

Pressure Study of BiS_2 -Based Superconductors $\text{Bi}_4\text{O}_4\text{S}_3$ and La(O,F)BiS_2

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We report the electrical resistivity measurements under pressure for the recently discovered BiS_2 -based layered superconductors $\text{Bi}_4\text{O}_4\text{S}_3$ and La(O,F)BiS_2 . In $\text{Bi}_4\text{O}_4\text{S}_3$, the transition temperature T_c decreases monotonically without a distinct change in the metallic behavior in the normal state. In La(O,F)BiS_2 , on the other hand, T_c initially increases with increasing pressure and then decreases above ~ 1 GPa. The semiconducting behavior in the normal state is suppressed markedly and monotonically, whereas the evolution of T_c is nonlinear. The strong suppression of the semiconducting behavior without doping in La(O,F)BiS_2 suggests that the Fermi surface is located in the vicinity of some instability. In the present study, we elucidate that the superconductivity in the BiS_2 layer favors the Fermi surface at the boundary between the semiconducting and metallic behaviors.

KEYWORDS: $\text{Bi}_4\text{O}_4\text{S}_3$, La(O,F)BiS_2 , pressure

The appearance of new superconductors with a BiS_2 layer has opened a new route in the field of fascinating layered superconductors.¹ Soon after the first discovery of superconductivity in $\text{Bi}_4\text{O}_4\text{S}_3$, another system with the same BiS_2 layer, La(O,F)BiS_2 , joined the family of this compound.² The discovery of superconductivity in this system is significant in many aspects, because it gives an opportunity for wide and thorough investigations using a variety of related materials possessing the BiS_2 layer along with the possible substitution of rare-earth ions as well as Fe-based superconductors. In fact, isostructural Nd(O,F)BiS_2 has also shown superconductivity.³ This derivative finding revealed that the superconductivity occurring in the BiS_2 layer is robust against magnetic elements. For either $\text{Bi}_4\text{O}_4\text{S}_3$ and La(O,F)BiS_2 , superconductivity can be obtained by carrier (electron) doping into the band insulators $\text{Bi}_6\text{O}_8\text{S}_5$ or LaOBiS_2 . The band calculation for the composition $\text{Bi}_4\text{O}_4\text{S}_3$ suggests that the Fermi level is located at the peak of the density of states, which mainly originates from the Bi 6p orbitals.¹ LaOBiS_2 also has a similar band structure, and the F-doping of $x = 0.5$ corresponds to the Fermi level with a high density of states in the rigid band picture.⁴ An important suggestion by the band calculations is that the bands possess a quasi-one-dimensional character, which originates from the difference in the contribution between the p_x and p_y orbitals, for both compounds. This gives a good nesting property, suggestive of the importance of electron correlations for superconductivity.^{1,4} Another notable point is that the Fermi level for the nominal composition is located in the vicinity of the topological change in the Fermi surface.⁴ If this superconductivity originates from the electric correlation, this suggests that the superconducting (SC) symmetry

can change depending on the doping level.⁴

Among the three compounds discovered thus far, the maximum T_c is ~ 10 K for La(O,F)BiS_2 . It is an intriguing issue how a high T_c is possible in the BiS_2 layer. The doping dependence of T_c has been investigated in Nd(O,F)BiS_2 , and the peak of T_c appears at $x = 0.3$ although it is not so sensitive to the doping level.³ In addition to the change in the doping level, the structural compression by applying pressure is also an effective method of exploring the optimized condition for superconductivity. The lattice constants at ambient pressure are different among the compounds: $a = 3.9592$ Å for $\text{Bi}_4\text{O}_4\text{S}_3$ and $a = 4.0527$ Å for La(O,F)BiS_2 .^{1,2} T_c is twofold higher in La(O,F)BiS_2 than in $\text{Bi}_4\text{O}_4\text{S}_3$. This suggests that the lattice parameter is an important factor for superconductivity.

A polycrystalline sample of $\text{Bi}_4\text{O}_4\text{S}_3$ was prepared by the solid-state reaction method,¹ while a polycrystalline sample of $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ was obtained by a two-step process including high-pressure annealing.² The composition expressed here is a nominal one for both compounds. Electrical resistivity (ρ) measurement at high pressures of up to ~ 4 GPa was carried out using an indenter cell.⁵ It was measured by a four-probe method using silver paint for contact. We used Daphne 7474 as a pressure-transmitting medium.⁶ The applied pressure was estimated from the T_c of the lead manometer. The present sample of $\text{Bi}_4\text{O}_4\text{S}_3$ contains Bi as an impurity, and it shows superconductivity above 2.55 GPa accompanied by a structural phase transition. We applied pressure of above 2 GPa to $\text{Bi}_4\text{O}_4\text{S}_3$, but it obstructs the evaluation of T_c intrinsic to $\text{Bi}_4\text{O}_4\text{S}_3$; thus we omitted the data from this paper.

Figures 1(a) and (b) show the temperature dependence of resistivity for $\text{Bi}_4\text{O}_4\text{S}_3$ at pressures of up to 1.92 GPa. The metallic behavior with a gradual temperature varia-

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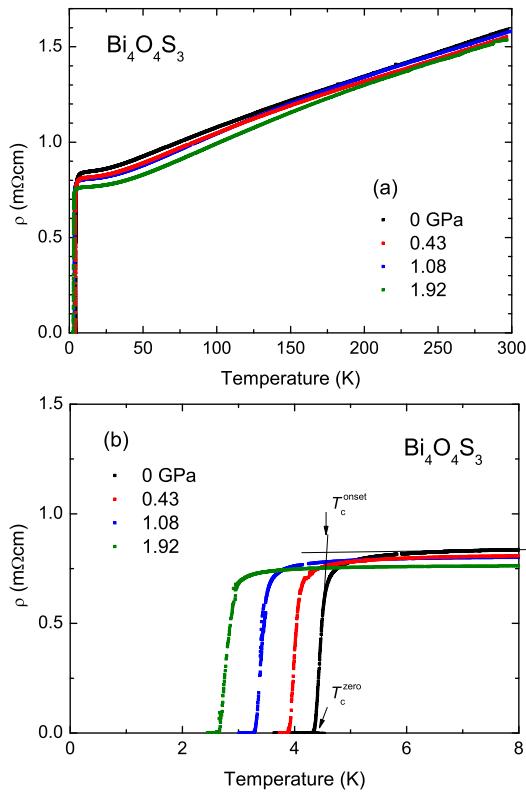


Fig. 1. (color online) (a) Temperature dependence of resistivity for $\text{Bi}_4\text{O}_4\text{S}_3$ under pressure. It shows the metallic behavior in the normal state, which is not sensitive to pressure. (b) Resistivity at low temperatures. T_c decreases monotonically with increasing pressure. We could not evaluate the intrinsic T_c above 2.5 GPa because of the superconductivity of the Bi impurity.

tion is insensitive to pressure. This behavior in the resistivity might be affected by the contribution of impurity phases; however, similar behavior is observed in the different samples synthesized by other groups.^{7–9} On the other hand, the evolution of T_c is noteworthy. As shown in Fig. 1(b), it decreases sensitively under pressure. If we determine T_c^{onset} and T_c^{zero} as shown in the figure, $T_c^{\text{onset}} \sim 4.6$ K at ambient pressure decreases to 2.9 K at 1.92 GPa. The pressure dependences of T_c^{onset} and T_c^{zero} are shown in Fig. 2. It is clear that T_c decreases

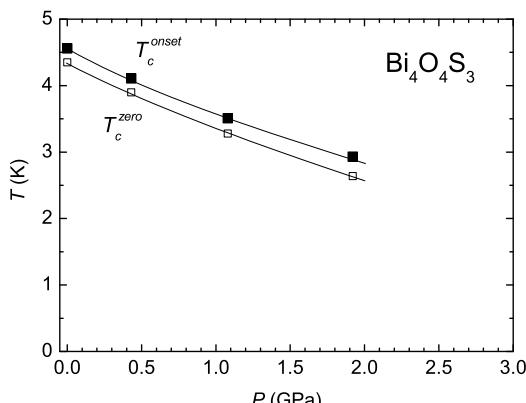


Fig. 2. Pressure dependences of T_c^{onset} and T_c^{zero} . Superconductivity for $\text{Bi}_4\text{O}_4\text{S}_3$ is suppressed under pressure.

monotonically. The initial slope is estimated to be -1.1 K/GPa.

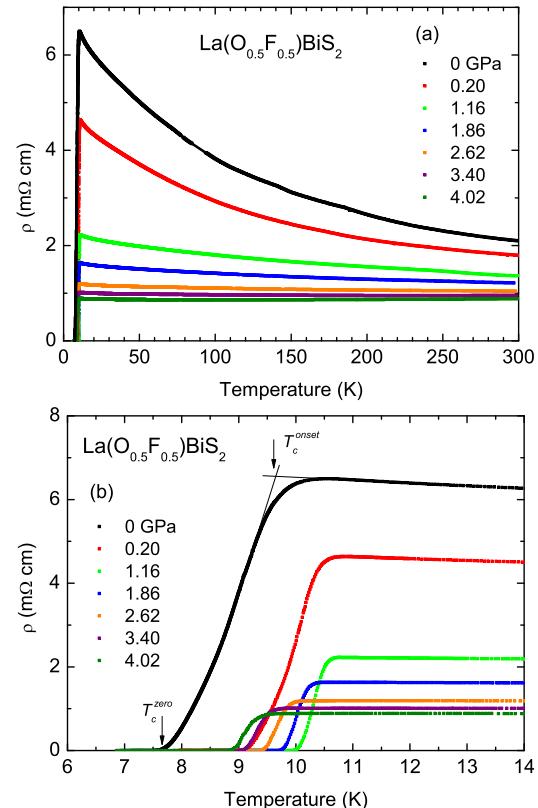


Fig. 3. (color online) (a) Temperature dependence of resistivity for $\text{La}(\text{O}_{0.5}\text{F}_{0.5})\text{BiS}_2$ under pressure. Semiconducting behavior is markedly suppressed with increasing pressure. Almost temperature-independent behavior is observed at ~ 4 GPa. (b) Resistivity at low temperatures. T_c initially increases and then decreases gradually above 1 GPa.

Figure 3(a) shows the temperature dependence of resistivity for $\text{La}(\text{O},\text{F})\text{BiS}_2$ below 300 K measured at several pressures of up to ~ 4 GPa. It shows semiconducting behavior at ambient pressure in contrast to that for $\text{Bi}_4\text{O}_4\text{S}_3$. This semiconducting behavior is extremely sensitive to pressure and is suppressed under pressure. We cannot see the obvious semiconducting behavior at ~ 4 GPa, at which resistivity is almost temperature-independent, which seems to be produced by the comparable contributions of phonon scattering and the semiconducting behavior. Figure 3(b) shows the data near T_c at low temperatures. T_c evidently increases by applying pressure up to ~ 1 GPa, however, it then decreases above ~ 1 GPa. Both T_c^{onset} and T_c^{zero} , which are determined as shown in the figure, have maxima at approximately 1 GPa; $T_c^{\text{onset}} = 10.5$ K and $T_c^{\text{zero}} = 10.0$ K.

We attempted to estimate the energy gap assuming that the semiconducting behavior in $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ originates in the small gap in the band structure. Figure 4 shows a semi-logarithmic plot for ρ vs $1/T$ up to 2.62 GPa. The lines in the figure correspond to the simple activation-type relation $\rho \propto \exp(\Delta_{1,2}/k_B T)$. As seen in the figure, the fitting by a single gap is impossible in the

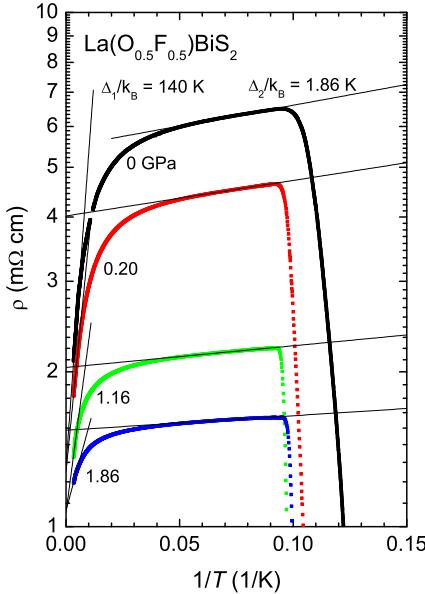


Fig. 4. (color online) ρ vs $1/T$ up to 1.86 GPa. The solid lines give simple activation-type temperature dependences. The respective gaps Δ_1 and Δ_2 are estimated at high and low temperatures.

whole temperature range. Δ_1 is estimated from the fitting in the temperature range of 200 – 300 K, while Δ_2 is obtained in the temperature range between ~ 20 K and T_c . Here, we neglected the contribution of scattering by phonons, but it is comparable to the semiconducting behavior at higher pressures; thus, the estimation of $\Delta_{1,2}$ above 2 GPa was not carried out. The gap sizes are estimated to be $\Delta_1/k_B \sim 140$ K and $\Delta_2/k_B \sim 1.86$ K at ambient pressure. The slopes of both lines in the figure gradually decrease and the semiconducting behavior is suppressed with increasing pressure.

Figure 5 shows the pressure dependences of T_c^{onset} and T_c^{zero} for $\text{La}(\text{O},\text{F})\text{BiS}_2$, the pressure dependence of ρ at 11 K just above T_c , and the tentatively estimated energy gaps $\Delta_{1,2}$. The high resistivity at low temperatures induced by the semiconducting behavior is markedly suppressed by applying pressure, especially up to ~ 1 GPa. The decrease in $\Delta_{1,2}$ is monotonic. T_c initially shows a steep increase; however, it gradually decreases above ~ 1 GPa. The slope above ~ 1 GPa is ~ -0.4 GPa/K. The highest T_c obtained at 0.5 – 1 GPa is achieved just after a large suppression of the semiconducting behavior, and T_c monotonically decreases upon approaching the metallic region.

We first discuss the origin of the strong suppression of the semiconducting behavior in $\text{La}(\text{O},\text{F})\text{BiS}_2$ under pressure. When we consider the present pressure effect along with the calculated band structure,^{1,4} we encounter a problem with the actual doping level of electrons. The band calculation based on the nominal composition has indicated that the Fermi energy is located at the peak position of the density of states in $\text{Bi}_4\text{O}_4\text{S}_3$.¹ A high density of states at the Fermi level is also expected in $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ for the nominal composition.⁴ Case 1 in Fig. 6 corresponds to the Fermi level close to the estimation from the nominal composition. If the Fermi

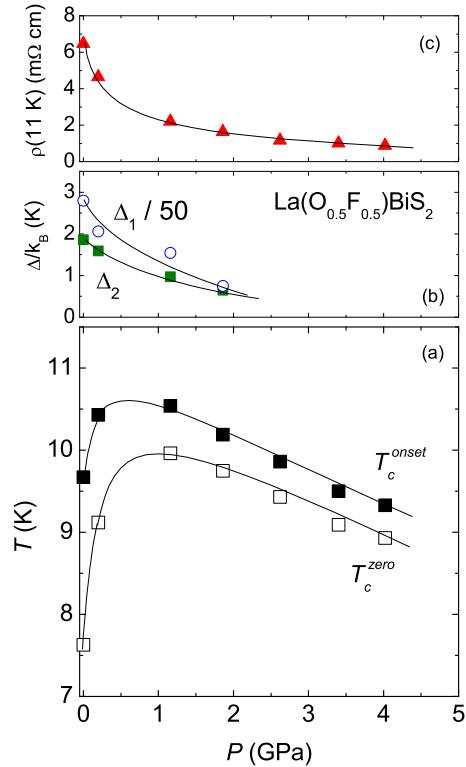


Fig. 5. (color online) (a) Pressure dependences of T_c^{onset} and T_c^{zero} for $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$. T_c initially increases with a relatively large slope and decreases above ~ 1 GPa. Pressure dependence of (b) tentatively estimated gaps and (c) ρ at 11 K just above T_c . The high resistivity induced by the semiconducting behavior is suppressed by applying pressure.

level only crosses the lower band near $(\pi, 0)$, and the upper band decreases relatively under pressure, then the change in the Fermi surface will give a large evolution of the resistivity. However this will be in contradiction to the semiconducting behavior in $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ because the Fermi surface is well established for the doping level of 0.5 electrons/unit cell. If the semiconducting behavior originates from the thermal change in carrier density, it is naturally conjectured that the carrier density in $\text{LaO}_{0.5}\text{F}_{0.5}\text{BiS}_2$ is much lower than that expected from the nominal composition, and that the Fermi level is most likely close to the edge of the conduction band. Here, we conjecture possible origin of the band gap or gap like behavior that explain the semiconducting behavior. The first one is the original band gap between the conduction band and the valence band. In the band structure of undoped LaOBiS_2 ,⁴ the band gap is estimated to be ~ 0.4 eV, but this tends to be reduced owing to the structural change by F doping, giving a semi metal-like band structure, as shown in Fig. 6.¹⁰ If the band gap is already small at ambient pressure, thermal excitation from the valence band, which is mainly formed by oxygen orbitals, into the conduction band is possible within the observed temperature range. Pressure may help to close the band gap. The second origin is the energy gap between the conduction band and the impurity level originating from the insufficient doping, as shown in Fig. 6 (Case 2). The third origin is the thermal hopping in the impurity level,

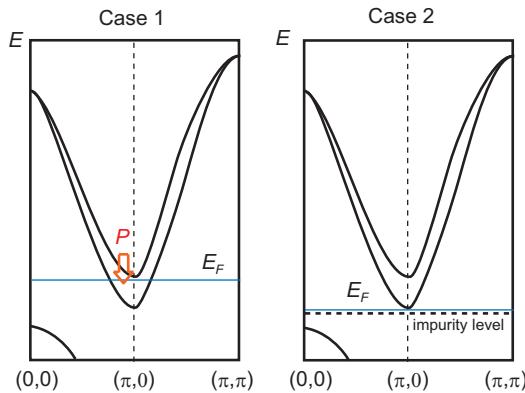


Fig. 6. (color online) Schematic band structures based on calculation for LaOBiS₂.⁴ In Case 1, the Fermi level is located near the position estimated from the nominal composition. The marked change in the resistivity under pressure might be explained by the topological change in the Fermi surface, but it is difficult to explain the semiconducting behavior. In Case 2, conduction is mainly governed by the impurity level or band. Pressure promotes the formation of the impurity band or the overlap of the impurity and conduction bands.

which gives gap like behavior. The semiconducting behavior is robust against magnetic field up to 5 T;² thus, the tentatively estimated small gap Δ_2 might not originate from a pure band-gap but be attributed in such thermal hopping in Case 2 scenario. Quantitative discussion is difficult at present; however, the semiconducting behavior in LaOBiS₂ seems to suggest the presence of an impurity level. In such a case, it can be conjectured that applying pressure promotes the formation of the impurity band or the overlap of the impurity and conduction bands, resulting in a decrease in the gaps.

Next, we discuss superconductivity in the BiS₂-based systems. The present pressure experiments suggest that a high T_c is obtained at the boundary between the semiconducting and metallic behaviors: T_c in semiconducting LaO_{0.5}F_{0.5}BiS₂ is twofold higher than that in metallic Bi₄O₄S₃, and once metallic behavior appears, T_c decreases monotonically as seen in LaO_{0.5}F_{0.5}BiS₂ above ~ 1 GPa and in Bi₄O₄S₃ from ambient pressure. Similarly, in the isostructural NdO_{1-x}F_xBiS₂, T_c is not sensitive to the doping level but its maximum is obtained at $x = 0.3$ at which slight semiconducting behavior is observed.³ These suggest that a high density of states is not important for a high T_c in these systems. The situation for achieving a high T_c is reminiscent of the doping dependence of Li_xZrNCl, whose electronic specific heat coefficient is $\gamma \sim 1$ mJ/molK².¹¹ T_c in Li_xZrNCl increases significantly upon approaching the band insulator.¹² The highest T_c in Li_xZrNCl is achieved when resistivity shows almost temperature-independent behavior. The evolution of T_c against the doping level cannot be explained by the framework of phonon-mediated superconductivity,¹³ and can be interpreted by the nest-

ing scenario.¹⁴ If the Fermi surface is well established by sufficient doping in the BiS₂-based system, the nesting scenario is a good candidate;⁴ if not, other mechanisms might be required.

In summary, we have measured the electrical resistivity under pressure for the BiS₂ based layered superconductors Bi₄O₄S₃ and LaO_{0.5}F_{0.5}BiS₂. T_c in metallic Bi₄O₄S₃ decreases monotonically with increasing pressure, whereas T_c in semiconducting LaO_{0.5}F_{0.5}BiS₂ initially increases and then decreases upon approaching the metallic region. The strong suppression of the semiconducting behavior in LaO_{0.5}F_{0.5}BiS₂ suggests that the Fermi surface is in the vicinity of some instability. It is plausible that the Fermi level is located near the edge of the conduction band. This indicates that superconductivity is realized in the complex Fermi surface including the impurity band with a low carrier density and a low density of states, and it rather provides benefit for achieving a higher T_c .

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