Electronic phase diagram in a new BiS$_2$-based Sr$_{1-x}$La$_x$FBiS$_2$ system

Yuke Li$^{1,2}$, Xi Lin$^1$, Lin Li$^1$, Nan Zhou$^1$, Xiaofeng Xu$^1$, Chao Cao$^1$, Jianhui Dai$^1$, Li Zhang$^3$, Yongkang Luo$^2$, Wenhe Jiao$^2$, Qian Tao$^2$, Guanghan Cao$^2$ and Zhuan Xu$^2$

$^1$ Department of Physics and Hangzhou Key Laboratory of Quantum Matters, Hangzhou Normal University, Hangzhou 310036, People’s Republic of China
$^2$ State Key Lab of Silicon Materials and Department of Physics, Zhejiang University, Hangzhou 310027, People’s Republic of China
$^3$ Department of Physics, China Jiliang University, Hangzhou 310018, People’s Republic of China

E-mail: yklee@hznu.edu.cn and xiaofeng.xu@hznu.edu.cn

Received 6 October 2013, revised 9 December 2013
Accepted for publication 20 December 2013
Published 11 February 2014

Abstract
In this paper, we systematically study the effect of electron doping in a new BiS$_2$-based system Sr$_{1-x}$La$_x$FBiS$_2$ (0 $\leq$ x $\leq$ 0.7) through the multiple techniques of x-ray diffraction, electrical transport, magnetic susceptibility, and Hall effect measurements. The parent compound SrFBiS$_2$ is found to possess a semiconductor-like ground state, with a thermal activation energy $E_g$ $\sim$ 38 meV. By the partial substitution of La for Sr, superconductivity emerges when x > 0.3, reaching its maximal superconducting transition temperature of $T_c$ $\sim$ 3.5 K at x = 0.55. In the normal state of superconducting samples, it is clearly seen that there exists a crossover from the metallic to the semiconducting state below a temperature $T_{min}$, which shifts to lower temperatures with increasing La content. Based on these measurements, the associated electronic phase diagram of the Sr$_{1-x}$La$_x$FBiS$_2$ system has thus been established.

Keywords: superconductivity, phase diagram

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

1. Introduction
In the past couple of decades, the discovery of a series of new superconducting compounds with relatively low transition temperatures $T_c$, yet displaying some unique properties, has triggered sustained research interest in the condensed matter physics community [1–3]. In particular, these compounds in some cases have led to the unveiling of entirely new families of superconducting materials [3–5] with $T_c$ far above the Bardeen–Cooper–Schrieffer (BCS) limit [6]. Interestingly, with few exceptions, these compounds possess a layered crystal structure, and exhibit exotic superconducting properties and complex physical features.

Very recently, a novel superconductor Bi$_4$O$_4$S$_3$ with a $T_c$ of 8.6 K has been reported [7, 8], which consists of a layered crystal structure built from the stacking of Bi$_2$S$_4$ superconducting layers and Bi$_4$O$_4$(SO$_4$)$_{1-x}$ block layers. Immediately after this work, several new BiS$_2$-based superconductors, LnO$_{1-x}$F$_x$BiS$_2$ (Ln = La, Ce, Pr, Nd) [9–13], which are composed of Bi$_2$S$_4$ layers and LnO$_2$ layers, have thus been discovered, with $T_c$ as high as 10 K. Evidently, these compounds share a common Bi$_2$S$_2$ layer, which serves as the basic building blocks for this new superconducting family. This feature is reminiscent of the situation encountered in the cuprate and pnictides superconductors, in which superconductivity arises predominantly from the CuO$_2$ planes and Fe$_2$Pn$_2$ layers, respectively. However, although these Bi$_2$S$_2$-based layered superconductors display a wealth of similarities to the iron pnictides, differences are also manifest. For instance, the parent compound of LnFeAsO shows an antiferromagnetic (AFM) transition and/or a structural phase transition [14], and superconductivity emerges from the suppression of this AFM order by chemical doping or pressure. In contrast, the
We find that superconductivity is successfully induced by La$_{1-x}$FeAs. The parent compound SrFBiS$_2$ is a semiconductor, and the 50% substitution of La for Sr induces superconductivity at room temperature using a D/Max-xA diffractometer with Cu Kα radiation and a graphite monochromator. Lattice parameters were obtained by Rietveld refinements. The electrical resistivity was measured with a standard four-terminal method between 300 and 0.4 K in a commercial Quantum Design PPMS-9 system with a $^3$He refrigeration insert. The Hall effect measurements were also performed in this system. The temperature dependence of dc magnetization was measured by means of a Quantum Design MPMS-5.

3. Results and discussion

Figure 1(a) shows the room-temperature powder XRD patterns of the Sr$_{1-x}$La$_x$FBiS$_2$ samples. The main diffraction peaks of these samples can be indexed well on the basis of a tetragonal cell structure with the $P4/nmm$ space group, except for some extra minor peaks arising from a possible impurity phase of Bi$_2$S$_3$ (note that the $x=0.4$ sample shows a single phase only). Figure 1(b) displays the (102) and (004) diffraction peaks on an enlarged scale. It is clearly seen that the (004) peak for La-doped samples shifts systematically towards higher 2θ angles with respect to that in the parent compound ($x=0$), while the (102) peak exhibits a much lower doping dependence. This observation is consistent with the variation of the lattice parameters at room temperature, as shown in figure 1(c), where the $c$-axis decreases quickly as $x$ grows, while the $a$-axis is almost independent of the La content. These suggest that La atoms are indeed incorporated into the lattice, resulting in a decrease in the cell volume. A similar feature was also reported in the case of LaO$_{1-x}$F$_x$BiS$_2$ [11]. To obtain the actual content of La impurities, EDX measurements (not shown here) are performed in a single-crystal grain of a polycrystalline sample for all La-doped samples. Those results suggest that the actual La content in all doped samples is very close to the nominal La concentration.

The temperature evolution of the resistivity $\rho(T)$ for all samples studied is summarized in figure 2. The parent compound SrFBiS$_2$, which has been widely studied in the literature [15, 16], is a semiconductor with a room-temperature
resistivity of $\sim 5 \times 10^2$ m$\Omega$ cm. This room-temperature value is about two orders of magnitude larger than that of iron-based superconductors with semi-metallicity [4]. No anomaly in resistivity is observed down to 2 K, contrasting with the prominent kink structure associated with the AFM phase transition in LnFeAsO systems [14]. Remarkably, the thermal energy $E_g$ extracted from fitting to the thermal activation formula $\rho(T) = \rho_0 \exp(E_g/k_B T)$ in the temperature range from 100 to 300 K, is about 38.2 meV for the parent compound. When 30% of La is introduced, however, the resistivity decreases sharply, yet remains semiconductor-like with its negative $T$-coefficient of the resistivity. Note that the thermal activation energy $E_g$ increases to 58 meV, which was ascribed to the impurity phase of Bi$_2$S$_3$, with sulfur deficiency [21]. As $x$ further increases to 0.4, the resistivity shows semiconducting behavior before a sharp superconducting transition with $T_{c\text{onset}}$ (the onset temperature at which the resistivity starts to drop) $\sim 2.0$ K, as clearly seen in the enlarged low-$T$ plot in figure 2(b). This result is comparable to the case of LaO$_{1.3}$F$_{0.7}$BiS$_2$, where the normal state shows semiconductor behavior and undergoes a superconducting transition below 10 K [9]. The $E_g$ fitted from high temperature decreases from 30 meV for $x = 0.4$ to 8.6 meV for $x = 0.5$, suggesting a decrease of the gap size due to electron doping. The highest $T_{c\text{onset}}$ is observed to be 3.5 K, at $x = 0.55$. Interestingly, for the superconducting samples, a crossover occurs from a metallic to semiconducting state as the temperature is lowered below $T_{\text{min}}$. While the value of $T_{\text{min}}$ shifts progressively towards lower temperatures with increasing La concentration up to $x = 0.7$, the superconducting $T_c$ remains almost unchanged above a doping level of 0.55, as observed in the figure 2(b).

To further confirm the bulk nature of the observed superconductivity, we performed dc magnetic susceptibility measurements in both zero-field-cooling (ZFC) and field-cooling (FC) modes under a 5 Oe magnetic field for the superconducting samples, as depicted in figure 3. For all the superconducting samples, strong diamagnetic signals are observed and the $T_c$ values determined from the magnetic susceptibility are overall consistent with the resistivity data. The estimated volume fraction of superconducting shielding from ZFC data is close to 30%. Note that the Meissner volume fraction estimated by FC data also exceeds 15%, which is larger than the previous report in the LaO$_{1.4}$F$_{0.6}$BiS$_2$ system [22].

Figure 4 shows the temperature dependence of resistivity for the $x = 0.55$ sample under various magnetic fields below 5 K. It can be seen that $T_{c\text{onset}}$ is about 3.5 K at zero field. With increasing magnetic fields, $T_{c\text{onset}}$ gradually suppresses and the superconducting transition becomes obviously broader. Above 0.3 T, $T_{c\text{onset}}$ becomes robust with the field and its value shows almost no change at around 2.6 K. For $B = 2$ T, however, the low-temperature resistivity increases rapidly, but a slight drop at 2.6 K is still detectable. The inset shows the temperature dependence of the upper critical field $\mu_0 H_c(0)$ below 5 K, determined by using the 99% normal state resistivity criterion. The value of $\mu_0 H_c(0)$ is almost linear with temperature, decreasing at low field but becoming constant as $H$ rises above 0.4 T. This may be ascribed to the residual Cooper pairs existing in the BiS$_2$-based system, where similar behaviors were also reported in the Bi$_2$O$_{0.5}$S$_{0.5}$ system [23]. According to the conventional one-band WHH formula [24], $\mu_0 H_c(0) = -0.69 T_{c_0} (\partial H_c/\partial T)_{T_{c_0}}$, the upper critical field $\mu_0 H_c(0)$ is estimated to be about 1.44 T. Apparently, this result from the one-band WHH model does not match our experimental data, indicating multi-band superconductivity in the Sr$_{1-x}$La$_x$Bi$_2$S$_3$ system. Recently, calculations [25] have claimed that in BiS$_2$ systems, the triplet pairing

---

**Figure 2.** (a) Temperature dependence of resistivity $\rho(T)$ for the Sr$_{1-x}$La$_x$FBiS$_2$ ($0 \leq x \leq 0.7$) samples. (b) A close-up view of the resistivity around $T_c$ for the superconducting samples.

**Figure 3.** Temperature dependence of the magnetic susceptibility under a 5 Oe magnetic field in the ZFC (solid) and FC (open) modes for $x = 0.5, 0.55, 0.6, 0.7$ samples. The Meissner volume fraction for those samples is over 15%, confirming the bulk superconductivity.
interaction is so strong that it may become dominant. Therefore, it would be intriguing to study its low-lying quasiparticle excitations in the present system [26, 27].

Recently, first-principles calculations [20] suggested a charge density wave instability or an enhanced correlation effect in this system. In order to study its normal state properties and obtain some useful insights into such a putative instability, the Hall effect measurement was performed. Figure 5 shows the temperature dependence of $R_H$ for the superconducting samples as $x \geq 0.4$. The inset gives the magnetic field dependence of the transverse resistivity $\rho_{xy}$ at various temperatures for the representative $x = 0.55$ sample. In the main panel of figure 5, a positive $R_H$ throughout the entire temperature range is observed, which displays a weak temperature dependence above 50 K for the $x = 0.4$ sample, suggesting dominant hole-type charge carriers regardless of the electron doping in this compound. In contrast, as $x \geq 0.5$, $R_H$ in the whole temperature region is negative, indicating that electron-type charge carriers are dominant for those compounds. Moreover, their $R_H$ values are seen to be independent of temperature at high temperatures and drop drastically below 100 K. The sign change of $R_H$ from positive to negative may be ascribed to the sudden topology change of the Fermi surface according to the calculations [28, 29]. On the other hand, as shown in the inset of figure 5, the magnetic field dependence of $\rho_{xy}$ shows weak nonlinear behavior at low temperatures for $x = 0.55$. The results are consistent with the multi-band effects in this system. Figure 6 distinguishes itself from those of LnO$_{1-x}$F$_x$BiS$_2$ systems in several aspects. First, the parent compound of the former is a semiconductor [15], while the latter is a bad metal [12]. Second, by electron doping, the resistivity decreases with the doping concentration in Sr$_{1-x}$La$_x$FBiS$_2$, which is distinct from LnO$_{1-x}$F$_x$BiS$_2$ [12] and La$_{1-x}M_x$OBiS$_2$ ($M = Ti, Zr, Hf, Th$) systems [32], where resistivity shows the opposite trend with the electron concentration. Third, no metal to semiconductor transition/crossover has been observed in LnO$_{1-x}$F$_x$BiS$_2$ and La$_{1-x}M_x$OBiS$_2$ systems.

![Figure 4](image1.png)

**Figure 4.** Temperature dependence of resistivity below 5 K under several magnetic fields for the $x = 0.55$ sample. Inset: $\mu_0H(T)$ as a function of temperature.

![Figure 5](image2.png)

**Figure 5.** Temperature dependence of the Hall coefficient $R_H$ measured at 5 T for different La doping samples. $R_H$ shows a weak temperature dependence at high temperature and drops at low temperature. The inset gives the Hall resistivity $\rho_{xy}$ as a function of the field at several representative temperatures for $x = 0.55$. The weak nonlinear behavior of $\rho_{xy}$ versus magnetic field suggests a multi-band effect in this system.

![Figure 6](image3.png)

**Figure 6.** Electronic phase diagram extracted from the resistivity measurements.
4. Conclusion

In summary, we have successfully synthesized a series of BiS$_2$-based Sr$_{1-x}$La$_x$Ba$_2$Bi$_2$ polycrystalline samples. Through measurements of the resistivity and magnetic susceptibility, the parent compound was found to be semiconductor-like, with a thermal activation energy $E_g \sim 38$ meV. Via partial La doping on Sr sites, however, the resistivity decreases sharply, and ultimately superconductivity emerges as $x > 0.3$, reaching a $T_c$ of 3.5 K at the optimal level of $x = 0.55$. The superconducting samples undergo a metal to semiconductor transition/crossover below $T_{min}$, which is seen to be gradually suppressed with further doping, whilst $T_c$ remains nearly unchanged above the optimal doping. Hall effect measurements for the La-doped samples confirm that the sign change of $R_H$ from positive to negative may be ascribed to a sudden topology change of the Fermi surface. A drop in $R_H$ and the nonlinear transverse resistivity $\rho_{xy}$ with field are associated with the multi-band effect or a CDW instability. According to these measurements, an electronic phase diagram is thus established.

Acknowledgments

Y K Li would like to thank Bin Chen, Jinhu Yang and Quanlin Ye for collaborative support. This work is supported by the National Basic Research Program of China (Grant Nos 111174247, 11104053, 61376094, 11104051). We thank Hangdong Wang for useful discussions, and Xuxin Yang and Y K Li would like to thank Bin Chen, Jinhu Yang and Quanlin Ye for collaborative support. This work is supported by the National Basic Research Program of China (Grant Nos 111174247, 11104053, 61376094, 11104051).

References

[1] Maeno Y, Hashimoto H, Yoshida K, Nishizaki S, Fujita T, Bednorz J G and Lichtenberg F 1994 Nature 372 532
[2] Takada K, Sakurai H, Muromachi T, Izumi E, Dilanian F and Sasaki R A T 2003 Nature 422 53
[3] Kamihara Y, Hiramatsu H, Hirano M, Kawamura R, Yanagi H, Kamiya T and Hosono H 2006 J. Am. Chem. Soc. 128 10012
[4] Kamihara Y, Watanabe T, Hirano M and Hosono H 2006 J. Am. Chem. Soc. 130 3296
[5] Chen X H, Wu T, Wu G, Liu R H, Chen H and Fang D F 2008 Nature 453 761
[6] McMillan W L 1968 Phys. Rev. 167 331
[7] Mizuguchi Y, Fujihisa H, Gotoh Y, Suzuki K, Usui H, Kuroki K, Demura S, Takano Y, Izawa H and Miura O 2012 Phys. Rev. B 86 220510(R)
[8] Singh S K, Kumar A, Gahtori B, Sharma G, Patnaik S and Awana V P S 2012 J. Am. Chem. Soc. 134 16504
[9] Mizuguchi Y, Demura S, Deguchi K, Takano Y, Fujihisa H, Gotoh Y, Izawa H and Miura O 2012 J. Phys. Soc. Japan 81 114725
[10] Demura S et al 2013 J. Phys. Soc. Japan 82 033708
[11] Awana V P S, Kumar A, Jha R, Singh S K, Pal A, Shruti, Saha J and Patnaik S 2013 Solid State Commun. 157 21
[12] Xing J, Li S, Ding X, Yang H and Wen H H 2012 Phys. Rev. B 86 214518
[13] Jha R, Singh S K and Awana V P S 2013 J. Superlatt. Novel Mag. 26 499
[14] Cruz C et al 2008 Nature 453 899
[15] Lin X et al 2013 Phys. Rev. B 87 020504
[16] Lei H C, Wang K F, Abeykoon M, Bozin E S and Petrovic C 2013 Inorg. Chem. 52 10685
[17] Li B, Xing Z W and Huang G Q 2012 arXiv:1210.1743
[18] Yazici D, Huang K, White B D, Jeon I, Burnett V W, Friedman A J, Lumi I K, Nallaiyan M, Spagna S and Maple M B 2013 Phys. Rev. B 87 174512
[19] Liang Y, Wu X X, Tsai W F and Hu J P 2012 arXiv:1211.5435
[20] Yildirim T 2013 Phys. Rev. B 87 020506(R)
[21] Chen B, Uher C, Iordanidis L and Kanatzidis M G 1997 Chem. Mater. 9 1655
[22] Deguchi K et al 2013 Europhys. Lett. 101 17004
[23] Li S, Yang H, Tao I, Ding X and Wen H H 2013 Sci. China Phys. Mech. Astron. 56 2019
[24] Wetheramer N R, Hel E and Hohenberg P C 1966 Phys. Rev. 147 295
[25] Yang Y, Wang W S, Xiang Y Y, Li Z Z and Wang Q H 2013 Phys. Rev. B 88 094519
[26] Xu X F et al 2013 Phys. Rev. B 87 224507
[27] Niu C Q et al 2013 Phys. Rev. B 88 104507
[28] Usuii H, Suzuki K and Kuroki K 2012 Phys. Rev. B 86 220501(R)
[29] Martins G B, Moreo A and Dagotto E 2013 Phys. Rev. B 87 081102(R)
[30] McGuire M A et al 2008 Phys. Rev. B 78 094517
[31] Sefat A S, McGuire M A, Sales B C, Jin R, Howe J Y and Mandrus D 2008 Phys. Rev. B 77 174503
[32] Yazici D, Huang K, White B D, Jeon I, Burnett V W, Friedman A J, Lumi I K, Nallaiyan M, Spagna S and Maple M B 2013 Phys. Rev. B 87 174512