Peculiar phase diagram with isolated superconducting regions in ThFeAsN$_{1-x}$O$_x$

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Abstract
ThFeAsN$_{1-x}$O$_x$ (0 $\leq$ x $\leq$ 0.6) system with heavy electron doping has been studied by the
measurements of x-ray diffraction, electrical resistivity, magnetic susceptibility and specific
heat. The non-doped compound exhibits superconductivity at $T_c^{\text{onset}}$ = 30 K, which is possibly
due to an internal uniaxial chemical pressure that is manifested by the extremely small value
of As height with respect to the Fe plane. With the oxygen substitution, the $T_c$ value decreases
rapidly to below 2 K for 0.1 $\leq$ x $\leq$ 0.2, and surprisingly, superconductivity re-appears in the
range of 0.25 $\leq$ x $\leq$ 0.5 with a maximum $T_c^{\text{onset}}$ of 17.5 K at x = 0.3. For the normal-state
resistivity, while the samples in intermediate non-superconducting interval exhibit Fermi
liquid behavior, those in other regions show a non-Fermi-liquid behavior. The specific heat
jump for the superconducting sample of x = 0.4 is $\Delta C/\gamma T_c$ = 0.89, which is discussed
in terms of anisotropic superconducting gap. The peculiar phase diagram in ThFeAsN$_{1-x}$O$_x$

presents additional ingredients for understanding the superconducting mechanism in iron-
based superconductors.

Keywords: iron-based superconductors, phase diagram, chemical pressure

(Some figures may appear in colour only in the online journal)

1. Introduction

Discovered in 2008, superconductivity in a group of iron-based compounds has become one of the hottest topics in
condensed matter physics [1]. It was not long before scientists realized that doping with either electrons or holes may
induce superconductivity [1–3]. On this basis, the substitution phase diagrams about tens of individual dopants have
been established [4, 5]. In the prototype ‘1111’ system, the carrier doping level is mostly limited by the heterovalent sub-
stitution solubility, such that the overdoped regime cannot be reached [1, 6–8]. However, recent experimental works show
that the high-pressure synthesis technique can remarkably

increase the substitution solubility and, the electron doping level is pushed to 0.53 electrons/Fe-atom in LaFeAsO$_{1-x}$H$_x$
[9], and 0.75 electrons/Fe-atom in LaFeAsO$_{1-x}$F$_x$ [10]. A sec-
ondary superconducting dome with a higher maximum super-
conducting transition temperature ($T_c$) was observed in both
systems. These findings shed light on the superconducting mechanisms in iron-based superconductors [11].

In the previous work of our group, we reported the dis-
covery of a new ‘1111’ type iron-based compound ThFeAsN,
which superconducts below 30 K without external chemical
doping [12]. Though theoretical calculations suggest a striped
anti-ferromagnetic (AFM) ground state [13, 14], the studies on $^{57}$Fe Mössbauer spectroscopy, neutron powder diffraction,
and μSR/NMR experiments found no magnetic order of the Fe moments down to 2.0 K [15–18]. To understand the absence of AFM ordering and the emergence of superconductivity in non-doped ThFeAsN, it is vitally necessary to look at the evolution of the superconducting phase with (preferably heavy) electron doping. In this work, we study the oxygen substitution effect in ThFeAsN\(_{1-x}\)O\(_x\). Unexpectedly, we find that the nominal oxygen solubility reaches as high as \(x = 0.6\) under ambient pressure. The measurement of electronic resistivity, as well as magnetic susceptibility, indicates that the 30 K superconductivity in ThFeAsN is rapidly suppressed to below 2 K at \(x = 0.1\). Following the quenching of superconductivity, as well as magnetic susceptibility, indicates that the 30 K superconductivity in ThFeAsN is rapidly suppressed to 2 K at \(x = 0.1\). Following the quenching of superconductivity in ThFeAsN, it is vitally necessary to look at the evolution of the superconducting phase with (preferably heavy) electron doping. In this work, we study the oxygen substitution effect in ThFeAsN\(_{1-x}\)O\(_x\). Unexpectedly, we find that the nominal oxygen solubility reaches as high as \(x = 0.6\) under ambient pressure. The measurement of electronic resistivity, as well as magnetic susceptibility, indicates that the 30 K superconductivity in ThFeAsN is rapidly suppressed to below 2 K at \(x = 0.1\). Following the quenching of superconductivity within \(0.1 < x < 0.2\), superconductivity re-appears in the region \(0.25 < x < 0.5\), with a maximum \(T_c\) of 17.5 K. While the two-superconductivity-region phenomenon somewhat resembles the aforementioned LaFeAsO\(_{1-x}\)H\(_x\) and LaFeAsO\(_{1-x}\)F\(_x\) systems [9, 10], the present system is remarkable for the isolated superconducting windows and, for the lower maximum \(T_c\) in the second superconducting region.

2. Experimental details

Polycrystalline samples of ThFeAsN\(_{1-x}\)O\(_x\) (\(0 \leq x \leq 0.6\)) were synthesized using powder of Th\(_3\)N\(_4\), ThO\(_2\), Th and FeAs as starting materials. The preparation of the precursors and the sintering condition of the final products are similar to those of the ThFeAsN parent compound [12]. Powder x-ray diffraction (XRD) was carried out at room temperature on a PANanalytical x-ray diffractometer (Model EMPYREAN) with a monochromatic Cu Kα1 radiation. Crystal structure data were obtained by Rietveld refinement using the step-scan XRD data with 20° < 2θ < 120° for all the samples. During the structural refinements, we fix the oxygen content at the nominal value as it is not reliable to detect light elements using the XRD technique. The typical R-factors of the refinements are: \(R_p \approx 3\%\), \(R_m \approx 4\%\), and \(R_w \approx 5\%\), indicating the good reliability of the refinement [19]. Magnetic measurements were performed on a Quantum Design Magnetic Property Measurement System (MPMS-XL5). The temperature-dependent resistivity was measured using a standard four-terminal method on a Cryogenic Mini-CFM measurement system equipped with a Keithley 2400 digital sourcemeter and a Keithley 2182 nanovoltmeter.

3. Results and discussion

3.1. Crystal structure

Figure 1(a) shows the XRD pattern of the synthesized ThFeAsN\(_{0.7}\)O\(_{0.3}\) sample. The XRD peaks can be well indexed with a tetragonal unit cell of \(a = 3.9955(4)\) Å and \(c = 8.4683(7)\) Å (detailed information is shown in Table 1). No obvious impurity peak is found for the samples with \(x < 0.5\), suggesting that oxygen is successfully incorporated into the lattice (the systematic changes in lattice parameters shown in figure 1(d) confirm this point). For the samples of \(x = 0.6\) and 0.7, the impurity peaks begin to show up in the XRD pattern, indicating that the oxygen solubility limit is near \(x = 0.6\). Note that, such a high solubility can be achieved only by means of high-pressure synthesis in \(LnFeAsO_{1-x}H_x\) (\(Ln\) stands for lanthanides) and LaFeAsO\(_{1-x}\)F\(_x\) systems [9, 10]. Thus the ThFeAsN\(_{1-x}\)O\(_x\) system is quite unique for the capacity of heavy electron doping under ambient pressure.

Figures 1(b) and (c) show the doping-dependent shift of the two separate reflections, (2 0 0) and (0 0 4), which are directly related to the \(a\) and \(c\) axes, respectively. While the (2 0 0) reflection drifts towards higher angles upon oxygen doping, the (0 0 4) peak shifts to higher angles for \(x < 0.2\), and then it moves to the opposite direction for \(x > 0.25\). Figure 1(d) plots the lattice parameters, obtained from the Rietveld analyses, as functions of nominal oxygen content. Indeed, the \(a\)-axis steadily shrinks with the oxygen substitution. In contrast, the \(c\)-axis first goes down rapidly to 8.4551(7) Å at \(x = 0.25\), and then gradually increases to 8.5006(2) Å at \(x = 0.6\). To our knowledge, such a non-monotonic change in \(c\)-axis has not been seen in other iron-based superconductors where the electron doping always leads to the monotonic decrease in \(c\) [1, 6, 8, 9, 20].

We plot selected crystallographic parameters versus nominal oxygen content in figure 2. Generally speaking, the substitution of \(O^2\) for \(N^3\) introduces extra positive (negative) charges in \([Th–N/O]\) ([Fe–As]) block layers, that enhances the interlayer Coulomb attraction. As shown in figure 2(a), the spacing between Th and As planar layers (\(H_{Th–As}\)) decreases monotonically from 1.781 Å to 1.591 Å. In contrast, the distance between As and Fe planar layers (\(H_{Fe–As}\)) and the one...
between Th and N/O planar layers ($H_{\text{Th-N/O}}$) abnormally increase with oxygen doping. We note that all the three data lines in figure 2(a) show a kink at $x \sim 0.25$, coincident with the minimum of c-axis in figure 1(d). For $x \geq 0.25$, all the interplanar spacings tend to change more mildly in response to the oxygen substitution. Among them, the change in $H_{\text{Fe-As}}$ is of particular significance because it correlates directly with the orbital-dependent band structures, which could control the emergence of superconductivity [11].

In the following statement, we cite the nominal oxygen content rather than measuring the oxygen content directly. The reasons as follows: (1) The $a$-axis basically decreases upon oxygen doping linearly, which is in line with expectation as O$^2-$ is smaller than N$^3-$ [21]. (2) No obvious impurity peak can be found in the XRD profile for $x \leq 0.5$. (3) The validity of using nominal oxygen content is supported by the similar experiments in NdFeAsO$_{1-x}$F$_x$, which indicated that the measured fluorine content is basically identical to the nominal content within the solubility limit [22]. (4) Our XPS and EDX experiments showed that, when exposed to the atmosphere, the sample will adsorb oxygen which strongly interferes with the analysis of elemental ratios [12]. As it is nearly impossible to isolate the sample from the air during the transfer, it is very difficult for us to accurately measure the oxygen content directly.

### 3.2. Characterization of physical properties

Figures 3(a) and (b) show the temperature dependence of magnetic susceptibility measured at 10 Oe near superconducting $T_c$ for ThFeAsN$_{1-x}$O$_x$ samples. The $\chi - T$ curves of different samples are shifted successively along the vertical axis for comparison. The shift steps are 0.5 and 0.02 for zero-field-cooling (ZFC) and field-cooling (FC), respectively.

Table 1. Crystallographic data of ThFeAsN$_{1-x}$O$_x$ ($x = 0.3$ and $0.6$) at room temperature. The space group is $P4/nmm$. The atomic coordinates are as follows: Th (0.25, 0.25, $z$); Fe (0.75, 0.25, 0.5); As (0.25, 0.25, 0); N/O (0.75, 0.25, 0). $H_{\text{Th-As}}$, $H_{\text{Th-N/O}}$ and $H_{\text{Fe-As}}$ represent the distance along the c-axis between Th and N/O, Th and As, Fe and As, respectively.

| Compounds             | ThFeAsN$_{1-x}$O$_{0.3}$ | ThFeAsN$_{1-x}$O$_{0.6}$ |
|-----------------------|--------------------------|--------------------------|
| $a$ (Å)               | 3.9955(4)                | 3.97125(9)               |
| $c$ (Å)               | 8.4683(7)                | 8.5006(2)                |
| $R_{\text{wp}}$ (%)   | 4.37                     | 5.21                     |
| $R_{\text{exp}}$ (%)  | 3.73                     | 3.55                     |
| $V$ (Å$^3$)           | 135.19(2)                | 134.06(5)                |
| $z$ of Th             | 0.14750(7)               | 0.1523(1)                |
| $z$ of As             | 0.6606(2)                | 0.6626(2)                |
| $H_{\text{Th-N/O}}$ (Å) | 1.2491(7)                | 1.2794(9)                |
| $H_{\text{Th-As}}$ (Å) | 1.626(2)                 | 1.591(3)                 |
| $H_{\text{Fe-As}}$ (Å) | 1.360(2)                 | 1.369(2)                 |
| As–Fe–As angle (°)    | 111.5(1)                 | 110.3(1)                 |

Figure 2. (a) Interplanar spacings, $H_{\text{Th-As}}$, $H_{\text{Fe-As}}$, and $H_{\text{Th-N/O}}$ (see the upper right structure), as functions of nominal oxygen content in ThFeAsN$_{1-x}$O$_x$. The solid lines are guides for the eye. (b) Oxygen-content dependent diagonal As–Fe–As bond angle.

Figure 3. (a) and (b) Magnetic susceptibility measured at 10 Oe near superconducting $T_c$ for ThFeAsN$_{1-x}$O$_x$ samples. The $\chi - T$ curves of different samples are shifted successively along the vertical axis for comparison. The shift steps are 0.5 and 0.02 for zero-field-cooling (ZFC) and field-cooling (FC), respectively.

Figure 4. (a) Temperature dependence of magnetic susceptibility measured at 1 kOe for the samples of $x = 0.15$ and $x = 0.6$ respectively. (b) The isothermal magnetization curves for the sample of $x = 0.6$ at various temperatures. (c) Derivative $dM/dH$ value as function of temperature. The $dM/dH$ values were obtained by a linear fitting for the high field (30–50 kOe) $M(H)$ data.
samples. As shown in the figure, the $T_c$ value depends dramatically on the nominal oxygen content. To begin with, the oxygen substitution at only 5% leads to the suppression of $T_c$ from 30 K to 15.5 K. For the sample of $x = 0.08$, $T_{c,\text{net}}$ is further reduced to 6.7 K and the magnetic shielding fraction (MSF) at 2 K is merely about 5%, indicating that most part of the sample is not superconducting. This is consistent with the transport property ($T_{\text{onset}} \approx 0.1 K$ to 15.5 K). Upon cooling (above 150 K), the susceptibility is not very sensitive to the temperature, suggesting Pauli paramagnetic behavior (the low temperature upturn is ascribed to small amount of paramagnetic impurities). No anomaly indicating long-range magnetic ordering can be observed in the $\chi - T$ plot. For $x = 0.6$, the room temperature susceptibility reaches $5.3 \times 10^{-2}$ emu mol$^{-1}$, which is significantly larger than that of LaFeAsO$_{1-x}$F$_x$ system ($\sim 4 \times 10^{-4}$ emu mol$^{-1}$) [23]. To understand its origin, we performed isothermal magnetization measurements, which are shown in figure 4(b). The plots of magnetization ($M$) versus applied field ($\mu_0 H$) clearly indicate existence of ferromagnetic impurity, whose Curie point is higher than 300 K. This is not surprising, as the the XRD profile shows that the sample is not single-phase. Thus, the extrinsic ferromagnetic contribution to $\chi$ can be removed by using the derivative $dM/dH$ in the high-field regime instead of $\chi = M/H$. The $dM/dH$ values were obtained by a linear fitting for the high field (30–50 kOe) $M(H)$ data, which are shown in figure 4(c). It can be seen that the $dM/dH$ value is $\sim 40$-times smaller than the $\chi$ value at 300 K. The nearly linear $dM/dH$ above $\sim 160 K$ is consistent with that of ThFeAsN parent compound [12]. Again, we cannot see any evident anomaly.

The temperature dependent resistivity near superconducting $T_c$ is shown in figure 5(a). The superconducting transition widths (defined as the temperature interval between 90%–10% of normal-state resistivity) vary from 1 K to 5 K, which are widely observed in ‘1111’ type polycrystalline samples [7–10]. The broadening of the superconducting transition may be due to doping inhomogeneity [24]. To track the variation of superconductivity, here we pay attention to the temperature-dependent normal-state resistivity $\rho(T)$. Knowing that most of the iron-based superconductors exhibit strong anisotropy and the resistivity along the $c$-axis could be as high as two orders of magnitude larger than that of the $ab$-plane [4]. So, when the current flows through a polycrystalline sample where the orientation of crystallites are supposed to be random with no preferred direction, most of the current will choose the path of low resistance route according to Kirchhoff’s current law. Thus, the $\rho(T)$ behavior of a polycrystalline sample is mainly determined by the low-resistivity $\rho_{ab}$, which reflect the intrinsic property [7, 25]. This is also supported by works in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ system, where the resistivity behavior of a polycrystalline sample is identical to that of the $ab$-plane in a single crystal [3, 26]. Figures 5(b)–(i) shows the $\rho - T$ curves up to the room temperature. We fit the $\rho(T)$ data in the temperature range 20 K $\leq T < 150$ K (for $x = 0.6$, the fitting range changes to 20 K $\leq T < 100$ K) using the equation $\rho(T) = \rho_0 + AT^n$ where the exponent $n$ marks the scattering mechanism [7, 25]. The $n$ value of the non-doped sample is 1.28, obviously deviated from 2.0 expected for a Landau-Fermi liquid. In the intermediate non-superconducting area (including $x = 0.08$ with very small superconducting fraction), the $n$ value is close to 2.0. With the re-emergence of superconductivity, the exponent decreases rapidly to about 1.5. For the non-superconducting sample $x = 0.6$, the exponent is 1.31.
Figure 6 show the temperature dependent specific heat for samples of $x = 0.4$ and $x = 0.6$. For the non-superconducting sample $x = 0.6$, the $C/T$ versus $T^2$ plot slightly deviates from linearity below 5 K. Similar phenomenon was also observed in ThNiAsN superconductor, which is ascribed to Schottky anomaly of magnetic impurities and/or some nuclei [27]. In the temperature range 5–25 K, the $C/T$ value is linearly related with $T^2$. This allows the estimation of Sommerfeld coefficient $\gamma = 32.4 \text{ mJ/mol/K}^2$, using the equation $C/T = \gamma T + \beta T^3$. As a comparison, the $\gamma$ value in heavily electron-doped LaFe$_{0.5}$Co$_{0.5}$AsO system is only 1.68 mJ/mol/K$^2$, nearly 20 times smaller [28]. The enhancement cannot be solely ascribed to the change in density of state, which means that there is a significant increase in the effective mass of electrons. For the superconducting sample of $x = 0.4$, the electronic specific heat in superconducting state can not be obtained by subtracting the specific heat measured in magnetic field, as the highest field available in our experiment (80 kGs) is not strong enough to suppress the superconducting state. Supposing that $C_{\text{normal}}(T) = \gamma T + \beta T^3$, we fit the normal state specific heat $(C_{\text{normal}})$ in the temperature range $11 \text{ K} \leq T \leq 25 \text{ K}$ where the $C/T$ value is linearly related with $T^2$. The derived $\gamma$ is 14.1 mJ/mol/K$^2$. By subtracting $C_{\text{normal}}(T)$ from the raw data, the specific heat jump due to the superconducting transition is revealed in the inset of figure 6. One may note that, the entropy of the superconducting transition does not conserve up to $T_c$. This suggest that the contribution from Schottky anomaly, which shows a broad peak at low temperatures [29], also exist in the data. Nevertheless, a jump of specific heat $(\Delta C/T_c = 12.5 \text{ mJ/mol/K}^2)$ is evidently observed below 13 K. The thermodynamic transition temperature determined by an entropy-conserving construction is 9.2 K, conforming with the $T_c^{\text{zero}}$ in the figure 5(a). Then, the $\Delta C/\gamma T_c$ value is determined as 0.89, which is significantly smaller than the weak-coupling limit of BCS superconductors $(\Delta C/\gamma T_c \approx 1.43)$. The reduction of $\Delta C/\gamma T_c$ value can be ascribed to an anisotropic superconducting gap within the $\alpha$-model of BCS theory [30, 31]. One may note an anisotropic superconducting gap was also proposed for the parent compounds ThFeAsN according to the measurements of specific heat $(\Delta C/T_c = 25 \text{ mJ/mol/K}^2)$ as well as $\mu$SR spectroscopy [17, 18]. In the rigid-band picture, the hole band at the $\Gamma$ point may gradually sink below the Fermi level upon electron doping, causing the shrink of the hole pocket [13]. This suggests that the anisotropic superconducting gap is more likely to be associated with the electron pocket.

Figure 6. Temperature dependence of the specific heat in $C/T$ versus $T^2$ plot in the low-temperature region for samples of $x = 0.4$ and $x = 0.6$. The blue straight line fits the normal state specific heat using the equation $C_{\text{normal}}(T) = \gamma T + \beta T^3$. The inset shows $(C - C_{\text{normal}})/T$ versus $T$ for $x = 0.4$.

Figure 7. Superconducting phase diagram of ThFeAsN$_{1-x}$O$_x$ system. $\chi^{\text{onset}}$, $\rho^{\text{onset}}$ and $\rho^{\text{zero}}$ represent the superconducting $T_c$ determined by the onset of $\chi - T$ curve, the onset of $\rho - T$ curve and the zero-resistivity temperature respectively. The pink star (right axis) shows the exponent $n$ extracted from the normal state resistivity. The dashed line near the bottom axis indicates the lowest temperature available in our experiments.
3.3. Doping phase diagram

We summarize superconducting $T_c$ and the exponent $n$ in resistivity fitting as functions of the nominal oxygen content in figure 7. The phase diagram shows two superconducting areas separated by a non-superconducting zone with $0.1 \leq x \leq 0.2$. Previous heavily electron-doped cases show two superconducting domes that are mostly connected [9, 10, 32]. Isolated superconducting phases are shown in LaFeAs$_{1-x}$P$_x$O [33] in which the intermediate non-superconducting phase is magnetically ordered [34]. Another distinct feature of the present ThFeAsN$_1$ system is that the maximum $T_c$ for the second superconducting region is significantly lowered, in sharp contrast with other systems mentioned above which shows the opposite. Interestingly, the emergence of superconductivity seems to correlate with the exponent $n$, which tends to deviate from 2.0 when superconductivity emerges. Nevertheless, although the $n$ value of the sample of $x = 0.6$ is 1.31, it does not superconduct.

The position of the non-superconducting phase in the phase diagram is another interesting issue, which could be related to the crystal structure of FeAs layers. Matsuishi et al [32] show that the $T_c$ valley between the two superconducting domes in LaFeAsO$_{1-x}$H$_x$ and SmFeAs$_{1-x}$P$_x$O$_{1-x}$H$_x$ systems locate at the electron doping level of $x_{val} \approx 0.16$ in which the diagonal As–Fe–As bond angle is $\alpha \approx 113^\circ$. Interestingly, the $\alpha$ is independent of both phosphorus doping and lanthanide species [32]. Coincidentally, the non-superconducting area in ThFeAsN$_{1-x}$O$_x$ is centered at $x = 0.15$ with the same bond angle of $\alpha = 113^\circ$. Nevertheless, their ‘starting points’ are quite different: the non-doped parent phases of LnFeAsO show an AFM ground state, while no magnetic order is detected in ThFeAsN [15–17]. This implies that, aside from the electron doping, there are additional factors controlling the ground states of ThFeAsN$_{1-x}$O$_x$.

We propose that the built-in chemical pressure could play an important role. Firstly, the axial ratio of ThFeAsN ($c/a \approx 2.11$) is the lowest among 1111-type iron arsenides [35]. Secondly, the $H_{Fe-As}$ value (1.305 A) is the smallest and, the $\alpha$ value (114.2°) is the largest, among FeAs-layer based compounds [36]. All these suggest that ThFeAsN bears an internal chemical pressure exerted along the $c$-axis. This viewpoint is supported by the recent structural analysis which shows that the $H_{Fe-As}$ value in ‘1111’ phases tends to decrease linearly with increasing physical pressure [37]. So, the parameter $H_{Fe-As}$ can be used as an indicator of the uniaxial chemical pressure, and the increase in $H_{Fe-As}$ upon oxygen doping (figure 2(a)) suggests that the chemical pressure is gradually released in ThFeAsN$_{1-x}$O$_x$. This partly explains the rapid suppression of superconductivity at low doping (note that the oxygen substitution also introduces electrons, therefore the AFM ground state cannot be recovered). Thus, the position and the width of the non-superconducting window on ThFeAsN$_{1-x}$O$_x$ phase diagram are actually determined by a combined effect of chemical pressure and electron doping. The lowered maximum $T_c$ of the second superconducting window could be caused by the remaining uniaxial chemical pressure.

Now let us discuss the origin of the two superconducting area in ‘1111’ systems. For the first (left) superconducting region, either carrier doping [1] or ‘applying’ chemical pressure with isovalent P/As doping [38] suppresses the magnetic order in the parent compounds, after which superconductivity appears with remaining spin fluctuations in the normal state [39–42]. This naturally leads to the picture that superconductivity is due to spin fluctuations associated with the nearby magnetic phase [43–45]. For the second (right) superconducting region, the relationship between superconductivity and magnetism becomes ambiguous. On the one hand, recent studies on LaFeAsO$_{1-x}$H$_x$ found a second AFM state below 100 K on the right side of the second superconducting dome, accompanied by an orthorhombic lattice distortion due to As atom off-centering [46, 47]. In LaFeAs$_{1-x}$P$_x$O$_2$, a second AFM state was also observed, but it locates at about half doping, in between the two superconducting domes [34]. Both cases still suggest a spin-fluctuation scenario for the second superconducting dome [34, 46, 47]. However, on the other hand, the study on heavily doped LaFeAsO$_{1−x}$F$_x$ found neither AFM ordering nor low-energy magnetic fluctuations [10]. Accordingly, an orbital-fluctuation mechanism was proposed for the second superconducting dome [10, 11]. As for ThFeAsN$_{1−x}$O$_x$, a long-range magnetic order seems unlikely according to the susceptibility measurement. In this aspect, further investigations using NMR, $\mu$SR or neutron diffractions are highly needed.

4. Conclusion

To summarize, we have successfully realized heavily electron doping in ThFeAsN$_{1-x}$O$_x$ ($0 \leq x \leq 0.6$) without using high-pressure synthesis. Our resistivity and susceptibility measurements reveal a peculiar phase diagram showing two isolated superconducting regions with maximum $T_c^{max}$ of 30 K at $x = 0$ and 17.5 K at $x = 0.3$, respectively. The absence of superconductivity in $0.1 \leq x \leq 0.2$ basically coincides with the structural anomaly featured with a minimum of $c$-axis as well as a kink in the As height. We argue that the built-in uniaxial chemical pressure, in addition to the electron doping, plays an important role for the quenching of superconductivity within $0.1 \leq x \leq 0.2$ as well as for the lowered $T_c^{max}$ of the second superconducting area. The specific-heat jump for the sample $x = 0.4$ implies anisotropic superconducting gap for the electron Fermi pocket. The present system supplies additional information for describing the global electronic phase diagram in iron-based superconductors, which could help to ultimately understand the superconducting mechanism.

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