

Electronic phase diagram in the new BiS₂-based Sr_{1-x}La_xFBiS₂ system

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Abstract. In this paper, we systematically study the electron doping effect in a new BiS₂-based system Sr_{1-x}La_xFBiS₂(0 ≤ x ≤ 0.7) through multiple techniques of X-ray diffraction, electrical transport, magnetic susceptibility, and Hall effect measurements. The parent compound SrFBiS₂ is found to possess a semiconducting-like ground state, with thermally 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 $T_c \sim 3.5$ K at $x = 0.55$. In the normal state of superconducting samples, it is clearly seen that there exists a crossover from metallic to 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 Sr_{1-x}La_xFBiS₂ system has thus been established.

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1. Introduction

In the last 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 community of condensed matter physics[1, 2, 3]. In particular, these compounds in some cases have led to the unveiling of entire new families of superconducting materials[3, 4, 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 $\text{Bi}_4\text{O}_4\text{S}_3$ with T_c of 8.6 K has been reported[7, 8], which consists of a layered crystal structure built from the stacking of Bi_2S_4 superconducting layers and $\text{Bi}_4\text{O}_4(\text{SO}_4)_{1-x}$ block layers. Immediately after this work, several new BiS_2 -based superconductors, $\text{LnO}_{1-x}\text{F}_x\text{BiS}_2$ ($\text{Ln}=\text{La, Ce, Pr, Nd}$)[9, 10, 11, 12, 13], which are composed of Bi_2S_4 layers and Ln_2O_2 layers, have thus been discovered, with T_c as high as 10 K. Evidently, these compounds share a common BiS_2 layer, which serves as the basic building blocks of 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_2Pn_2 layers, respectively. However these BiS_2 -based layered superconductors display a wealth of similarities to the iron pnictides, the 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 parent compound LnOBiS_2 displays no magnetic/structural transition, implying that magnetism is of less relevance to superconductivity in BiS_2 -based systems. On the other hand, it is noted that superconductivity is in close proximity to an insulating normal state for the BiS_2 -based compounds [12]. Yet for the discovered superconducting materials, superconductivity grows from a metallic normal state.

More recently, a new BiS_2 based superconductor $\text{Sr}_{1-x}\text{La}_x\text{FBiS}_2$ ($x=0.5$) has been synthesized and studied[15, 16]. This compound is iso-structural to LaOBiS_2 , where the $[\text{Ln}_2\text{O}_2]^{2-}$ layer is replaced by iso-charged $[\text{Sr}_2\text{F}_2]^{2-}$ block, in analogy to the case of LaOFeAs and SrFFeAs . The parent compound SrFBiS_2 is a semiconductor, and the 50% substitution of La for Sr induces superconductivity with T_c of 2.8 K.

To date, most studies about BiS_2 -based systems have focused on their electronic structures[17], superconducting transition temperature[18] and the pairing symmetry[19, 20], with only few reports on the study of their electronic phase diagrams. In this paper, we report the successful synthesis and the detailed characterization of a series of La-doped $\text{Sr}_{1-x}\text{La}_x\text{FBiS}_2$ samples. We find that superconductivity is successfully induced by La doping when $x > 0.3$, with maximal T_c of 3.5 K at $x = 0.55$, above which T_c shows less doping dependence. Interestingly, for the superconducting samples, their normal state undergoes a metal to semiconductor transition/crossover

at T_{min} , which shifts to lower temperatures with increasing La content. For all superconducting samples studied, a strong diamagnetic signal was observed, confirming the bulk superconductivity. As a consequence, we established the electronic phase diagram of this $\text{Sr}_{1-x}\text{La}_x\text{FBiS}_2$ system based on our experimental data.

2. Experiment

The polycrystalline samples of $\text{Sr}_{1-x}\text{La}_x\text{FBiS}_2$ ($0 \leq x \leq 0.7$) used in this study were synthesized by two-step solid state reaction method. The detailed synthesis procedures can be found in our previous report[15]. Crystal structure characterization was performed by powder X-ray diffraction (XRD) at room temperature using a D/Max-rA diffractometer with $\text{CuK}\alpha$ 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 K to 0.4 K in a commercial Quantum Design PPMS-9 system with a ^3He refrigeration insert. The Hall effect measurements were also performed in this system. The temperature dependence of d.c. magnetization was measured by a Quantum Design MPMS-5.

3. Results and Discussion

Figure 1 (a) shows the room temperature powder XRD patterns of the $\text{Sr}_{1-x}\text{La}_x\text{FBiS}_2$ samples. The main diffraction peaks of these samples can be well indexed based on a tetragonal cell structure with the P4/nmm space group, except for some extra minor peaks arising from the possible impurity phase of Bi_2S_3 (note that $x = 0.4$ sample shows a single phase only). Fig. 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 much less doping dependence. This observation is consistent with the variation of the lattice parameters at room temperature, as shown in Fig. 1(c), where the c -axis decreases quickly as x grows, while the a -axis is nearly independent of the La content. These suggest that La atoms are indeed incorporated into the lattice, resulting in the decrease in the cell volume. Similar feature was also reported in the case of $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$ [11]. To obtain the actual content of La impurities, the EDX measurements (not shown here) are performed in a single crystal grain of polycrystalline sample for all La-doped samples. Those results suggest that the real 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 Fig. 2. The parent compound SrFBiS_2 , which has been broadly studied in the literature[15, 16], is a semiconductor with room temperature resistivity of $\sim 5 \times 10^2 \text{ m}\Omega\cdot\text{cm}$. 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 the fitting to the thermal activation formula $\rho(T) = \rho_0 \exp(E_g/k_B T)$ at the temperature range from 100 K 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 semiconducting-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_2S_3 with sulfur deficiency[21]. As x further increases to 0.4, resistivity shows semiconducting behavior before a sharp superconducting transition with T_c^{onset} (the onset temperature at which the resistivity starts to drop) ~ 2.0 K sets up, as clearly seen in the low- T enlarged plot in Fig. 2(b). This result is comparable to the case of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$, where the normal state shows semiconducting behavior, and it 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 the decrease of gap size due to electron doping. The highest T_c^{onset} is observed to be 3.5 K at $x = 0.55$. Interestingly, for the superconducting samples, there occurs a crossover from a metallic to semiconducting state as the temperature is lowered below T_{min} . While the T_{min} shifts progressively towards lower temperatures with increasing La concentration up to $x=0.7$, superconducting T_c remains almost unchanged above the doping level of 0.55, as observed in the Fig. 2(b).

To further confirm the bulk nature of the observed superconductivity, we performed the d.c. magnetic susceptibility measurement with both zero field cooling (ZFC) and field cooling (FC) modes under 5 Oe magnetic field for the superconducting samples, as depicted in Fig. 3. For all superconducting samples, strong diamagnetic signals are observed and the T_c values determined from the magnetic susceptibility are overall consistent well 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 $\text{LaO}_{1-x}\text{F}_x\text{BiS}_2$ system[22].

Fig. 4 shows the temperature dependence of resistivity for $x = 0.55$ sample under various magnetic fields below 5 K. It can be seen that T_c^{onset} is about 3.5 K at zero field. With increasing magnetic fields, T_c^{onset} is gradually suppressed and the superconducting transition becomes obviously broader. Above 0.3 T, T_c^{onset} becomes robust in fields and its value shows nearly no changes 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 upper critical field $\mu_0 H_c(T)$ below 5 K, determined by using 99% normal state resistivity criterion. The $\mu_0 H_c(T)$ is nearly linear with temperature decreasing at low field but becomes constant as H is over 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 $\text{Bi}_4\text{O}_4\text{S}_3$ system[23]. According to the conventional one band WHH formula[24] $\mu_0 H_{c2}(0) = -0.69 T_{c0} (\partial H_{c2}/\partial T)|_{T_{c0}}$, the upper critical field $\mu_0 H_{c2}$ estimated is about 1.44 T. Apparently, this result from one band WHH model does not match to our experimental data, indicating the multiband

superconductivity in the $\text{Sr}_{1-x}\text{La}_x\text{FBiS}_2$ system. Recently, the calculations[25] have claimed that in BiS_2 systems, the triplet pairing 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, the 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. Fig. 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 ρ_{xy} at various temperatures for the representative $x = 0.55$ sample. In the main panel of Fig. 5, the positive R_H throughout the entire temperature range is observed and displays a weak temperature dependence above 50 K for $x = 0.4$ sample, suggesting the dominant hole-carriers regardless of electron doping in this compound. In contrast, as $x \geq 0.5$, the R_H in the whole temperature region is negative and indicates that the electron-type charge carriers is dominant for those compounds. Moreover, their R_H are seen to be T -independent at high temperatures and drop drastically below 100 K. The sign change of R_H from positive to negative may be ascribed to the suddenly topology change of the Fermi Surface according to the calculations[28, 29]. On the other hand, as shown in the inset of Fig. 5, the magnetic field dependence of ρ_{xy} shows weak nonlinear behaviors at low temperatures for $x = 0.55$. The results are consistent with the multi-band effects in the present system, similar to the case of CeOFBiS_2 [12]. However, another possibility of the spin (charge) density wave (SDW/CDW) formation[30] can not be ruled out at this stage, as the similar sharp drop in R_H was also observed in the iron-based superconductors below AFM transition[31].

On the basis of the above experimental findings, the electronic phase diagram of $\text{Sr}_{1-x}\text{La}_x\text{FBiS}_2$ system is mapped out in Fig. 6. The parent compound SrFBiS_2 is a semiconductor. With La doping on Sr sites, superconductivity emerges as $x \geq 0.3$ and it reaches a maximal $T_c \sim 3.5$ K at $x = 0.55$. Meanwhile, a crossover from metallic to semiconducting-like behavior is observed in the normal state of the superconducting samples, with the resistivity minimum T_{min} shifting progressively towards lower temperatures with doping.

The above phase diagram of $\text{Sr}_{1-x}\text{La}_x\text{FBiS}_2$ system distinguishes itself from those of $\text{LnO}_{1-x}\text{F}_x\text{BiS}_2$ 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 $\text{Sr}_{1-x}\text{La}_x\text{FBiS}_2$, which is distinct from $\text{LnO}_{1-x}\text{F}_x\text{BiS}_2$ [12] and $\text{La}_{1-x}\text{M}_x\text{OBiS}_2$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{Th}$) systems[32], where resistivity shows the opposite trend with the electron concentration. Third, no metal to semiconductor transition/crossover has been observed in $\text{LnO}_{1-x}\text{F}_x\text{BiS}_2$ and $\text{La}_{1-x}\text{M}_x\text{OBiS}_2$ systems.

4. Conclusion

In summary, we have successfully synthesized a series of BiS_2 -based $\text{Sr}_{1-x}\text{La}_x\text{FBiS}_2$ polycrystalline samples. Through the measurements of resistivity and magnetic susceptibility, the parent compound was found to be semiconducting-like with an thermal activation energy $E_g \sim 38$ meV. Via the partial La doping on Sr sites, however, the resistivity decreases sharply, and ultimately superconductivity emerges as $x > 0.3$ and it reaches 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 the suddenly topology change of the Fermi Surface. A drop in R_H and the non-linear transverse resistivity ρ_{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

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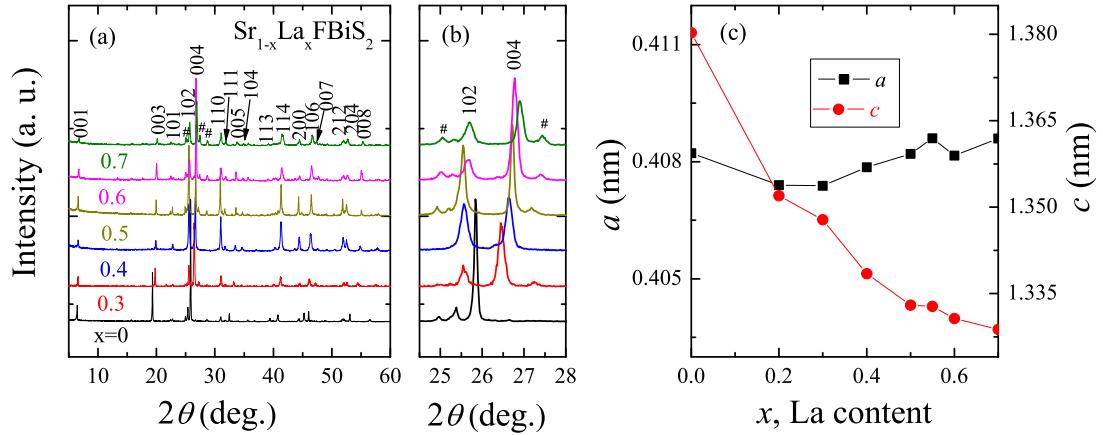


Figure 1. (color online). Crystal structure of $\text{Sr}_{1-x}\text{La}_x\text{FBiS}_2$ (a) Room temperature powder X-ray diffraction patterns of $\text{Sr}_{1-x}\text{La}_x\text{FBiS}_2$ ($0 \leq x \leq 0.7$) samples. The # peak positions designate the impurity phase of Bi_2S_3 . (b) An enlarged plot of the XRD diffraction peaks around (102) and (004). (c) Lattice parameter as a function of La content x .

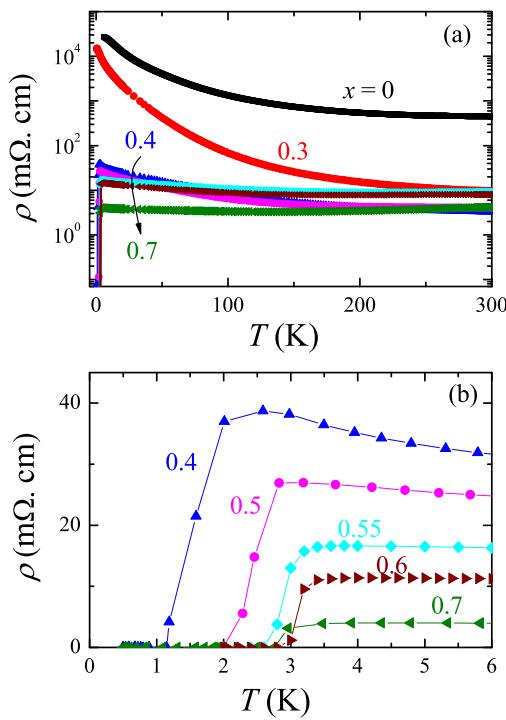


Figure 2. (color online). (a) Temperature dependence of resistivity $\rho(T)$ for the $\text{Sr}_{1-x}\text{La}_x\text{FBiS}_2$ ($0 \leq x \leq 0.7$) samples. (b) A close-up view of the resistivity around T_c for the superconducting samples.

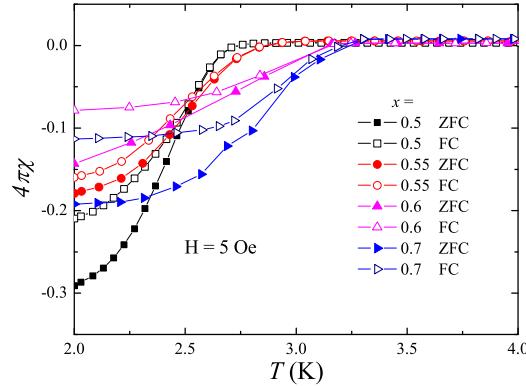


Figure 3. (color online). Temperature dependence of the magnetic susceptibility under 5 Oe magnetic field with ZFC(Solid) and FC(Open) modes for $x = 0.5, 0.55, 0.6, 0.7$ samples. The Meissner volume fraction for those samples is over 15%, confirming the bulk superconductivity.

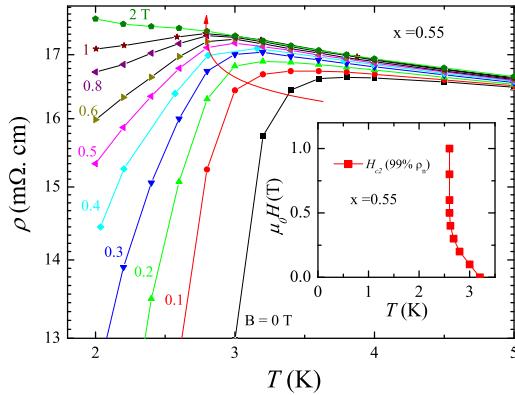


Figure 4. (color online) Temperature dependence of resistivity below 5 K under several magnetic fields for $x = 0.55$ sample. The inset: $\mu_0 H(T)$ as a function of temperature.

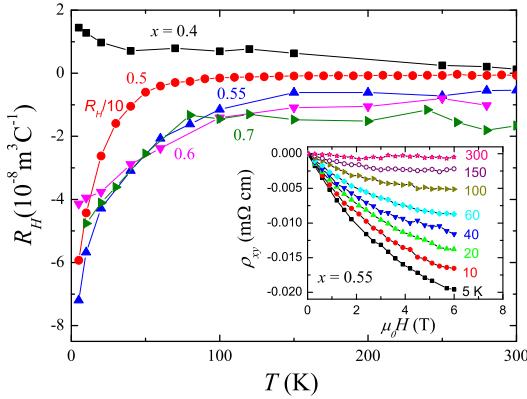


Figure 5. (color online) Temperature dependence of Hall coefficient R_H measured at 5 T for the different La doping samples. R_H shows weak temperature dependence at the high temperature and drops at low temperature. The inset gives the Hall resistivity ρ_{xy} as a function of fields at several representative temperature as $x = 0.55$. The ρ_{xy} vs. magnetic field with weak nonlinear behaviors suggests the multi-band effect in this system.

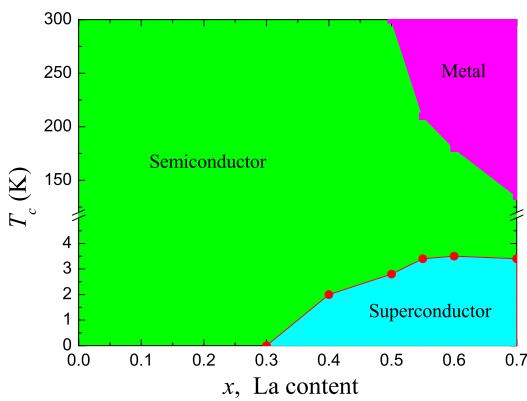


Figure 6. (color online) The electronic phase diagram extracted from the resistivity measurements.