature magnetoresistivity under various magnetic fields below 6 K for the Sr$_{0.5}$La$_{0.5}$FBS$_2$ 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 polycrystalline sample. A relatively weak $H$ ($\sim$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 $\mu_0 H_c^2(T)$, determined by using the 90% normal state resistivity criterion. The $H_c^2$ at zero temperature estimated by using the Werthamer–Helfand–Hohenberg formula $H_c^2(T) = -0.69T_c^2\frac{\partial \rho}{\partial T}$, is about 5.5 T for $T_c^{\text{onset}}$. This value is rather large compared to that of the Sr$_{0.5}$La$_{0.5}$FBS$_2$ system [11].

A logarithmic plot of the magnetoresistivity versus temperature below 50 K with the applied magnetic field up to 9 T is shown in figure 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 $T_{\text{min}}$, followed by a near log$T$-dependent feature at lower temperatures. The similar behavior was also observed in the LaO$_{0.5}$F$_{0.5}$BiS$_2$ crystal at 2.0 GPa [21]. As a result, the phase diagram in terms of magnetic field and temperature is mapped in figure 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 figure 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$_{0.5}$FBS$_2$ sample is in contrast to other BiS$_2$-based superconductors such LnO$_{1-x}$F$_x$BiS$_2$ and Sr$_{1-x}$Ln$_x$FBS$_2$ systems [29], where the $T_c$ is enhanced to 10 K by pressure. In the LaO$_{1-x}$F$_x$BiSe$_2$ and Eu$_3$F$_4$Bi$_2$S$_4$ systems [21, 30, 31], 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.

Figure 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 $T_{\text{min}}$, where the resistivity takes a local minimum. Apparently, $T_{\text{min}}$ shifts toward higher temperatures with pressures. It is noted that the value of $\rho_{300 K}$ decreases with pressure, while $\rho_{10 K}$ 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$_{0.5}$FBS$_2$ 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$_{0.5}$FBS$_2$ could be completely killed by pressure.

The phase diagram of pressure versus temperature is summarized in figure 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$_x$BiSe$_2$ 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$_2$ [32], 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 [32]. 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).

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