Phase diagram and physical properties of NaFe$_{1-x}$Cu$_x$As single crystals

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A series of high quality NaFe$_{1-x}$Cu$_x$As single crystals has been grown by a self-flux technique, which were systematically characterized via structural, transport, thermodynamic, and high pressure measurements. Both the structural and magnetic transitions are suppressed by Cu doping, and bulk superconductivity is induced by Cu doping. Superconducting transition temperature ($T_c$) is initially enhanced from 9.6 to 11.5 K by Cu doping, and then suppressed with further doping. A phase diagram similar to NaFe$_{1-x}$Co$_x$As is obtained except that insulating instead of metallic behavior is observed in extremely overdoped samples. $T_c$’s of underdoped, optimally doped, and overdoped samples are all notably enhanced by applying pressure. Although a universal maximum transition temperature ($T_{c\text{max}}$) of about 31 K under external pressure is observed in underdoped and optimally doped NaFe$_{1-x}$Co$_x$As, $T_{c\text{max}}$ of NaFe$_{1-x}$Cu$_x$As is monotonously suppressed by Cu doping, suggesting that impurity potential of Cu is stronger than Co in NaFeAs. The comparison between Cu and Co doping effect in NaFeAs indicates that Cu serves as an effective electron dopant with strong impurity potential, but part of the doped electrons are localized and do not fill the energy bands as predicted by the rigid-band model.

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I. INTRODUCTION

The discovery of iron-based superconductors gives another opportunity to study the physics of high-temperature superconductivity besides the cuprates. The parent compounds of iron-based superconductors are antiferromagnetic semimetals, and superconductivity can be induced by hole, electron doping or applying pressure. For example, superconductivity was induced in BaFe$_2$As$_2$ by the doping of Co, Ni, and Cu. In the case of Co and Ni doping, the doped electron numbers predicted by rigid band model are $x$ and $2x$, respectively. The study on phase diagram of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ and Ba(Fe$_{1-x}$Ni$_x$)$_2$As$_2$ by angle-resolved photoemission spectroscopy (ARPES) indicates that the doped electron number roughly follows the rigid-band model. Therefore, it is natural to expect that superconductivity could be induced by Cu doping and the doped electron number is $3x$. However, superconductivity was observed in a very narrow range of doping in Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ and no superconductivity was observed in Sr(Fe$_{1-x}$Cu$_x$)$_2$As$_2$.

Although the doping effect of Co and Ni is clear now, the role of Cu doping is still under debate. X-ray photoelectron spectroscopy (XPS) and x-ray absorption (XAS) measurements show that Cu 3$d$ states locate at the bottom of the valence band in a localized 3$d^{10}$ shell, so that the formal valence state of Cu is +1 and the substitution of Fe$^{2+}$ by Cu$^{1+}$ results in hole doping. The theoretical and experimental studies on SrCu$_2$As$_2$, the end member of Sr(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ series, indicate that it is an sp-band metal with hole-type carries dominate and Cu in the nonmagnetic 3$d^{10}$ electronic configuration corresponds to the valence state Cu$^{1+}$. which further supports the result of XPS and XAS. In addition, the doping effect of Cu is similar to that of Mn, which is also considered as hole doping and no superconductivity has been found. On the other hand, electron doping by Cu was proved by ARPES and further confirmed by hall measurement on Ba$_0.6$K$_0.4$(Fe$_{1-x}$Cu$_x$)$_2$As$_2$. Similar superconducting dome to that of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ was observed in the phase diagram of Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ ($x$ $\sim$ 0.022 and $x$ $\sim$ 0.047) indicating the similar doping effect between Co and Cu, and suggesting electron doping induced by Cu substitution. To reconcile this controversial situation, it is of great interest to further investigate the Cu doping effect in other family of iron-pnictide superconductors.

Besides BaFe$_2$As$_2$, high quality of NaFeAs single crystal is also available now, which turns out to be suitable for studying the Cu doping effect. NaFeAs is regarded as a filamentary superconductor, and the superconductivity cannot be detected by specific heat. By substituting Co or Ni on Fe sites, bulk superconductivity was obtained. The Ni doping doubles the amount of electron doping of Co which follows the rigid band model. Moreover, it has been reported that $T_c$ of analogous compound LiFe$_{1-x}$Cu$_x$As is suppressed linearly by Cu doping. Hence, we study the role of Cu doping in NaFe$_{1-x}$Cu$_x$As, and compare it with the effect of Cu doping in BaFe$_2$As$_2$ and LiFeAs. In this paper, we report the study on the physical properties and phase diagram of NaFe$_{1-x}$Cu$_x$As by measuring x-ray diffraction (XRD), resistivity, magnetic susceptibility, Hall coefficient, specific heat, and high pressure. A phase diagram

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similar to NaFe$_{1-x}$Co$_x$As is established. The comparison of the physical properties and phase diagrams between NaFe$_{1-x}$Cu$_x$As and NaFe$_{1-x}$Co$_x$As clearly indicates that Cu doping is electron doping and the electron concentration deviates from the expected 3x. The deviation can be explained that part of the doped electrons fill the impurity band which is located deep below the Fermi level ($E_F$) and do not fill the energy bands as predicted by the rigid-band model.\textsuperscript{14,15}

II. EXPERIMENTAL DETAILS

A series of NaFe$_{1-x}$Cu$_x$As single crystals was grown by adopting the NaAs flux method. Its growth procedure resembles to that of NaFe$_{1-x}$Co$_x$As, and the details can be found in our previous work.\textsuperscript{15} XRD was performed on a Smartlab-9 diffractometer (Rikagu) from 10° to 70°, with a scanning rate of 6° per minute. The actual chemical composition of the single crystal was determined by energy dispersive x-ray spectroscopy (EDX). The Cu content $x$ hereafter is the actual composition determined by EDX. The resistivity and specific heat measurements were carried out by using the PPMS-9T (Quantum Design), and resistivity down to 50 mK were measured in a dilution refrigerator on PPMS. The magnetic susceptibility was measured using a vibrating sample magnetometer (VSM) (Quantum Design). The Hall coefficient was measured on PPMS with the four-terminal ac technique by switching the polarity of the magnetic field $H//c$ to remove any magnetoresistive components due to the misalignment of the voltage contacts.\textsuperscript{12} The pressure was generated in a Teflon cup filled with Daphne Oil 7373, which was inserted into a Be-Cu pressure cell, and the pressure applied in the resistivity measurement was determined by shifting the superconducting transition temperature of pure Sn.

III. RESULTS

A. X-ray diffraction

Figure 1(a) shows the selected single-crystalline XRD patterns for the NaFe$_{1-x}$Cu$_x$As single crystals. Only (00l) reflections can be recognized, indicating that the crystals are well orientated along the $c$ axis. The lattice parameter $c$ is estimated from the (00l), and the evolution of all the single crystals’ lattice parameter $c$ with the doping level is shown in Fig. 1(b). The lattice parameter $c$ decreases with increasing doping concentration, which roughly obeys the Vegard’s law. Comparing with undoped NaFeAs, the amplitude of lattice parameter change is about 0.8% with Cu doping concentration up to 0.30, a little smaller than that of Co doped NaFeAs with the same doping level.\textsuperscript{14,15}

FIG. 1: (color online). (a) Selected XRD patterns for the NaFe$_{1-x}$Cu$_x$As single crystals. (b) Doping dependence of the $c$-axis parameter.

FIG. 2: (color online). (a)-(c) Temperature dependence of in-plane resistivity for NaFe$_{1-x}$Cu$_x$As single crystals. (d) Enlargement of the low temperature resistivity in panels (a) and (b). The criteria used to determine the onset and offset temperature for the superconducting transitions is also shown in (d).

B. Electrical resistivity

The temperature dependence of in-plane electrical resistivity for NaFe$_{1-x}$Cu$_x$As single crystals are shown in Fig. 2. To make the graphs easier to read, the data are grouped into three sets. The resistivity at room temperature is about 0.4-1.7 mΩ cm.\textsuperscript{15,18} The error bar of the absolute resistivity is relatively large comparing to the evolution of resistivity caused by the doping effect, which is mainly coming from the uncertainty of geometric factor. So we cannot observe a systematic evolution of the room temperature resistivity in the whole doping range. The superconducting transitions for most of the samples
are quite broad and the onset is very round, so we define \( T_{\text{offset}} \) as \( T_c \), as shown in Fig. 2(d). \( T_c \) stands for \( T_{\text{offset}} \) for convenience hereafter. The kinks associated with the structural/spin density wave (SDW) transition are clearly resolved in the low temperature resistivity of underdoped crystals. We use the same criteria to define the structural and SDW transition as described in Ref. 15.

The structural and SDW transitions are progressively suppressed with increasing Cu concentration, similar to NaFe\(_{1-x}\)Co\(_x\)As. \( T_c \) increases slightly with Cu doping in the underdoped region. The maximum \( T_c \) about 11.5 K is reached at \( x = 0.019 \), but the amplitude of \( T_c \) enhancement (2K) is much smaller than that in Co doped NaFeAs (10K). \( T_c \) decreases quickly with further increasing Cu doping, and no trace of superconducting transition is observed in crystals with doping concentration larger than 0.045. Metal-insulator transition is observed in the crystals with doping level higher than 0.033. Ultimately, insulating behavior in the whole temperature range is observed in the extremely overdoped crystals, which is quite different from the metallic behavior in extremely overdoped NaFe\(_{1-x}\)Co\(_x\)As.\(^{15}\) A weak semiconducting behavior is also observed in Ba(Fe\(_{1-x}\)Cu\(_x\))\(_2\)As\(_2\) and Sr(Fe\(_{1-x}\)Cu\(_x\))\(_2\)As\(_2\).\(^{5,2}\) In addition, when \( x \sim 4\% \) Fe was substituted by Cu, a metal-insulator transition was observed in Fe\(_{1.01-x}\)Cu\(_x\)Se.\(^{20,21}\) It is reported that the insulator phase of Fe\(_{1.01-x}\)Cu\(_x\)Se is an Anderson localized system arising from disorder rather than a conventional semiconductor.\(^{22}\) Whether the metal-insulator transition in NaFe\(_{1-x}\)Cu\(_x\)As and Fe\(_{1.01-x}\)Cu\(_x\)Se have common origination need further investigation.

C. Magnetic susceptibility

Figure 3 shows the zero-field-cooling (ZFC) magnetic susceptibility taken at 10 Oe with \( H \) perpendicular to the \( c \) axis for the superconducting NaFe\(_{1-x}\)Cu\(_x\)As single crystals. As reported previously, a tiny diamagnetic signal was observed below 9 K in undoped NaFeAs.\(^{15}\) With Cu doping, the superconducting shielding fraction rises rapidly. Bulk superconductivity with large shielding fraction is observed in the composition range of 0.006 ∼ 0.024, indicating that Cu doping is beneficial to the superconductivity of NaFeAs. \( T_c \) inferred from the diamagnetic signal is consistent with that determined by resistivity measurement. As shown in Fig. 3, \( x = 0.019 \) is the optimally doped composition with maximum \( T_c \) and largest shielding fraction. Both shielding fraction and \( T_c \) decrease with further Cu doping, and no diamagnetic signal above 2 K is detected in samples with the Cu doping level higher than 0.033.

Figure 4 (a) presents the normal state in-plane magnetic susceptibility \( \chi \) for NaFe\(_{1-x}\)Cu\(_x\)As under a magnetic field of 5 T. (b) Temperature dependence of the normalized magnetic susceptibility, which is shifted upward by 0.1 for clarity.

![Graph](image-url)
cooled (FC) susceptibility of NaFe$_{0.70}$Cu$_{0.30}$As is also presented. Rapid drops associated with superconducting transition can still be observed at low temperature for the superconducting samples. Kinks corresponding to the structural and SDW transitions are observed in the undoped and underdoped samples, which are suppressed with Cu doping and consistent with the observation of resistivity. It is worth noting that $\chi$ shows an almost linear temperature dependence in high temperature for concentration up to 0.16. The slope of the linear dependence of high-temperature susceptibility slightly decreases with Cu doping, similar to Co doping. The linear temperature dependence of high temperature susceptibility is a common feature in iron-based superconductors, which has been observed in NaFe$_{1-x}$Co$_2$As$^{15,16}$ Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ and LaFeAsO$_{1-x}$F$_x$. An explanation based on the $J_1$-$J_2$ model of localized spins ascribes this behavior to the spin fluctuations arising from the local SDW correlation.$^{25}$ It is also argued that the behavior can be explained based on the spin susceptibility of a 2D Fermi-liquid with nearly nested electron and hole pockets of the Fermi surface.$^{26}$ There is a Curie-Weiss like upturn in the low temperature magnetic susceptibility of overdoped NaFe$_{1-x}$Cu$_x$As, which has been reported in many Fe-based superconductors.$^{2,15,27,28}$ The susceptibility upturn is usually attributed to extrinsic origin, such as defects or impurities. A small separation between the ZFC and FC occurs at NaFe$_{0.70}$Cu$_{0.30}$As, which is considered as spin glass transition.$^{28}$ The sharp drop in the $x = 0$ and $x = 0.006$ single crystals is due to structural transition, and the temperature of the transition determined from resistivity, magnetic susceptibility, and Hall coefficient is consistent with each other. The negative Hall coefficient of all the single crystals indicate that the dominated carrier is electron. A systematic evolution is observed on the absolute value of Hall coefficient at 200 K. The value decreases with Cu doping up to optimally doped crystal with $x = 0.019$, and then increases with further Cu doping. Due to the multi-band effect and different mobility of electron and hole carries, the Hall behavior is complex. If we simply take the single band expression $n_H = 1/(eR_H)$ the behavior of Hall coefficient of NaFe$_{1-x}$Cu$_x$As indicates that the Cu doping is electron doping, similar to that of Co doping in NaFe$_{1-x}$Co$_x$As. As the Cu doping, Hall coefficients of Ba$_{0.6}$K$_{0.4}$(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ gradually change from positive values to negative values, clearly showing electron carriers are introduced. The result of Hall measurement on NaFe$_{1-x}$Cu$_x$As is similar to the result of Ba$_{0.6}$K$_{0.4}$(Fe$_{1-x}$Cu$_x$)$_2$As$_2$. As shown in Fig. 5(b), The Hall angle is plotted as $\cot \theta_H = \rho / \rho_{xy}$ vs $T^4$, where $\rho$ is in-plane resistivity and $\rho_{xy}$ is Hall resistivity. It has been reported that $\cot \theta_H$ shows power-law temperature dependence for all the single crystals of NaFe$_{1-x}$Co$_2$As: $T^4$ for the parent compound, approximately $T^3$ for the superconducting crystals and $T^2$ for the heavily overdoped non-superconducting sample.$^{15}$ But $T^2$-dependent $\cot \theta_H$ with $\beta \approx 4$ is observed in these NaFe$_{1-x}$Cu$_x$As single crystals. This value is different from NaFe$_{1-x}$Co$_2$As, Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ and hole doped cuprates, but similar to electron-doped cuprates.$^{22}$ Since the $T^4$-dependence in cuprate is interpreted by the multi-band effect with different contributions from various bands, the different power law dependence between NaFe$_{1-x}$Cu$_x$As and NaFe$_{1-x}$Co$_2$As indicates the different band evolution of NaFeAs by Cu/Co doping.

E. Specific heat

To verify the bulk thermodynamic nature of the superconducting transition, specific heat measurement were performed on optimally doped NaFe$_{0.981}$Cu$_{0.019}$As, as shown in Fig. 6. Remarkable jump in specific heat corresponding to superconducting transition is observed, while no anomaly can be observed on NaFeAs single crystal. The obvious jump in specific heat suggests that bulk superconductivity in NaFeAs is obtained by Cu doping.

The red line is the best fit of the normal state specific heat between 13 and 30 K by $C_p = \gamma_n T + \beta T^3 + \eta T^5$, where $\gamma_n T$ and $\beta T^3 + \eta T^5$ are electron and phonon contributions, respectively. It is found that $\gamma_n = 7.44$ mJ mol$^{-1}$ K$^{-2}$, $\beta = 0.238$ mJ mol$^{-1}$ K$^{-4}$, and $\eta = -5.00 \times 10^{-5}$ mJ mol$^{-1}$ K$^{-6}$. The estimated Debye temperature is 290 K, almost same to the corresponding value for NaFe$_{0.972}$Co$_{0.028}$As.$^{15}$ $\Delta C_p / T_c$ at

FIG. 5: (color online). (a) Temperature dependence of the Hall coefficient $R_H$ for selected NaFe$_{1-x}$Cu$_x$As single crystals. (b) The $\cot \theta_H$ of NaFe$_{1-x}$Cu$_x$As single crystals plotted in power-law temperature scale. The legends in (b) are same as (a).

D. Hall effect

Figure 5(a) shows the temperature dependence of Hall coefficients for selected single crystals of NaFe$_{1-x}$Cu$_x$As.
$T_c = 10.65$ K is estimated to 9.85 mJ mol$^{-1}$ K$^{-2}$ by isentropic construction sketched in Fig. 6. The value roughly follow the expanded BNC scaling, which is proposed by Bud’ko, Ni, and Canfield (BNC) and expanded by J. S. Kim et al. The BNC scaling is considered as a simple text of whether a material belongs to the iron-based superconductors. So the pairing symmetry of NaFe$_{0.981}$Cu$_{0.019}$As may be similar to Ba(Fe$_{0.925}$Co$_{0.075}$)$_2$As$_2$ and NaFe$_{0.972}$Co$_{0.028}$As. It has been reported that $\Delta C_p/\gamma_0T_c = 2.11$ in NaFe$_{0.972}$Co$_{0.028}$As. Based on the data obtained above, $\Delta C_p/\gamma_0T_c$ in NaFe$_{0.981}$Cu$_{0.019}$As is estimated to 1.32, a little smaller than 1.43 expected for weak-coupling BCS superconductor. The different value between optimally Cu and Co doped NaFeAs suggests that the coupling strength in Cu doped NaFeAs is weaker than Co doped. As a result, NaFe$_{0.981}$Cu$_{0.019}$As may be a two band s-wave superconductor with a weaker coupling strength.

F. Phase diagram

The $T - x$ phase diagram of NaFe$_{1-x}$Cu$_x$As is plotted in Fig. 7, where $T_s$, $T_{SDW}$, and $T_c$ stand for structural, SDW, and superconducting transition, respectively. The data in Fig. 7 is obtained from resistivity, which is consistent with magnetic susceptibility, Hall, and specific heat measurements. As the Cu doping, both structural and SDW transitions are progressively suppressed to low temperature, and $T_c$ is enhanced slightly from 9.6 K in NaFeAs to 11.5 K in optimally Cu doped NaFeAs. $T_c$ decreases with Cu concentration in overdoped region, and metal-insulator transition is observed in the normal state resistivity of overdoped superconducting samples. Extremely overdoped samples exhibit insulating behavior, which is different from the overdoped nonsuperconducting NaFe$_{1-x}$Co$_x$As, where metallic behavior is observed. A weak semiconductor behavior is also observed on overdoped Ba(Fe$_{1-x}$Cu$_x$)$_2$As$_2$ and Sr(Fe$_{1-x}$Cu$_x$)$_2$As$_2$. Although the magnitude of $T_c$ enhancement of NaFeAs is only 1.9 K by Cu doping, the negligible small shielding fraction is greatly enhanced to nearly 100%. The full shielding fraction indicates Cu doping is beneficial for the superconductivity of NaFeAs, contrast to the case of LiFe$_{1-x}$Cu$_x$As. But the maximum $T_c$ is obviously lower than 20 K in NaFe$_{1-x}$Co$_x$As under ambient pressure, the maximum $T_c$ may be suppressed by stronger impurity potential of Cu. Microscopic coexistence of SDW and superconductivity has been proved by scanning tunneling microscopy (STM) in underdoped NaFe$_{1-x}$Co$_x$As. As shown in Fig. 7, superconductivity also coexists with SDW in underdoped NaFe$_{1-x}$Cu$_x$As.

G. Pressure effects

Resistivity measurements under pressure were performed in underdoped sample with $x = 0.006$, optimally doped $x = 0.019$, and overdoped $x = 0.037$ samples. As shown in Fig. 8 (a), for underdoped single crystal with $x = 0.006$, the resistivity upturn associated with the structural or SDW transitions is suppressed to low temperature by pressure and eventually become indistinguishable. $T_c$ initially increased by applying pressure, and maximum $T_c = 26.2$ K is observed at 2.2 GPa, the $T_c$ decreases with further increasing pressure, the data is summarized in Fig. 8 (b). For optimally doped and overdoped samples, where structural and SDW transitions have been suppressed by Cu doping, $T_c$ are monotonously enhanced up to the maximum pressure in our measurement.

As shown in Figs. 8(d) and 8(f), the $T_c^{max} = 24.6$ and 12.9 K are obtained for $x = 0.019$ and $x = 0.037$,
If we only consider the impurity effect on the maximum NaFeAs, it is mainly the impurity effect that responds by other transition metal can induce carries as well as im-

37

T

1

p

K in Ba

T

tion. The large T

1

−0.7 K in NaFe

optimally doped and overdoped NaFe

−

maximum is 5.2, 4.9, and 5.1 K GPa

NaFe

FIG. 8: (color online). Left panels: in-plane resistivity of NaFe

1−x

Cu

x

As (x=0.006 (a), 0.019 (c) and 0.037 (e)) under various pressures, arrows indicate the direction of the increasing pressure. Right panels: the T(p) phase diagrams of the samples corresponding to the left panels.

respectively. The pressure coefficient between ambient pressure and the pressure at which Tc reaches its maximum is 5.2, 4.9, and 5.1 K GPa−1, comparable to the optimally doped and overdoped NaFe

1−x

Co

x

As plotted as functions of the Co/Cu substitution. x.

The maximum transition temperature (Tc,max) of NaFe

1−x

Co

x

As and NaFe

1−x

Cu

x

As obtained under pressure is plotted on Fig. 9. As shown in Fig. 9, the maximum Tc obtained by combining the effect of doping and pressure in NaFe

1−x

Cu

x

As decreases with Cu concentration, contrast to the pressure effect on NaFe

1−x

Co

x

As, where maximum Tc about 31 K is observed from un-
doped to optimally doped samples.

Substitution of Fe by other transition metal can induce carries as well as impurities. Because both Co and Cu can dope electron into NaFeAs, it is mainly the impurity effect that responds for the different Tc,max evolution as a function of doping. If we only consider the impurity effect on the maximum transition temperature of NaFeAs, Tc-suppression rate for Cu is ΔTc/Cu-1% = −4.3 K, slightly larger than −3.5 K in Ba0.6K0.4(Fe1−xCu)x2As2 but much larger than −0.7 K in NaFe

1−x

Co

x

As with similar doping concentration. The large Tc-suppression rate of NaFe

1−x

Cu

x

As suggests that the impurity potential of Cu is stronger

H. Anisotropy of the upper critical field

In Fig. 10, we present the temperature dependence of resistivity for NaFe

1−x

Cu

x

As (x=0.006, 0.019) under various magnetic fields. The transition temperature of superconductivity (the criteria is shown in Fig. 2(d)) is suppressed gradually and the transition is broadened with increasing magnetic field. The effect of magnetic field is much larger when the field is applied along the c axis of the single crystals instead of within the ab plane. For underdoped sample NaFe0.994Cu0.006As, the positive magnetoresistance appears well below the temperature which is defined as the SDW transition.

The similar phenomenon was observed in NaFeAs single crystal and confirmed by neutron scattering. Temperature dependent Hc2 curves for NaFe0.994Cu0.006As and NaFe0.981Cu0.019As is shown in Figs. 7(c) and 7(f), respectively. In order to determine the upper critical field in the low-temperature region, we adopt the Werthamer-Helfand-Hohenberg (WHH) formula Hc2(0) = 0.693[−(dHc2/dT)Tc]Tc for single band BCS superconductor. We obtain [−(dHc2/dT)]Tc = 4.23 T/K and [−(dHc2/dT)]Tc = 2.24 T/K at Tc = 10.40 K from Fig. 7(c) for NaFe0.994Cu0.006As, so the Hc2(0) can be estimated to be 30 and 16 T with the field parallel and perpendicular to the ab plane, respectively. In the same way, Hc2(0) = 49 T and Hc2(0) = 22 T are obtained for NaFe0.981Cu0.019As single crystal. As a result, the anisotropy parameter γH = Hc2(0)/Hc2(0) can be estimated to be 1.88 and 2.22 for NaFe0.994Cu0.006As and NaFe0.981Cu0.019As, respectively. The smaller anisotropy γH of underdoped samples than the overdoped samples has also observed on
from Co except carries doping effect. Overdoped samples, indicating Cu doping effect distinct of the metallic phase is observed in the extremely Co doped NaFeAs lies in that the insulating phase in- NaFe

Cu doping definitely introduces electron carries into the overall phase diagram of NaFe

larger than 1.7 - 1.86 in Ba

K

are close to 2.25 - 2.35 for NaFe

x

−

But recent ARPES result on Ba(Fe

−

Cu

2)

As

(TM = Co, Ni, and Cu) suggests that although electrons are indeed doped, part of them may be localized and do not fill the energy bands as predicted by the rigid-band model. Theory calculation found that the substitution with strong impurity potential induces an impurity band split-off below the original host band, which reduces the electron occupy from the host band, result in decrease of the electron occupation. ARPS and density functional theory (DFT) studies found that the impurity potential of the substituted atoms enhances from Co, Ni, to Cu. As a result, the number of electron doped by Cu is less than the value expected from the simple rigid-band model.

As also suggested by high pressure measurement, the impurity effect of Cu is stronger than Co. The dome of superconductivity is mainly controlled by the balance of carrier concentration and impurity scattering induced by the dopants. So the narrow or even absence of superconducting dome in the phase diagram of Cu doped BaFe

2

As

 arises from that enough carriers are doped and so many impurities are induced. Therefore, the expanded superconducting dome of Ba(Fe

x−

Cu

y)

As

 (x ∼ 0.022 and 0.047) than Ba(Fe

x−

Cu

y)

As

 can be understood that fewer carriers are needed when BaFe

2

As

 have been electron doped with Co. While in NaFeAs, whose structural/SDW transition temperature is much lower than BaFe

2

As

, fewer electrons are required to suppress SDW and induce superconductivity. Therefore, Cu doping can provide enough carriers to map out a phase diagram similar to NaFe

x−

Cu

y)

As

 and Ba(Fe

x−

Cu

y)

As

. Meanwhile, as the Cu concentration further increases, density of States (DOS) at E

F

 is gradually removed by the impurity band induced by Cu doping. As a result, metal-insulator transition is observed as a function of doping.

This scenario can also explain the contradiction between results of XPS/XAS and ARPES. Since Cu 3d states are located deeper below the E

F

 than Co, the extra 3 electrons for Cu almost totally locate around the substituted site. Hence, closed 3d shell is observed by XPS and XAS, although there is a little delocated electron introduced by Cu dopant. It is found that substitutions of Cu for Fe in (Ba, Sr)Fe

2

As

 at low level result in electron doping, while in SrCu

2

As

, the end member of Sr(Fe

x−

Cu

y)

As

, is an sp-band metal with hole-type carries dominate. The contradictory result has been interpreted that there is a crossover between electron and hole doping with increasing x, which is induced by tetragonal (T) to collapsed tetragonal (cT) phase transition as a function of doping. Thus, in the case of NaFe

x−

Cu

y)

As

, where no cT phase has been observed, it is natural to observe electron doping at low-

IV. DISCUSSION

Although the T

c

 of optimally doped NaFe

x−

Cu

y)

As

 is lower than that in NaFe

x−

Cu

y)

As

 and the superconducting dome is much narrower than that of NaFe

x−

Co

y)

As

, the overall phase diagram of NaFe

x−

Cu

y)

As

 is similar to those of NaFe

x−

Co

y)

As

 and Ba(Fe

x−

y)

Co

y)

As

 (x ∼ 0.022 and 0.047). This indicates that the similar doping effect of Cu and Co. A result, the Cu doping definitely introduces electron carries into NaFe

x−

Cu

y)

As

. The main difference between Cu and Co doped NaFeAs lies in that the insulating phase instead of the metallic phase is observed in the extremely overdoped samples, indicating Cu doping effect distinct from Co except carries doping effect.
level substitution of Cu for Fe.

V. SUMMARY AND CONCLUSIONS

In conclusion, we have performed structural, transport, thermodynamic, and high pressure measurements on NaFe$_{1-x}$Cu$_x$As single crystals. Enough carriers can be provided by Cu doping to map out a phase diagram similar to NaFe$_{1-x}$Co$_x$As. In underdoped region, both the structural and SDW transition are monotonically suppressed by Cu doping. $T_c$ and the superconducting shielding fraction are enhanced with the doping. Bulk superconductivity with $T_c = 11.5$ K is observed at optimally doped sample, and a metal-insulator transition is observed with further doping. Finally, insulating instead of metallic behavior in NaFe$_{1-x}$Co$_x$As is observed in extremely overdoped non-superconducting samples. $T_c$ is obviously enhanced by pressure, but the $T_{c,\text{max}}$ decreases with Cu concentration. The Hall measurements and comparison between Cu and Co doped NaFeAs phase diagrams indicate that Cu doping introduces electron into system, but the number of electron is far from 3$x$ as predicted by rigid-band model.

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