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# Pressure effects on the superconducting properties of single-crystalline Co doped NaFeAs

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**Abstract.** Resistivity and magnetic susceptibility measurements under external pressure were performed on $NaFe_{1-x}Co_xAs$ ($x = 0$, 0.01, 0.028, 0.075 and 0.109) single crystals. For both underdoped and optimally doped $NaFe_{1-x}Co_xAs$, the maximum $T_c$ reached as high as 31 K under certain pressures. Meanwhile the overdoped sample with $x = 0.075$ also exhibits a positive pressure effect on $T_c$, and an enhancement of $T_c$ by 13 K is achieved under a pressure of 2.3 GPa. All of these superconducting samples show large positive pressure coefficients on superconductivity, being distinct from those of $Ba(Fe_{1-x}Co_x)_2As_2$. However, the superconductivity cannot be induced by pressure in heavily overdoped non-superconducting $NaFe_{0.891}Co_{0.109}As$. These studies reveal that the electronic structure is very different between superconducting and heavily overdoped non-superconducting $NaFe_{1-x}Co_xAs$, consistent with the observation of angle-resolved photoemission spectroscopy.

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## Contents



## 1. Introduction

Since the discovery of superconductivity in F-doped LaOFeAs [1], extensive experimental and theoretical efforts have been made to study the iron-based superconductors. Most of the parent compounds of the iron-based superconductors undergo structural and spin density wave (SDW) transitions. With doping or high pressure, both the structural and SDW transitions are suppressed and superconductivity emerges. The so-called '111'-type iron–arsenide compounds with the PbFCl structure, including LiFeAs and NaFeAs [2, 3], have been regarded as a unique family which is superconducting without purposeful doping or application pressure. Although no long-range antiferromagnetic order has been observed in LiFeAs [4], NaFeAs is reported to undergo three successive phase transitions around 52, 41 and 23 K, which correspond to structural, magnetic and superconducting transitions, respectively [5]. Although the resistivity of NaFeAs drops to zero at about 10 K, its superconductivity is filamentary rather than a bulk phenomenon [6, 7]. With Co substitution on Fe sites, both magnetism and structural distortion are suppressed, and bulk superconductivity with zero resistivity up to 20 K can be achieved [8, 9]. Full shielding fraction and large specific heat jump can be observed in single-crystalline optimally doped $NaFe_{0.972}Co_{0.028}As$ samples [7].

Application of pressure has been proved as an effective way to enhance $T_c$ in many types of iron-based superconductors. It was revealed that the $T_c$ of F-doped LaOFeAs was enhanced up to 43 K with pressure soon after the discovery of superconductivity in this system [10]. In tetragonal FeSe, $T_c$ increases from 8.5 K at ambient pressure to about 37 K under $P = 8.9$ GPa, which has been the largest pressure effect reported in iron-based superconductors so far [11]. Pressure effects in electron-doped 122-system $Ba(Fe_{1-x}Co_x)_2As_2$ with different doping levels have been thoroughly studied. Applying pressure dramatically enhances $T_c$ in the underdoped regime, whereas the effect of pressure on $T_c$ is rather small in the optimally doped and overdoped regimes [12, 14]. For the '111'-type Fe-pnictides, it was reported that the transition temperature of LiFeAs is suppressed linearly with pressure [15], whereas the $T_c$ of a $Na_{1-x}FeAs$ polycrystal can be enhanced up to 31 K at about 3 GPa [16]. This difference was attributed to the different ionic radius between Li and Na. However in former high-pressure studies, the superconducting transition has been found to be rather broad due to the highly hygroscopic nature of the polycrystalline NaFeAs sample. In order to study the intrinsic properties of this system, it is of great interest to investigate the combined effect of doping and pressure on the superconducting properties of single-crystal samples. In this paper, we report the results of resistivity measurements under hydrostatic pressure for single-crystalline $NaFe_{1-x}Co_xAs$, tracking $T_c$ as a function of both pressure and doping level in different regions of the phase diagram. The initial slope of the pressure dependence of $T_c$, $(dT_c/dP)_P = 0$,

is positive in the whole superconducting doping regime of the phase diagram. The value of the pressure coefficient is comparably large among Fe-pnictides, even in the overdoped region. For the extremely overdoped non-superconducting sample, the pressure effect is negligible. High $T_c^{offset}$ (31 K), generally being consistent with the maximum $T_c$ under pressure in polycrystalline NaFeAs, can be obtained in both underdoped and optimally doped samples. The identical maximum $T_c$ under pressure in under and optimally doped regions indicates that a universal maximum transition temperature of about 31 K in electron-doped NaFeAs, which can be obtained by applying high pressure or combining the effect of pressure and doping.

## 2. Experimental details

High-quality $NaFe_{1-x}Co_xAs$ single crystals were grown by the conventional high temperature solution growth method using the NaAs self-flux technique. Details of the growth procedures were provided in our previous work [7]. Electrical resistivity was measured using the ac four-probe method. Pressure was generated using a Be–Cu pressure cell with a Teflon cup which was filled with Daphene Oil 7373. The pressure applied in the resistivity measurement was determined by shifting the superconducting transition temperature of pure Sn [18]. The magnetic susceptibility was measured under pressures up to 6.1 GPa in a diamond anvil cell (DAC) made of Be–Cu alloy. The sample was placed inside the hole (initial diameter 300 $\mu$m) of a gasket and the diamond culet size was 600 $\mu$m. The pressure transmitting medium was Daphene Oil 7373 and the pressure was measured at room temperature by ruby fluorescence spectroscopy. The background of the magnetic susceptibility was measured first, before placing the samples inside the hole. The resistivity measurements were performed using a Quantum Design physical properties measurement system (PPMS-9), and the magnetic susceptibility was measured using a superconducting quantum-interference device magnetometer (SQUID-MPMS-7T, *Quantum Design*).

## 3. Results and discussion

Figure 1(a) shows the temperature dependence of resistivity for NaFeAs under different pressures. Two anomalies in the resistivity curve are observed at 51 and 41 K under ambient pressure, which are consistent with previous reports [5]. These anomalies have been proved by neutron scattering experiments to arise from the structural and SDW transitions, respectively [6]. With increased pressure, the anomalies corresponding to the SDW transition are gradually suppressed to lower temperatures, whereas the structural transition quickly becomes undetectable. The suppression of the anomalies could also be observed in the derivative of resistivity shown in figure 1(c). We use the same criteria to infer the structural and SDW transitions from the resistivity as described in [19], which has been confirmed by specific heat and magnetic susceptibility measurements [7]. As shown in figure 1(b), the superconducting transition is rather broad, and the three transitions take place in a narrow temperature range, thus it is difficult to define the $T_c^{onset}$. Therefore we use the criterion $T_c^{offset}$ to describe the superconducting transition temperature in this paper, the definition of which is shown in figure 1(b). As the applied pressure increases, $T_c^{offset}$ firstly decreases slightly, and then increases quickly with pressures higher than 1 GPa. The highest $T_c^{offset}$ is 11.9 K at $P = 1.79$ GPa. The data of NaFeAs under pressure are summarized in figure 1(d). The phase diagram $T(P)$ is

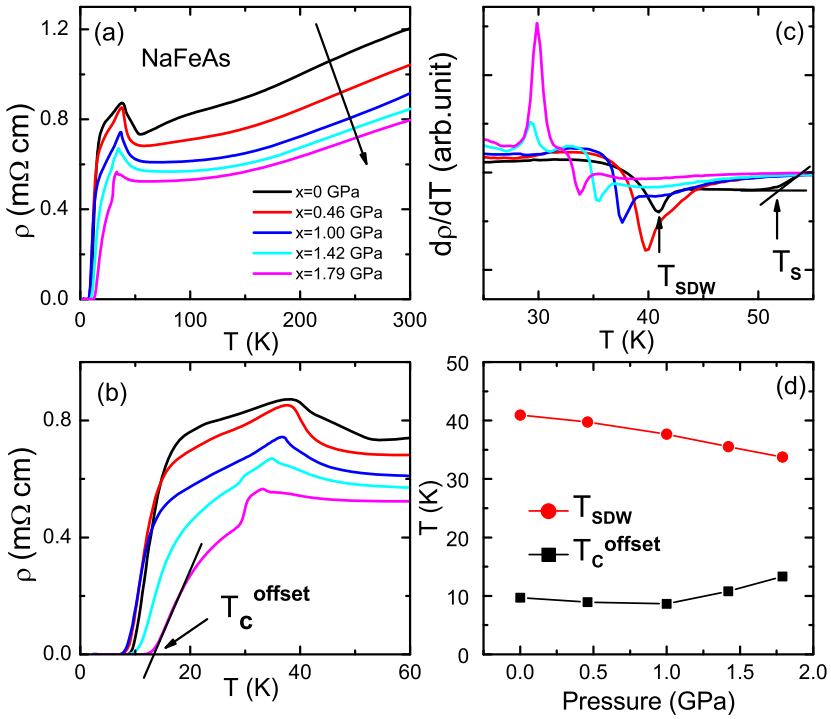


**Figure 1.** (a) Temperature dependence of in-plane resistivity for NaFeAs under different pressures. The arrow indicates the direction of the increasing pressure. (b) Expanded plot of the temperature dependence of resistivity under various pressures around $T_c$. (c) The derivative of the in-plane resistivity $d\rho/dT$ and the criteria by which we infer $T_s$ and $T_{SDW}$. (d) $T_c$ and $T_{SDW}$ as a function of pressure for the parent compound NaFeAs.

similar to that of underdoped $Ba(Fe_{1-x}Co_x)_2As_2$ [12], in which $T_{SDW}$ is suppressed gradually and superconductivity is enhanced by the applied pressure.

For the underdoped sample $NaFe_{0.99}Co_{0.01}As$ with $T_c^{offset} \sim 16$ K, the kinks in the resistivity curves associated with the structural and SDW transitions are distinct at ambient pressure. Once the external pressure is applied, the kinks quickly become obscure and then indistinguishable, similar to the case in the doped 122-system [12]. As shown in figure 2(a), the low-temperature resistive upturn corresponding to the structural and/or magnetic transitions was progressively suppressed, and ultimately vanished at $P = 2.05$ GPa, at which the highest superconducting transition temperature, about 30.7 K, occurs. The criteria used to determine the onset and offset temperatures of the superconducting transition are shown in figure 2(b). Since the onset temperature of superconductivity is ambiguous in $NaFe_{1-x}Co_xAs$, $T_c$ stands for $T_c^{offset}$ for convenience hereafter. As reported in underdoped $Ba(Fe_{1-x}Co_x)_2As_2$, the critical pressure at which the high temperature transition disappears coincides rather well with the pressure at which $T_c$ is the highest and the superconducting transition is the narrowest [14]. The pressure coefficient $dT_c/dP$ is 9.6 K GPa$^{-1}$ below 1.28 GPa, and the pressure coefficient between ambient and the pressure at which $T_c$ reaches its maximum is 7.06 K GPa$^{-1}$, even larger than that of FeSe (3.2 K GPa$^{-1}$) [11]. The pressure effect coefficient based on the $T_c^{onset}$ is about 4.7 K GPa$^{-1}$ which is still relatively large in iron pnictides. In the phase diagram shown in figure 2(c), it is

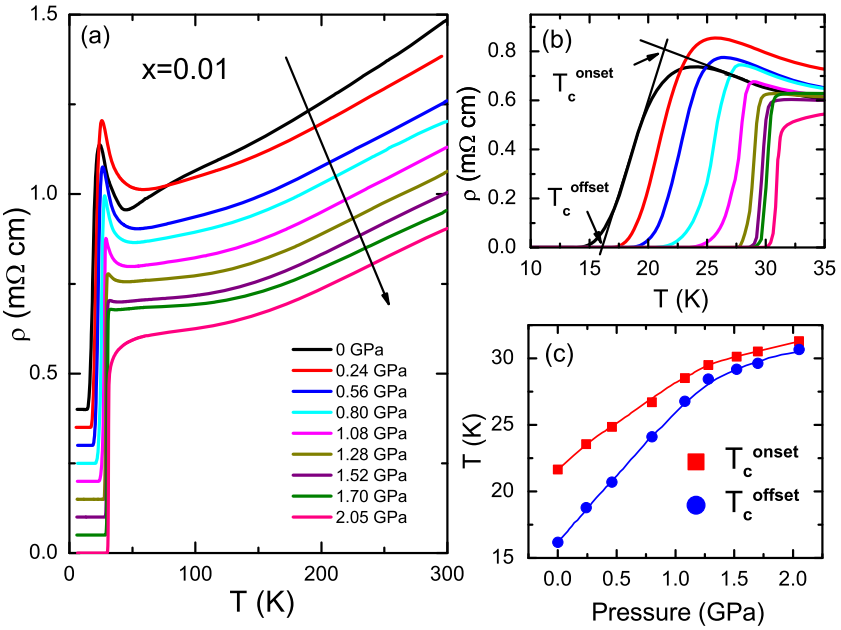


**Figure 2.** (a) Temperature dependence of the resistivity under different pressures up to 2.05 GPa for $NaFe_{0.99}Co_{0.01}As$. Each subsequent data set is shifted downward by 0.05 mΩ cm for clarity. (b) Enlargement of the low temperature resistivity and the criteria used to determine the onset and offset temperatures for the superconducting transitions. (c) $T_c$ as a function of pressure for the underdoped single crystal $NaFe_{0.99}Co_{0.01}As$.

obvious that the superconducting transition width becomes narrower with increasing pressure. The sharp superconducting transition observed at 2.05 GPa indicates that the pressure condition is homogeneous.

For the optimally doped sample $NaFe_{0.972}Co_{0.028}As$, the anomalies associated with the structural or SDW transition are suppressed completely by Co doping. As shown in figure 3(a), $T_c$ measured by in-plane resistivity increases monotonously from 20.4 to 31.0 K by increasing the applied pressure from 0 to 2.28 GPa. The pressure coefficient is 4.67 K $GPa^{-1}$, which is much larger than 1 K $GPa^{-1}$ in optimally doped $Ba(Fe_{1-x}Co_x)_2As_2$ [12] and comparable with 5 K $GPa^{-1}$ in optimally doped $LaFeAsO_{1-x}F_x$ [10]. In order to establish the complete superconducting dome in the phase diagram, we carried out the magnetic susceptibility measurement adopting the DAC technology. Pressure up to 6.1 GPa was applied to the $NaFe_{0.972}Co_{0.028}As$ single crystal. The values of $T_c^M$ under various pressures are determined from the beginning of the deviation from the extrapolated line of the normal state $M$–$T$ curve as shown in figure 3(c). Figure 3(d) exhibits the $T(P)$ phase diagram based on the resistivity and magnetic susceptibility measurements. The $T_c^M$ measured by DAC technology initially increases monotonously, and begins to decrease when the pressure is higher than 2.3 GPa. The transition temperatures obtained by resistivity and magnetic susceptibility are highly consistent with each other. The highest transition temperature obtained by our measurement is 31.0 K, with a considerably sharp transition width of 0.5 K. The $T_c = 31.0$ K presented here is comparable to the highest $T_c$ ever reported in the 111 system [13].

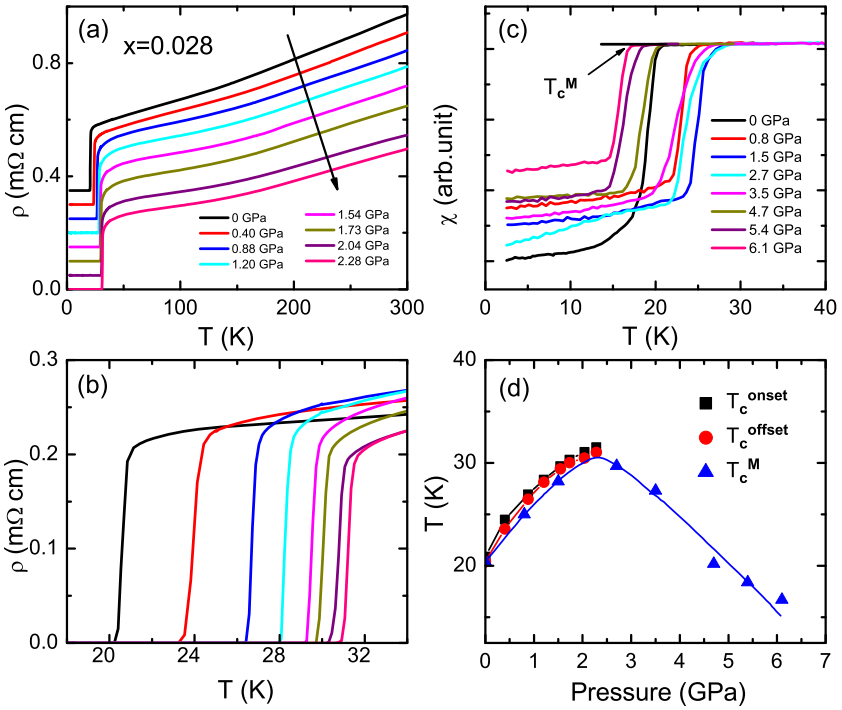


**Figure 3.** (a) Temperature dependence of in-plane resistivity for $NaFe_{0.972}Co_{0.028}As$ under various pressures. Successive data sets are offset vertically by 0.05 mΩ cm for clarity. (b) The data in panel (a) is plotted in the low temperature range for clarity. (c) The plot of magnetic susceptibility as a function of temperature in zero-field cooled measurements up to 6.1 GPa. (d) Evolution of $T_c$ determined by resistivity and susceptibility measurements with the applied pressure.

Figures 4(a) and (c) display the pressure dependence of the in-plane resistivity and magnetic susceptibility of the overdoped sample $NaFe_{0.925}Co_{0.075}As$, respectively. The superconducting transition temperature of this overdoped sample is 11.5 K at ambient pressure. Similar to the case in optimally doped $NaFe_{0.972}Co_{0.028}As$, the $T_c$ increases monotonously up to 24.5 K by increasing the applied pressure to 2.32 GPa. A domelike shape of $T_c(P)$ was revealed by magnetic susceptibility measurement, from which we can deduce that the highest superconducting transition temperature in $NaFe_{0.925}Co_{0.075}As$ is about 24.5 K with the uncertainty less than 1 K. A large enhancement of $T_c$ of 13 K, which is comparable to those in underdoped and optimally doped samples, still exists in this overdoped composition. The pressure coefficient of $NaFe_{0.925}Co_{0.075}As$ is 5.57 K $GPa^{-1}$, even higher than that of the optimally doped sample. The large pressure coefficient of overdoped $NaFe_{0.925}Co_{0.075}As$ is obviously different from those in other iron-pnictide superconductors, which are rather small or could even change their sign from positive to negative in the overdoped regime in the phase diagram [12, 20–22].

When external pressure was applied to the extremely overdoped sample $NaFe_{0.891}Co_{0.109}As$, which shows no superconductivity down to 2 K at ambient pressure, we cannot observe the pressure-induced superconductivity with applied pressure up to 2.32 GPa

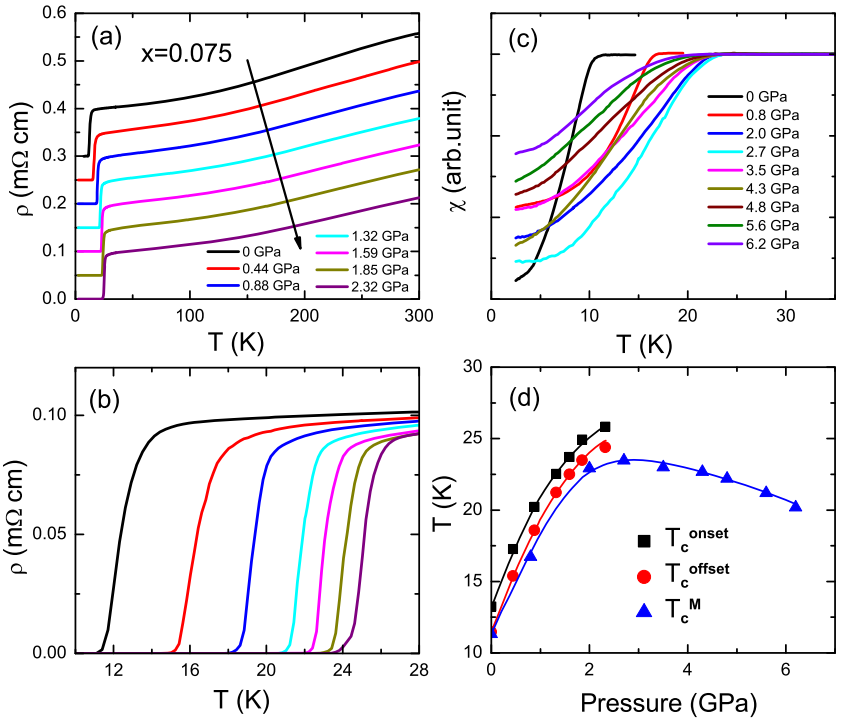


**Figure 4.** (a) Temperature dependence of in-plane resistivity for $NaFe_{0.925}Co_{0.075}As$ under various pressures; successive data sets are offset vertically by 0.05 mΩ cm for clarity. (b) The same data shown in (a) around the superconducting transition. (c) Temperature dependence of magnetic susceptibility under different pressures for $NaFe_{0.925}Co_{0.075}As$. (d) The $T_c$ obtained from resistivity and susceptibility measurements as a function of pressure.

(figure 5). Besides, both the magnitude and the behavior of the resistivity do not change much with the applied pressure.

The effect of applied pressure on the superconducting transition temperature of $NaFe_{1-x}Co_xAs$ is illustrated in figure 6(a), where the maximum $T_c$ under pressure and $T_c$ at ambient pressure are plotted as a function of doping level $x$. Because the maximum transition temperature has not been obtained in undoped NaFeAs, we use the maximum value reported by Zhang *et al* [16] for this composition. A large positive pressure coefficient $dT_c/dP$ is observed in all the superconducting compositions, even in the overdoped regime. The maximum transition temperatures in NaFeAs, $NaFe_{0.99}Co_{0.01}As$ and $NaFe_{0.972}Co_{0.028}As$ are all around 31 K. The $T(P)$ phase diagram of the $NaFe_{1-x}Co_xAs$ system with respect to various $x$ is shown in figure 6(b). It is obvious that the maximum transition temperature in the undoped, underdoped and optimally doped samples is strikingly similar. These results indicate that there is a universal maximum transition temperature in $NaFe_{1-x}Co_xAs$ of about 31 K, which can be achieved by applying a critical pressure of $P = 2$–3 GPa. Although the Daphne 7373 freezes at room temperature at 2.2 GPa, we do not think it is related to the maximum in $T_c$, since $Na_{1-x}FeAs$ also exhibited a maximum $T_c$ near the same pressure (2–3 GPa) by using a solid pressure medium MgO [16]. We compared the resistivity curves for the samples with different doping $x$ but similar $T_c$ around 30 K induced by pressure as shown in figure 6(c). The $T_c$ of NaFeAs

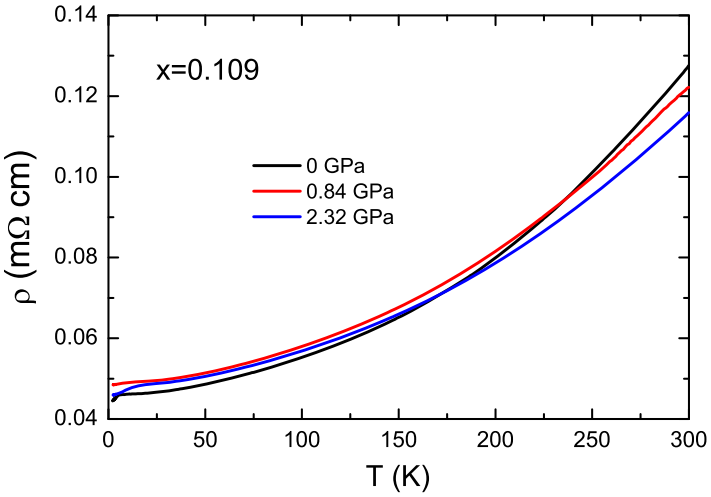


**Figure 5.** Temperature dependence of in-plane resistivity for heavily overdoped non-superconducting crystal $NaFe_{0.891}Co_{0.109}As$ under various pressures.

can also be enhanced to 30 K through interaction with environment [17] and we compared the resistivity curve with our samples. We found the resistivities are almost the same for the two $NaFe_{1-x}Co_xAs$ samples with $T_c$ around 30 K under pressure. However, the resistivity behavior of NaFeAs which interacts with the environment is quite different, though the $T_c$ is almost the same.

For the undoped and underdoped samples, applied external pressure suppresses the SDW transition, and enhances superconductivity simultaneously. This behavior is similar to the pressure effect in $LaFeAsO_{1-x}F_x$ [10] and 122-systems [12, 21, 23, 24]. Although the $T_c$ and normal state resistivity behavior evolve systematically with Co doping, the maximum transition temperature enhancement and corresponding critical pressure is nearly the same in all the superconducting samples. These properties are distinct from the case in most of the iron-based superconductors where the pressure effect is different in various regions of the electronic phase diagram. An identical maximum $T_c$ of 31 K for underdoping as well as pressure has also been reported in $BaFe_2(As_{1-x}P_x)_2$ [25]. In the P-doped Ba-122 system, phosphorous substitution could be regarded as chemical pressure, which changes Fe–Pn distance and causes similar effects on superconductivity as the physical pressure. Although the Co-substitution in NaFeAs is referred to as electron doping, being different from the replacement of As by P which is referred to as an isovalent substitution, it is likely that the pressure-induced enhancement of $T_c$ in $NaFe_{1-x}Co_xAs$ is also associated with the optimization of the structural parameters of FeAs layers, including the As–Fe–As bond angle and anion height [26]. One possible reason for the lower maximum transition temperature obtained in overdoped $NaFe_{0.925}Co_{0.075}As$ single crystal is that the superconductivity is disturbed by the disorder or additional scattering induced by excess cobalt doping. This phenomenon is different from the case of overdoped $LaFeAsO_{1-x}F_x$, in which the conducting layer is not affected by F doping and the highest transition temperatures acquired in optimally and overdoped samples are almost the same [10].

The overdoped superconducting sample $NaFe_{0.925}Co_{0.075}As$ still has a considerable positive pressure coefficient, which is rare in Fe-pnictide superconductors. However, when the pressure is applied on the extremely overdoped non-superconducting sample, no superconductivity

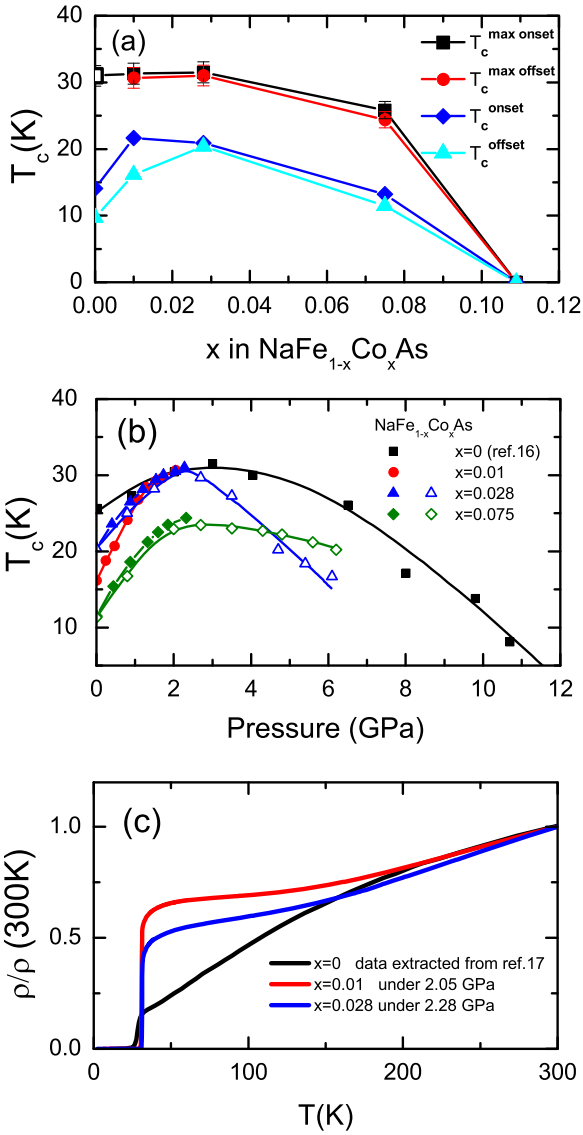


**Figure 6.** (a) Comparison of $T_c$ at ambient pressure and the maximum $T_c$ achieved under applied pressure at various Co concentrations. The open square represents the $T_c^{onset}$ reported by Zhang *et al* [16]. (b) $T(P)$ phase diagram of $NaFe_{1-x}Co_xAs$ with different doping levels. Open and filled symbols represent data obtained from susceptibility and resistivity measurements, respectively. (c) The normalized resistivity curves for our samples with $T_c$ around 30 K under pressure and environmental-interacted NaFeAs extracted from [17].

induced by pressure can be observed. It has also been reported that linear temperature dependent susceptibility can be observed in high temperatures for all the superconducting samples, and the breakdown of the linear temperature dependent susceptibility in the overdoped region coincides with the disappearance of superconductivity [7]. These phenomena indicate that there is an abrupt change in the electronic structure between the superconducting compositions and the heavily overdoped non-superconducting phase. This conclusion is supported by the

experimental results of scanning tunneling microscopy (STM) investigations [27] and the angle-resolved photoemission spectroscopy (ARPES) studies [28]. The STM study revealed that the high energy $dI/dV$ spectra of superconducting $NaFe_{1-x}Co_xAs$ remain nearly the same, whereas the high energy spectrum suddenly starts to shift to the lower energy substantially for the sample with $x = 0.109$. The direct measurements of the electronic structure of $NaFe_{1-x}Co_xAs$ by ARPES revealed that all the superconducting $NaFe_{1-x}Co_xAs$ compounds have similar band structures and small relative Fermi level shifts. However, the $x = 0.109$ compound in the heavily overdoped regime shows a large Fermi level shift (about 100 meV) relative to the optimally doped compounds, and its band structure is significantly changed as the hole-like bands around the zone center disappear and an electron pocket appears, which means the consequent Fermi surface consists of electron pockets only in this sample. The drastic change in electronic structure for the heavily overdoped non-superconducting samples could explain the observed properties of the pressure effect.

## 4. Summary

In conclusion, we have performed resistivity and magnetic susceptibility measurements on $NaFe_{1-x}Co_xAs$ ($x = 0$, 0.01, 0.028, 0.075 and 0.109) single crystals under various pressures. In the undoped and underdoped compounds, the SDW transition is gradually suppressed while superconductivity is enhanced by applied external pressure. A universal maximum transition temperature of about 31 K under external pressure is observed in underdoped and optimally doped $NaFe_{1-x}Co_xAs$. The superconducting transition temperature of $NaFe_{1-x}Co_xAs$ is strongly enhanced in the whole superconducting regime of the phase diagram, and the pressure effect is considerably large compared to other iron pnictides. The large positive pressure coefficient in the optimally and overdoped region is different from that in $Ba(Fe_{1-x}Co_x)_2As_2$, and disappears simultaneously with the superconductivity in the phase diagram. These results could be caused by the similarity of electron structures within the superconducting dome, and a drastic change of the electron structures between the superconducting overdoped regime and the non-superconducting heavily overdoped regime, which coincides with the conclusions of STM and ARPES measurements.

## Acknowledgments

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