Abnormal T-linear susceptibility and Phase diagram of 
\( \text{BaFe}_{2-x}\text{Co}_x\text{As}_2 \) single crystals

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Abstract

We study systematically transport, susceptibility and heat capacity for \( \text{BaFe}_{2-x}\text{Co}_x\text{As}_2 \) single crystals. In the underdoped region, spin density wave (SDW) transition is observed in both resistivity and susceptibility. The magnetic susceptibility shows unusual T-linear dependence above SDW transition up to 700 K. With Co doping, SDW ordering is gradually suppressed and superconductivity emerges with a dome-like shape. Electrical transport, specific heat and magnetic susceptibility indicate that SDW and superconductivity coexist in the sample \( \text{BaFe}_{2-x}\text{Co}_x\text{As}_2 \) around \( x = 0.17 \), being similar with \( \text{(Ba,K)Fe}_2\text{As}_2 \). When \( x>0.34 \), the superconductivity completely disappears. A crossover from non-Fermi-liquid state to Fermi-liquid state is observed with increasing Co doping. A detailed electronic phase diagram about evolution from SDW to superconducting state is given.

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I. INTRODUCTION

Recent discovery of iron-based arsenide high-Tc superconductor\cite{1, 2, 3, 4, 5} attracts much interesting. Up to now, the pnictide superconductors with two main kinds of crystallographic structure have been widely studied: ZrCuSiAs-type (1111) and ThCr$_2$Si$_2$-type (122). Similar to cuprates, such pnictide superconductors are also believed to have a quasi-2D conducting layer—Fe$_2$As$_2$ layer, which is separated by LnO (Ln = La, Sm etc.) or R (R = Ba, Sr etc.) charge reservoir. Electron and hole can be introduced to FeAs layer to realize superconductivity by replacing elements in charge reservoir\cite{1, 6, 7, 8, 9, 10, 11}. However, in contrast to high-Tc cuprates, doping by replacing Fe atom with Co or Ni atom in FeAs layer can also produce superconductivity in both 1111 and 122 structures\cite{12, 13, 14, 15, 16, 17, 18}. For example, in Co-doped BaFe$_2$As$_2$, the superconducting temperature reach up to 22 K, lower than 38 K in K-doped BaFe$_2$As$_2$\cite{5, 12}. It seems that superconductivity in FeAs layer is very robust, and the integrality of FeAs layer is not important for superconductivity, being in sharp contrast to the case of cuprates in which any doping in Cu site destroyed the superconductivity. It makes the origin of superconductivity in iron-arsenide very complicated. However, detailed study on Co-doping system is very limit\cite{12, 13, 14, 15, 16, 17, 18}. Systematic study on Co-doped system and phase diagram are urgent needs to elucidate the role of Co-doping and to understand the superconductivity. In this paper, systematic study on transport, magnetism and heat capacity of BaFe$_{2-x}$Co$_x$As$_2$ single crystals are reported. In the underdoped region, spin density wave (SDW) transition is observed in both transport and magnetism. Interestingly, the magnetic susceptibility shows unusual T-linear dependence above SDW transition up to 700 K. It indicates strong antiferromagnetic coupling above SDW ordering in this system. With Co doping, SDW transition is suppressed and superconducting state gradually emerges with a dome-like shape. A crossover from non-Fermi-liquid to Fermi-liquid behavior is evidenced by transport. The coexistence of SDW and superconductivity is observed around x=0.17. When x>0.34, the superconducting state completely disappears and T-linear susceptibility gradually changes to Curie-weiss law. A detailed electronic phase diagram about evolution from SDW to superconducting state is presented.
II. EXPERIMENT

Single crystals of $BaFe_{2-x}Co_xAs_2$ were grown by self-flux method. In order to avoid contamination from incorporation of other elements into the crystals, FeAs was chosen as the flux\cite{19}. FeAs and CoAs powder was mixed together, then roughly grounded. The Ba pieces were added into the mixture. All procedures above are achieved in glove box in which high pure argon atmosphere is filled. The total proportion of $Ba:(2-xFeAs+xCoAs)$ is 1:4. The details have been reported elsewhere\cite{19}. Single crystals were characterized by x-ray diffractions (XRD) using Cu $K_\alpha$ radiations. As shown in Fig. 1, only (00l) peaks is observed, indicating that the single crystals are perfect c-orientation. The parameter of the c-axes linearly decreases with increasing Co-doping, being consistent with the results previously reported\cite{20}. The actual chemical composition of the single crystals is determined by inductively coupled plasma (ICP) atomic emission spectroscopy (AES) (ICP-AES) technique and X-ray Energy Dispersive Spectrum (EDS). The electrical transport was measured using the ac four-probe method with an alternative current (ac) resistance bridge system (Linear Research, Inc.; LR-700P). Hall effect is measured by four-terminal ac technique. The magnetic susceptibility was measured by SQUID (Quantum Design). The in-plane magnetoresistivity was measured by Physical Properties Measurement System (PPMS, Quantum Design).

III. RESULTS AND DISCUSSIONS

Fig.2 shows the temperature dependence of in-plane and out-of-plane resistivity for $BaFe_{2-x}Co_xAs_2$ (0.08$\sim x$\sim 0.60). For $x < 0.18$, an upturn behavior in ab-plane resistivity is clearly observed. With Co doping, the upturn temperature decreases and superconductivity emerges at $x=0.17$. In $BaFe_2As_2$, this abnormal behavior in resistivity is ascribed to SDW transition/structural transition\cite{5}. Here, the upturn behavior is also believed to originate from SDW transition or structural transition. For out-of-plane resistivity, a similar behavior is also observed. It is very surprising that the SDW transition seems to coexist with superconductivity for the samples with $x = 0.17$ and $x = 0.18$. Similar results is also observed in K-doped $BaFe_2As_2$ system\cite{21}. This issue will be further discussed later. With further doping, the upturn behavior is completely suppressed and superconductivity can reach to the maximum 25 K at $x = 0.2$ sample, being consistent with the previous report\cite{12}. The
superconducting transition temperature decreases with further doping, and superconductivity disappears for the samples with $x>0.34$. As shown in Fig. 2(c), the anisotropic ratio monotonously decreases with Co doping. A weak temperature dependence for the anisotropy ($\rho_c/\rho_a$) is observed for all doping. It indicates that in-plane and out-of-plane transport shares the same scattering mechanism, and interplane correlation is enhanced with Co doping, being consistent with the fact that the parameter of c-axis decreases with doping Co. We also fit resistivity in the whole temperature range for the samples without SDW ordering by the formula: $R=A+BT^n$. The values of parameter $n$ are listed in Table I. The value of $n$ increases from 1.25 for underdoped sample with $x=0.18$ to 2.01 for overdoped sample with $x=0.38$. It is well known that the T-linear behavior is believed to arise from non-Fermi-liquid system as observed in cuprates, while $T^2$ behavior originates from Fermi-liquid system. These results indicate that this system seems to show a crossover from non-Fermi-liquid state to Fermi-liquid state.

Fig. 3 shows the field-cooling (FC) and zero-field-cooling (ZFC) magnetic susceptibility for the superconducting samples in the temperature range from 2 K to 30 K at a fixed magnetic field 5 Oe. All the samples show a sharp superconductivity transition. We have estimated the superconducting volume by ZFC susceptibility. For the samples with $x = 0.17, 0.25$ and $0.18$, the superconductivity volume fraction reaches to 100% at 2 K. For $x = 0.20$, the volume is reach to 80% at 2 K. It indicates a bulk superconductivity in these samples.

Fig. 4 shows the temperature dependent in-plane susceptibility for all samples in the whole temperature range under $H = 6.5$ T. As shown in Fig. 3(a), a T-linear behavior is observed for the samples with SDW ordering above SDW temperature. The value of room-temperature susceptibility decreases with Co doping. But the slope does not change with Co doping for the samples with $x < 0.16$. For $x = 0.17$, the slope begins to decrease, but T-linear behavior keeps. For $x = 0.2$, T-linear behavior is broken and an upturn behavior is observed in low temperature region. In order to investigate the T-linear behavior, we have expanded the temperature range up to 700 K. As shown in Fig.3(b), a well-defined T-linear is observed for $x = 0$ and 0.17 samples up to 700 K. Recently, Zhang et al. have given an explanation to understand the T-linear behavior in susceptibility[22]. These data definitely indicates a strong antiferromagnetic coupling above the SDW transition. Strong magnetic fluctuation is believed to be the key point. Here, a T-linear behavior up to 700 K indicates
that strong magnetic fluctuation exists in this system, and it remains in superconducting samples. As shown in Fig.3(c), for overdoped sample, the deviation from T-linear behavior becomes more obvious and a Curie-Weiss like behavior is observed for $x = 0.6$ samples. It indicates that superconductivity is somewhat related to strong antiferromagnetic correlation. Interestingly, both T-linear behavior and superconductivity disappear at the meantime.

Fig. 5 is temperature-dependent Hall coefficient for the crystals $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ ($x=0.08, 0.16, 0.20, 0.60$). For $x = 0.08$ and 0.16, the Hall coefficient shows a large slope at the temperature corresponding to the anomaly in resistivity, being similar to that observed in $\text{BaFe}_2\text{As}_2$. For $x = 0.2$ sample, strong temperature-dependent behavior is observed above the superconducting temperature. However, a weak temperature dependence is observed for $x = 0.6$ sample. It is well known that temperature-independent Hall coefficient is expected in Fermi liquid state. Strong temperature dependence in Hall coefficient is always ascribed to non-Fermi-liquid state, such as cuprates. The evolution of Hall coefficient with Co doping observed here indicates that the system evolves from non-Fermi-liquid state with Co-doping. This result is consistent with the transport result as shown in Fig.2.

Fig. 6 shows the in-plane magnetoresistivity for the crystals $\text{BaFe}_{2-x}\text{Co}_x\text{As}_2$ under a fixed magnetic field of 14 Tesla rotating H within ab plane. A two-fold symmetry is observed only below the SDW/structure transition temperature for all the samples with SDW ordering, and disappears above SDW ordering temperature as shown in Fig.6. Such two-fold symmetry disappears for the samples without SDW ordering. In $\text{BaFe}_2\text{As}_2$, a similar two-fold symmetry is also observed and it is ascribed to SDW ordering[19]. These results indicate that SDW transition in Co-doped $\text{BaFe}_2\text{As}_2$ has a similar magnetic symmetry to that of $\text{BaFe}_2\text{As}_2$. For the samples with $x=0.17$ and 0.18, two-fold symmetry also supports coexistence of superconductivity and SDW. In order to study the coexistence of superconductivity and SDW, heat capacity for $x = 0.17$ sample is studied. As shown in Fig.7, an apparent jump is observed around SDW temperature. At low temperatures, superconductivity also shows a peak in heat capacity although it is very weak. In order to see clearly, we have also measured the $x = 0.17$ sample under magnetic field of 14 Tesla. The data shown in down-inset in Fig. 7 is obtained by substracting the heat capacity of the sample measured under magnetic field of 14 Tesla. As shown in the inset, a clear jump can be seen around superconducting temperature determined by resistivity. These results clearly prove that the superconductivity and SDW ordering coexist in Co-doped $\text{BaFe}_2\text{As}_2$ system. For $x = 0.20,$
a clear jump is observed in heat capacity as shown Fig. 7(b) with $T_c = 25.3$ K. It indicates a bulk superconductivity in this sample, being consistent with magnetization data.

Finally, a detailed electronic phase diagram is given for the BaFe$_{2-x}$Co$_x$As$_2$ with $0 \leq x \leq 0.40$. The $T_s$ and $T_c$ was defined as the anomaly in resistivity and the superconductivity transition by resistivity and susceptibility, respectively. The cyan area refers to the SDW state and the yellow area represents SC state. As been the same as the $Ba_{1-x}K_xFe_2As_2$ system, there exists a region in which the SDW and superconductivity coexist (red area).

In BaFe$_{2-x}$Co$_x$As$_2$ system, the region is in the doping range of $0.15 \leq x \leq 0.20$. It is strong evidence that in iron-based superconducting system, the SDW and the superconductivity coexist. In addition, these results also indicate that a crossover form non-Fermi-liquid state to Fermi-liquid state happens with Co doping. For underdoped samples, strong antiferromagnetic fluctuation above SDW ordering and strong temperature-dependent Hall coefficient are evidence for non-Fermi-liquid state. The power law temperature dependence for the resistivity in underdoped samples indicates that the value of $n$ evolves from 1 to 2 with increasing Co doping. With further increasing Co doping, Curie-Weiss like behavior and almost temperature-independent Hall coefficient emerge. $T^2$ behavior is fitted well in the whole temperature range for the overdoped samples. All these results support that Fermi-liquid state emerges with Co doping. In other hand, T-linear behavior up to 700 K in susceptibility indicates a strong magnetic fluctuation above the SDW ordering. Such T-linear behavior can be also observed in the superconducting samples. It suggests that strong magnetic fluctuation could be related to the superconductivity. This could be very important for the superconducting mechanism.

IV. CONCLUSIONS

Systematic study on transport, susceptibility and heat capacity for BaFe$_{2-x}$Co$_x$As$_2$ single crystals is performed. A crossover from non-Fermi-liquid state to Fermi-liquid state with Co-doping is evidenced by transport and susceptibility. The magnetic susceptibility shows unusual T-linear dependence above SDW transition up to 700 K, indicating strong magnetic fluctuation in this system. Electrical transport, specific heat and magnetic susceptibility indicate that SDW and superconductivity coexist in the sample BaFe$_{2-x}$Co$_x$As$_2$ with $x = 0.17$, being similar with (Ba,K)Fe$_2$As$_2$. A detailed phase diagram with evolution from SDW
to superconducting state with Co doping is given.

**Note:** When we are preparing this manuscript, the competing work is reported by N. Ni et al., arXiv:0811.1767 and J. H. Chu et al., arXiv:0811.2463.

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TABLE I: The value of parameter $n$ fitted by power law $\rho = A + BT^n$.

| Co content $x$ | 0.18 | 0.20 | 0.25 | 0.27 | 0.32 | 0.34 | 0.38 |
|---------------|------|------|------|------|------|------|------|
| $n$           | 1.25 | 1.27 | 1.33 | 1.55 | 1.79 | 1.90 | 2.01 |
FIG. 1: (a): X-ray diffraction patterns for $BaFe_{2-x}Co_xAs_2$ single crystals; (b): Doping dependence of c-axis parameter.
FIG. 2: Temperature dependent resistivity for the $BaFe_{2-x}Co_xAs_2$ single crystals. (a): In-plane resistivity (0.08-red, 0.12-green, 0.17-blue, 0.18-cyan, 0.20-magenta, 0.25-yellow, 0.60-pink, respectively; (b): out-of-plane resistivity; (c): Temperature-dependent anisotropy; (d): power law fitting for $x=0.18$, 0.27 and 0.34. The red solid line is the fitting line.
FIG. 3: Temperature dependent susceptibility for BaFe$_{2-x}$Co$_x$As$_2$ ($x=0.17, 0.18, 0.20, 0.25$) with magnetic field 5 Oe.
FIG. 4: Temperature dependent in-plane susceptibility for BaFe$_{2-x}$Co$_x$As$_2$ single crystals under $H$ = 6.5T. (a): in the temperature range from 2 K to 300 K for $x \leq 0.2$; (b): in the temperature range from 2 K to 700 K for $x = 0$ and 0.17; (c): in the temperature range from 2 K to 300 K for $x = 0.20, 0.25$ and 0.60.
FIG. 5: Temperature dependent Hall coefficient for single crystals BaFe$_{2-x}$Co$_x$As$_2$ ($x=0.08$, 0.16, 0.20 and 0.60).
FIG. 6: Isothermal in-plane magnetoresistivity for $BaFe_{2-x}Co_xAs_2$ single crystals with rotating H within ab plane. The measuring magnetic field is 14 T.
FIG. 7: Temperature dependent specific heat for $BaFe_{2-x}Co_xAs_2$ single crystals with $x=0.17$ and 0.20. (a): $C_p/T$ vs $T^2$ for the crystal with $x = 0.17$. Up-inset: the jump of specific heat around SDW transition; Down-inset: the jump of specific heat around superconducting transition, $\Delta C_p/T$ is obtained by substracting the heat capacity of sample with low superconducting volume. (b): specific heat for $x=0.20$. 
FIG. 8: Phase diagram of BaFe$_{2-x}$Co$_x$As$_2$ within the range 0≤x≤0.40. Both $T_s$ and $T_c$ are determined by resistivity.