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Superconductivity induced by La doping in $Sr_{1-x}La_xFBiS_2$

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Through a combination of x-ray diffraction, electrical transport, magnetic susceptibility, and heat-capacity measurements, we report the effect of La doping on Sr in the newly discovered $SrFBiS_2$ system. Superconducting transition with critical temperature T_c of 2.8 K, developed from a semiconducting-like normal state, was found in $Sr_{0.5}La_{0.5}FBiS_2$. A strong diamagnetic signal and a clear specific-heat anomaly associated with this transition were observed, confirming bulk superconductivity. The upper critical field $H_{c2}(0)$ was estimated to be 1 T by using the Ginzburg-Landau approach. Our experiments therefore demonstrate that bulk superconductivity can be achieved by electron doping in the $SrFBiS_2$ system.

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Superconductivity within layered crystal structures has attracted sustained interest in the community of correlated electron systems, primarily due to the exotic superconducting properties they exhibit. Notable examples include the high-T_c cuprates with the CuO_2 plane and the Fe-based superconductors with Fe_2An_2 (An = P, As, and Se) superconducting (SC) layers. Recently, superconductivity in the novel BiS_2-based superconductor $Bi_4O_4S_3$ with a superconducting transition temperature (T_c) of 8.6 K has been reported.[1] Immediately following this result, several $LnO_{1-x}F_xBiS_2$ (Ln = La, Ce, Pr, and Nd) superconductors, with the highest T_c of 10 K,[2–6] have then been discovered. While T_c is largely determined by a $[Ln_2O_2]^{2-}$ blocking layer in these systems, all these superconductors share the common BiS_2 layer. Although these BiS_2-based layered superconductors show a wealth of similarities to the iron pnictides, some differences are also manifest. First, the parent compound $LnOBiS_2$ is a bad metal without detectable antiferrimagnetic transition or structure phase transition, implying that magnetism is of less importance to superconductivity in BiS_2-based systems. Second, resistivity measurements in BiS_2-based systems suggest that superconductivity appears in close proximity to an insulating normal state for the optimal superconducting sample,[5] in sharp contrast to the iron-based superconductors where superconductivity grows from a metallic state. Interestingly, pairing symmetry in layered BiS_2-based compounds has yet to be determined albeit some theorists conjectured that BiS_2-based compounds are strongly electron-phonon coupled superconductors, and the pairing symmetry may be an extended s wave with full gaps on different parts of Fermi surfaces,[7,8] in analogy to the iron-based superconductors.[9,10] However, the experimental evidence of pairing symmetry is still lacking thus far.

Very recently, a new BiS_2-based layered compound $SrFBiS_2$ has been reported.[11] This compound is isostructural to $LaOBiS_2$, with the $[Ln_2O_2]^{2-}$ layer being replaced by an isocharged $[Sr_2F_2]^{2-}$ block, similar to the case of LaOFeAs and SrFFeAs. The resistivity of $SrFBiS_2$ shows the semiconducting behavior, however, no superconductivity has been reported in this system.

In this Rapid Communication, we report the successful synthesis and the detailed characterization of La-doped $Sr_{1-x}La_xFBiS_2$ ($x = 0,0.5$) samples. The parent compound $SrFBiS_2$ exhibits thermally excited resistivity down to low temperature, consistent with the existing literature.[11] As $x = 0.5$, resistivity at normal state still shows the semiconducting behavior, but its absolute value drops by a factor of 2, followed by a sharp superconducting transition below 2.8 K. The strong diamagnetic signal and a clear specific-heat jump provide compelling evidence of bulk superconductivity in the $Sr_{1-x}La_xFBiS_2$ system. Finally, the specific-heat data show evidence of strong-coupling nature of the observed superconductivity.

The polycrystalline samples of $Sr_{1-x}La_xFBiS_2$ ($x = 0,0.5$) used in this study were synthesized by a two-step solid state reaction method. The starting materials—La pieces, SrF_2 powder, Bi and S powder—are all of high purity ($\geqslant$99.9%). First, La_2S_3 was presynthesized by reacting stoichiometric S powder and La pieces at 873 K for 10 h. After that, the as-grown La_2S_3 and the powder of SrS, SrF_2, Bi, and S as starting materials were weighted according to their stoichiometric ratio and then fully ground in an agate mortar. The mixture of powder was then pressed into pellets, heated in an evacuated quartz tube at 1073 K for 10 h, and finally furnace cooled to room temperature. The whole process was repeated once again in order to get the pure phase.

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 obtained by Rietveld refinements. The electrical resistivity was measured with a standard four-terminal method covering the temperature range from 0.4 to 300 K in a commercial Quantum Design PPMS-9 system with a ^{3}He refrigeration insert. Specific-heat and Hall-effect measurements were also performed in this system. The temperature dependence of dc magnetization was measured on a Quantum Design MPMS-5.

Figure 1(a) shows the powder XRD patterns of the $Sr_{1-x}La_xFBiS_2$ ($x = 0,0.5$) samples. Overall, the main diffraction peaks of these two samples can be well indexed based on a tetragonal cell structure with the $P4/nmm$ space group. Extra minor peaks arising from the impurity phase of Bi_2S_3 can also be seen. The content of impurity phase Bi_2S_3 estimated by Rietveld fitting is about 15% and 12%

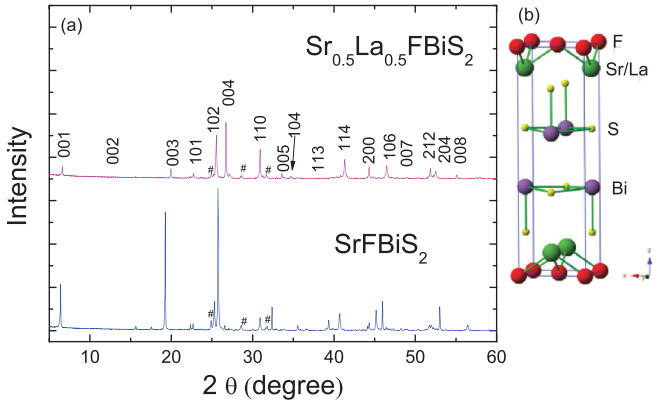

FIG. 1. (Color online) (a) Powder x-ray diffraction patterns of $Sr_{1-x}La_xFBiS_2$ ($x = 0,0.5$) samples. The # peak positions designate the impurity phase of Bi_2S_3. (b) Crystal structure of $Sr_{1-x}La_xFBiS_2$. The solid line indicates the unit cell.

for the parent compound ($x = 0$) and the $x = 0.5$ sample, respectively. The lattice parameters of the parent compound $SrFBiS_2$ are extracted to be $a = 4.0820$ Å and $c = 13.8025$ Å by Rietveld fitting, in good agreement with the previous report.[11] For the La-doped sample, however, the $(00l)$ peaks shift discernibly towards higher 2θ angles, suggesting the smaller c-axis constant. Thus, while the a-axis lattice parameter increases slightly to 4.0822 Å in the La-doped sample, the c axis decreases significantly to 13.335 Å, implying that the La impurity was indeed doped into the lattice, given that the ionic radius of the La ion is known to be smaller than that of Sr. This is quite similar to the case of $LaO_{1-x}F_xBiS_2$.[4] The resultant crystal structure is therefore schematically shown in Fig. 1(b), which is composed of a stacked rocksalt-type BiS_2 layer alternating with a fluorite-type SrF layer along the c axis.

The zero-field temperature dependence of the electrical resistivity (ρ) of these two samples is plotted in Fig. 2(a). For the parent $SrFBiS_2$ compound, the resistivity clearly shows thermally activated behavior with decreasing temperature from 300 K, and no resistivity anomaly can be observed down to 2 K. The thermal activation energy (E_a) obtained by fitting with the thermal activation formula $\rho(T) = \rho_0 \exp(E_a/k_BT)$ for the temperature range from 100 to 300 K is about 38.2 meV, consistent with previous studies.[11] However, it is noted that its absolute value is nearly two-thirds smaller than the reported value by Lei *et al.*[11] We attribute this to the impurity phase of Bi_2S_3 with sulfur deficiency[12] in our sample which may decrease the absolute value of resistivity. As Sr is partially replaced by La ($x = 0.5$), the resistivity remains semiconducting-like at high temperatures, with the magnitude of resistivity substantially reduced compared to the undoped sample. Meanwhile, the E_a fitted at high temperature also decreases to 8.6 meV, suggesting the decrease of gap size because of electron doping. With further cooling down, a sharp superconducting transition with T_c of 2.8 K is clearly seen. This result is reminiscent of $LaO_{0.5}F_{0.5}BiS_2$, where the normal state shows semiconducting behavior, and it undergoes superconducting transition below 10 K.[2] Interestingly, the first-principles calculations[7] have suggested that there may be a charge density wave instability or an enhanced correlation

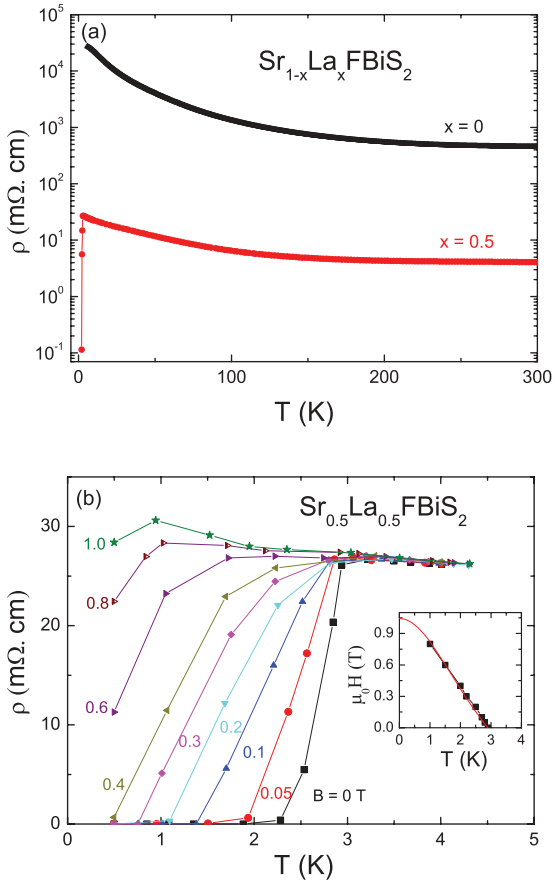

FIG. 2. (Color online) (a) Temperature dependence of resistivity (ρ) for the $Sr_{1-x}La_xFBiS_2$ ($x = 0,0.5$) samples. (b) Temperature dependence of resistivity for $Sr_{0.5}La_{0.5}FBiS_2$ samples under several different magnetic fields ($B = 0,0.05,0.1,0.2,0.3,0.4,0,6,0.8,1$ T).

effect in this system. Yet, no such instability can be detected merely from the resistivity measurement given in this study.

Figure 2(b) shows the close-up view of the low-temperature resistivity for $Sr_{0.5}La_{0.5}FBiS_2$ samples under various magnetic fields below 4 K. The inset gives the temperature dependence of the upper critical field $\mu_0 H_{c2}(T)$, determined by using 90% normal state resistivity criterion. The temperature dependence of $\mu_0 H_{c2}(T)$ is nearly linear in the temperature range studied. According to the Ginzburg-Landau theory, the upper critical field H_{c2} evolves with temperature following the formula

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

where t is the renormalized temperature T/T_c. It is found that the upper critical field H_{c2} as drawn can be well fitted by this model and its zero-temperature limit is estimated to be 1.04 T.

In order to verify the bulk nature of the observed superconductivity, the temperature dependence of dc magnetic susceptibility was measured under 5 Oe magnetic field with both zero-field-cooling (ZFC) and field-cooling (FC) modes for the superconducting samples (Fig. 3). The strong diamagnetic signal was observed for the $Sr_{0.5}La_{0.5}FBiS_2$ sample. The T_c value determined from the magnetic susceptibility agrees well with the one extracted from the resistivity data. The estimated volume fraction of magnetic shielding from ZFC data is over 30%, bearing out the bulk superconductivity. Note that the

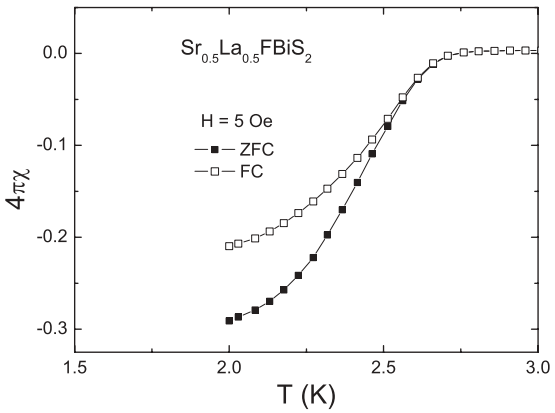

FIG. 3. The diamagnetic signal vs temperature under a magnetic field of 5 Oe with ZFC (solid) and FC (open) modes for $Sr_{0.5}La_{0.5}FBiS_2$.

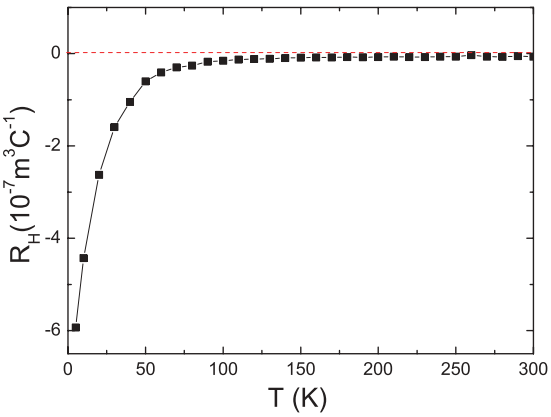

FIG. 5. (Color online) Temperature dependence of Hall coefficient R_H measured at 5 T for the $Sr_{0.5}La_{0.5}FBiS_2$ sample.

Meissner volume fraction estimated by FC measurement data also exceeds 20%, indicating the high-quality superconducting sample.

To further study its superconducting properties, the specific-heat measurement of the $Sr_{0.5}La_{0.5}FBiS_2$ sample was performed in the temperature range from 0.5 to 5 K. As plotted in Fig. 4, a clear specific-heat jump can be observed at $T_c = 2.8$ K, further confirming the bulk superconductivity. Below 1.5 K, however, the low-temperature heat capacity undergoes a moderate upturn which very likely arises from Schottky anomaly associated with the impurities phase or the freezing out of La nuclear spins.[13] Taking into account the Schottky anomaly component, the overall specific heat can be written as

$$C/T = \gamma + \beta T^2 + \alpha/T^3, \tag{2}$$

where γ and βT^2 account for the electronic and lattice contributions, respectively, and the last term, α/T^3, is the Schottky anomaly. The plot of C/T-α/T^3 versus T^2 shows a linear behavior in the high-temperature range from 2.9 to 5 K (data not explicitly shown here). The resultant electronic coefficient γ and the lattice coefficient β are 1.42 mJ/mol K^2 and $\beta = 0.414$ mJ/mol K^4, respectively. The Debye temperature is then estimated to be 265 K. This value is somewhat smaller that

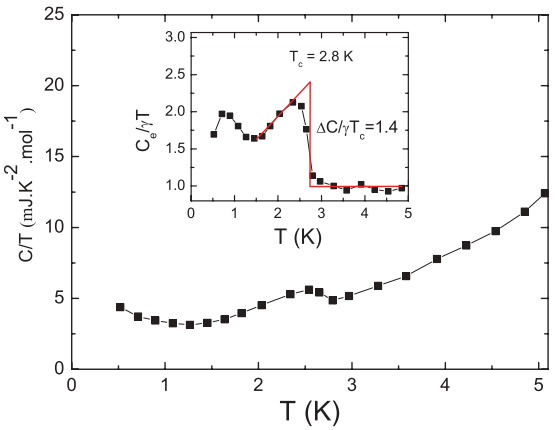

FIG. 4. (Color online) The specific heat of $Sr_{0.5}La_{0.5}FBiS_2$ samples under zero field below 5 K. The inset shows $\Delta C_e/\gamma T_c$ as a function of temperature, where C_e is the electronic specific heat.

those of LaONiAs,[14] LaOFeP,[15] and $LaO_{0.89}F_{0.11}FeAs$.[16] The lattice contribution was further subtracted in the inset in order to see the clear specific-heat jump at the SC transition. The corresponding electronic specific jump at T_c, therefore, is estimated to be $\Delta C_e/\gamma T_c = 1.4$, very close to the weak-coupling Bardeen-Cooper-Schrieffer (BCS) value of 1.43. Considering the relatively low volume fraction of magnetic shielding suggested from susceptibility measurement, the real size of $\Delta C_e/\gamma T_c$ ought to be much larger than the BCS value, implying that SC in $Sr_{0.5}La_{0.5}FBiS_2$ likely involves a strong electron-phonon coupling, consistent with the theoretical prediction.[7]

Finally, the temperature dependence of Hall coefficient R_H for the $Sr_{0.5}La_{0.5}FBiS_2$ sample is shown in Fig. 5. The negative R_H signal covers the whole temperature region, indicating that the electron-type charge carrier is dominant in this sample. Clearly, R_H is T independent at the high-temperature regime, and drops drastically below 50 K. The result reminds us of the similar behavior observed in iron-based SC, where R_H decreases sharply due to spin-density-wave (SDW) formation.[17] In the present sample, however, no SDW/CDW anomaly has been observed in the measurements of resistivity and magnetization. On the other hand, it is known that the inherent impurity phase may act to smear out the anomalies in the resistivity and susceptibility. In this regard, it would be interesting to clarify this problem by first-principles calculations[7] or further improving the sample quality. In a single-band metal, the Hall coefficient R_H is associated with carrier density (n) as $R_H = 1/ne$. We therefore estimate the charge-carrier density to be $1.05 \times 10^{19}/\text{cm}^3$ at 5 K, which is similar to the $Bi_4O_4S_3$ system[18] and iron-based superconductors[19] with a very low superfluid density. In addition, we cannot rule out the multiband effect[5] as the origin of the drop in R_H.

In summary, we study the electron doping effect, i.e., partially substituting La for Sr, in the newly discovered $SrFBiS_2$ system. The parent compound shows semiconducting-like resistivity with decreasing temperature. Via electron doping, we discovered a BiS_2-based superconductor $Sr_{0.5}La_{0.5}FBiS_2$ with a T_c as high as 2.8 K. Importantly, this superconductivity was found to develop on the background of an insulating normal state, raising a question of whether this superconductor is in proximity to a Mott insulator or a band insulator. Based

on the heat-capacity measurement, we speculate that the superconducting electron pairs might have a strong-coupled nature. In this regard, it would certainly be interesting to identify the symmetry of superconducting order parameter in this system along with other BiS_2-based superconductors.

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