Multi-Band Exotic Superconductivity in the New Superconductor \( \text{Bi}_4\text{O}_4\text{S}_3 \)

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Resistivity, Hall effect and magnetization have been investigated on the new superconductor \( \text{Bi}_4\text{O}_4\text{S}_3 \). A weak insulating behavior has been induced in the normal state when the superconductivity is suppressed. Hall effect measurements illustrate clearly a multiband feature dominated by electron charge carriers, which is further supported by the magnetoresistance data. Interestingly, a kink appears on the temperature dependence of resistivity at about 4 K at all high magnetic fields when the bulk superconductivity is completely suppressed. This kink can be well traced back to the upper critical field \( H_{c2}(T) \) in the low field region, and is explained as the possible evidence of residual Cooper pairs on the one dimensional chains.

\[ \text{PACS numbers: 74.70.Dd, 74.20.Mn, 74.25.Dw, 74.25.fc} \]

Superconductivity is induced by the quantum condensation of large number of paired electrons. The original proposal about the pairing by the electron-phonon coupling is gradually replaced by the more exotic pairing mechanism, such as through exchanging the magnetic spin fluctuations, and the superconducting transition temperature can be increased to a higher level. The superconducting (SC) pairing mechanism of the cuprates\[3–5\] and the iron pnictides\[6\] with the electron correlations of the electrons from the 3d orbits.\[3–5\] In the heavy Fermion systems\[6\] and organic materials\[7\], a similar conclusion may be achieved. In this regard, it is natural to explore new superconductors with possible higher transition temperatures in the compounds with transition metal elements. The electrons in the p-orbital, especially those from the 5p or 6p orbits, are normally assumed to have weak repulsive potential \( U \) and quite wide band width \( w \), and hence have very weak correlation effect. It would be surprising to find out superconductivity with exotic feature in the p-orbital based compounds. Very recently, Mizuguchi et al.\[8\] discovered superconductivity with \( T_{c}^{\text{onset}} = 8.6 \) K and \( T_{c}^{\text{zero}} = 4.5 \) K in the so-called \( \text{Bi}_2\text{S}_3 \) based compound \( \text{Bi}_4\text{O}_4\text{S}_3 \). This compound has a layered structure with the space group of \( I4/mmm \) or \( I - 42m \). After just three days, the same group reported superconductivity at about 10.6 K in another system \( \text{LaO}_{1-x}\text{F}_x\text{Bi}_2\text{S}_2 \) by doping electrons into the material through substituting oxygen with fluorine.\[9\] Recalling that the same doping technique was used by Kamihara et al.\[2\] in the discovery of superconductivity in the FeAs-based superconductor \( \text{LaO}_{1-x}\text{F}_x\text{FeAs} \). Quickly followed is the theoretical work based on the first principles band structure calculations.\[10\] which predicts that the dominating bands for the electron conduction as well as for the superconductivity are derived from the Bi 6\( \text{p}_x \) and 6\( \text{p}_y \) orbits. In this Letter, we present the first set of data for an intensive study on the transport and magnetic properties of the new superconductor \( \text{Bi}_4\text{O}_4\text{S}_3 \). Our results clearly illustrate the multi-band, strong fluctuation and some unexpected anomalous properties of superconductivity, putting this interesting superconductor as an exotic one.

The polycrystalline samples were synthesized by using a two-step solid state reaction method. First, the starting materials Bi powder (purity 99.5%, Alfa Aesar) and sulfa powders (purity 99.99%, Alfa Aesar) were mixed in 2:3 ratio, ground and pressed into a pellet shape. Then it was sealed in an evacuated quartz tube and followed by annealing at 500°C for 10 hours. The resultant pellet was smashed and ground together with the \( \text{Bi}_2\text{O}_3 \) powder (purity 99.5%, Alfa Aesar) and sulfa powder, in stoichiometry as the formula \( \text{Bi}_4\text{O}_4\text{S}_3 \). Again it was pressed into a pellet and sealed in an evacuated quartz tube and burned at 510°C for 10 hours. Then it was cooled down slowly to room temperature. The second step was repeated in achieving good homogeneity. The resultant sample looks black and very hard. We cut the sample and obtained a specimen with a rectangular shape (length 4.2 mm, width 2.0 mm and thickness of 0.125 mm). Since it is very hard, we can polish the sample with very fine sand paper and obtained shiny and mirror like surface. The crystallinity of the sample was checked by using the x-ray diffraction (XRD) with the Brook Advanced D8 diffractometer with Cu K\( \alpha \) radiation. The analysis of XRD data was done with the softwares Powder-X, Fullprof and Topas. The XRD pattern looks very similar to that reported by Mizuguchi et al.\[8\]. The Rietveld fitting was done with the GSAS program, yielding a 90% volume of \( \text{Bi}_4\text{O}_4\text{S}_3 \) with 10% of impurities which are mainly \( \text{Bi}_2\text{S}_3 \). The resistivity, Hall effect were measured with Quantum Design instrument PPMS-16T and PPMS-9T, and the magnetization was detected by the Quantum Design instrument SQUID-VSM with a resolution of about 5 \times 10^{-8} \text{emu}. The six-lead method was used in the transport measurement on the longitudinal and the transverse resistivity at the same time. The resistance and Hall effect was measured by either sweeping magnetic field at a fixed temperature or sweeping temperature at a fixed field, both set of data coincide very well. The tempera-
and spin-down electrons will become asymmetric given is applied, the density of states (DOS) of the spin-up band has a very shallow band edge, as illustrated by the temperature here. Another possibility is that the conduction which is far beyond the superconducting transition tem-
perature stabilization was better than 0.1% and the resolution of the voltmeter was better than 10 nV.

In Fig. 1(a) we present the temperature dependence of resistivity measured at three magnetic fields: $\mu_0 H = 0$, 6 and 14 T. In addition to the moderate magnetoresistance, one can see that a weak insulating behavior is induced by the magnetic field. This is of course ant
intuitive for a normal state with Fermi liquid characteristic. A simple explanation would be that the insulating feature is given by an adjacent competing order here, once the superconductivity is suppressed, the latter is promoted. However, we should mention that the insu-
lating behavior starts actually at 25 K (at 6 and 14 T) which is far beyond the superconducting transition tem-
perature here. Another possibility is that the conduction band has a very shallow band edge, as illustrated by the band structure calculations.\cite{10} When a magnetic field is applied, the density of states (DOS) of the spin-up and spin-down electrons will become asymmetric given by the Zeeman effect. Therefore we have some polarized electrons which induce the weak insulating behavior. In Fig. 1(b) we present the magnetization data measured in the zero-field-cooled (ZFC) and the field-cooled mode (FC). The superconducting magnetic transition starts at about 3.6 K, far below the onset transition temperature which is about 10 K (determined by the deviating from the normal state background of resistivity) and 4.6 K (determined in using the crossing point of the normal state line and the extrapolation of the steep transition line). Therefore strong superconducting fluctuation is clearly present in this sample. This is actually expected by the band structure calculations which predict a low dimen-
sionality of the electronic structure, and can be corrob-
orated by the quickly broadened transition under mag-
netic fields, as shown in Fig. 1(c). One can see that the bulk superconductivity can be suppressed above 2 K by a magnetic field as low as 0.9 T. However, even the bulk superconductivity can be easily suppressed, a kink appears on the $\rho$ vs $T$ curve. If following the onset transition of the resistivity, as shown in Fig. 1(d), we can clearly see

![FIG. 1: (color online) (a) Temperature dependence of resistivity at three magnetic fields: $\mu_0 H = 0$, 6 and 14 T. It is clear that, beside a moderate magnetoresistance effect, a weak insulating behavior is induced by the magnetic field. (b) The temperature dependence of magnetization near the superconducting transition measured with $H = 4.8$ Oe in the field-cooled (FC) and zero-field-cooled processes (ZFC). (c) An enlarged view for the temperature dependence of resistivity at magnetic fields of (from bottom to top) 0, 0.1 to 0.8 T with increments of 0.1 T; 1, 1.5 to 7 T with increments of 1 T; and 9, 12, 14 T. It is found that the bulk superconductivity can be quickly suppressed by the magnetic field, while the onset transition temperature changes slightly, indicating a strong fluctuation effect. (d) Temperature dependence of the resistivity (as shown in c) normalized at 10 K. A kink can be clearly seen at about 4 K when the magnetic field is high and the bulk superconductivity is suppressed completely. The red arrowed line traces out the evolution from the superconducting onset transition in the low field region to a kink at high magnetic fields.](image1)

![FIG. 2: (color online)(a) The transverse resistivity $\rho_{xy}$ versus the magnetic field $\mu_0 H$ at different temperatures. The curves are extremely curved, indicating a very strong multi-band effect and/or the shallow band edge effect. (a) The Hall coefficient $R_H$ calculated at 9 T, a clear temperature dependence can be seen here, again supporting the multi-band effect. The symbols represent the data measured by sweeping the magnetic field at fixed temperatures. The solid line shows the data measured at -9T and 9T by sweeping temperature. Both set of data coincide very well.](image2)
determine the Hall coefficient of $d$ is extremely curved, it is not possible to use the slope feature at all temperatures, prohibiting any single band of the Hall coefficient is shown in Fig. 2 (b). A clear temperature dependence the field dependence of carriers as the dominating one. It is remarkable that Pauli limit given by the zero temperature limit, which certainly exceeds the point of the insulating behavior as seen from the resistivity data. Taking the value at 2 K, and using a single band assumption, we get the charge carrier density of $4.5 \times 10^{19} / \text{cm}^3$. This indicates that the superconductor, as the cuprates and the iron pnictides, has a very low superfluid density.

In the study of the Hall effect of clean $MgB_2$ superconductors, our group has also observed a curved $\rho_{xy}$ vs. $H$ and a strong temperature dependence of $R_H$, this was explained very well by the multiband scattering effect. As explained in that paper, a natural consequence of the multiband effect is that one should see a strong magnetoresistance effect. It is well known that the magnetoresistance is a very powerful tool to investigate the electronic scattering process and the message of the Fermi surface. As mentioned above, in MgB$_2$, a large magnetoresistance (MR) was found which is closely related to the multiband property. For the present new superconductor, we also measured and found a moderate MR, as shown in Fig. 1(a) and (c). In Fig. 3 (a) we present the field dependence of the longitudinal resistivity. Clearly a 40% to 50% increase of resistivity can be observed at a magnetic field of 9 T. In Fig. 3(b) we present the MR ratio, i.e., $\Delta \rho / \rho_0$, where $\rho_{xx}$ is the resistivity and $\rho_0$ is the resistivity at zero field. One can see that the MR is about 52% at 10 K and 9 T. This MR ratio is significant and difficult to be understood with a single band picture of the Fermi liquid. Considering that the sample is a polycrystalline sample, the MR effect may be weakened by mixing the transport components with the magnetic field along different directions of the crystallographic axes. For a single band metal with a symmetric Fermi surface, the Kohler’s law is normally obeyed. Kohler’s law shows that the magnetoresistance $\Delta \rho_{xx} / \rho_0$ measured at different temperatures should be scalable with the variable $H / \rho_0$. For MgB$_2$, the Kohler’s law is not obeyed because of the multiband property. We also do the scaling based on the Kohler’s law for this sample, the result is shown in Fig. 3 (b). Clearly, the data measured at different temperatures do not overlap and the Kohler’s law is seriously violated for this material. This discrepancy indicates that in this new superconductor there is clear multiband effect, as expected by the theoretical calculations. However, the MR in this sample do show some specialty. For two-band or multiband materials with weak MR, the MR ratios could be well described by the expression $\Delta \rho / \rho_0 \propto H^2$ in the low field region. This is because the contribution of the higher order even terms of $\mu_0 H$ could be omitted at a low field (the odd terms are absent here according to the Boltzmann equation for electronic transport). But for the present material, the MR ratio exhibits a roughly linear feature in the low field region, deviating from the expectation. This effect is also found in NbSe$_2$ which has a complex Fermi surface structure. In this sense, the
anomalies mentioned above in the present new superconductor may also be induced by multiband effect together with complex Fermi surfaces.

Next we have a look at whether there is a sizable local magnetic moment. For a system with the magnetic fluctuation given by the local moments, the magnetization have two major origins: Pauli susceptibility and the ionic (orbital and the nuclei) contribution. Assuming the total magnetic susceptibility is given by

\[ \chi(T) = \chi(0)[1 - (T/T_E)^2] + C/(T + T_0) \]

The first term comes from the Pauli susceptibility corrected with a temperature dependence of the DOS at the Fermi energy. The \( T_E \) is a parameter proportional to the Fermi energy. The second term is related to the magnetism arising probably from the contributions of the local moments. In Fig. 4 we show the temperature dependence of the magnetic susceptibility measured at a field of 3 Tesla. One can see a plateau of the magnetic susceptibility above 100 K, which is mainly contributed by the conduction electrons (the Pauli susceptibility). In the low temperature region, one can clearly see a divergence of the susceptibility. By fitting the data to above equation, we get

\[ \chi(0) = 0.000736 \text{ emu/mol Oe}, \quad T_E = 1335 \text{ K}, \quad C = 0.0034 \text{ emu K/mol Oe} \text{ and } T_0 = 3.32 \text{ K}. \]

Once \( C \) is determined, we can get the magnetic moment given by each Bi atom. It turns out that \( \mu_{eff}/\mu_B = 0.096 \mu_B \). This indicates that the local moment of the Bi atom is very weak although with a finite value.

Finally we present a phase diagram based on our transport and magnetization measurement and give discussions on the possible mechanism of superconductivity. As shown in Fig. 5 the onset superconducting transition point giving rise to the upper critical field \( H_{c2} \) determined by 99% \( \rho_n \) is shown by the red filled circles. The bulk superconductivity is established in a very small area covered by the curve name \( H_{c2}(T) \) (blue down triangles). The large area between them indicates a strong superconducting phase fluctuation. The curve marked with \( H_{c2} \) (cross) marks the upper critical field determined using the usual crossing point of the normal state background and the extrapolated line of the steep resistive transition part. The curve \( H_c \) (kink) shows the point determined from the kink point of the resistive data shown in Fig. 1(d).
weak correlation effect in the Bi 6p electrons, some other novel mechanism, such as the valence fluctuation of the Bi$^{2+}$ and Bi$^{3+}$, may play an important role in this new superconductor.

In summary, resistivity, Hall effect and magnetization have been intensively investigated on the new superconductor $Bi_4O_4S_3$. A weak insulating behavior is induced in the normal state when a high magnetic field is applied. This can be induced either by an adjacent competing order, or the very shallow $p_x$ and $p_y$ band and small Fermi energy. Both the strong non-linear Hall effect and the magnetoresistance indicate the multiband feature. A kink appears on the temperature dependence of resistivity at all high magnetic fields when the bulk superconductivity is completely suppressed. This kink can be well traced back to the upper critical field $H_{c2}(T)$ in the low field region. We argue that the superconducting pairing, for some reason, could be very strong and occur first in the one dimensional chains, then the bulk superconductivity is established through the Josephson coupling between them.

We appreciate the useful discussions with Qianghua Wang and Jianxin Li. This work is supported by the NSF of China, the Ministry of Science and Technology of China (973 projects: 2011CBA00102), and Chinese Academy of Sciences.

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