CHIN. PHYS. LETT. Vol. 36, No. 10 (2019) 107403

# Neutron Powder Diffraction Study on the Non-Superconducting Phases of $ThFeAsN_{1-x}O_x$ ($x = 0.15, 0.6$) Iron Pnictide *

Hui-Can Mao(毛慧灿)[1,2], Bing-Feng Hu(胡丙锋)[3**], Yuan-Hua Xia(夏元华)[3], Xi-Ping Chen(陈喜平)[3], Cao Wang(王操)[4], Zhi-Cheng Wang(王志成)[5], Guang-Han Cao(曹光旱)[5,6], Shi-Liang Li(李世亮)[2,7,8], Hui-Qian Luo(罗会仟)[2,7**]

[1]*Department of Physics and Center for Advanced Quantum Studies, Beijing Normal University, Beijing 100875*
[2]*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190*
[3]*Key Laboratory of Neutron Physics, Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621999*
[4]*Department of Physics, Shandong University of Technology, Zibo 255049*
[5]*Department of Physics and State Key Lab of Silicon Materials, Zhejiang University, Hangzhou 310027*
[6]*Collaborative Innovation Centre of Advanced Microstructures, Nanjing 210093*
[7]*Songshan Lake Materials Laboratory, Dongguan 523808*
[8]*School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 100190*

(Received 14 July 2019)

*We use neutron powder diffraction to study the non-superconducting phases of $ThFeAsN_{1-x}O_x$ with $x = 0.15$, 0.6. In our previous results of the superconducting phase ThFeAsN with $T_c = 30$ K, no magnetic transition is observed by cooling down to 6 K, and possible oxygen occupancy at the nitrogen site is shown in the refinement [Europhys. Lett. 117 (2017) 57005]. Here in the oxygen doped system $ThFeAsN_{1-x}O_x$, two superconducting regions ($0 \leqslant x \leqslant 0.1$ and $0.25 \leqslant x \leqslant 0.55$) are identified by transport experiments [J. Phys.: Condens. Matter 30 (2018) 255602]. However, within the resolution of our neutron powder diffraction experiment, neither the intermediate doping $x = 0.15$ nor the heavily overdoped compound $x = 0.6$ shows any magnetic order from 300 K to 4 K. Therefore, while it shares the common phenomenon of two superconducting domes as most 1111-type iron-based superconductors, the magnetically ordered parent compound may not exist in this nitride family.*

*PACS:* 74.70.Xa, 74.62.Bf, 61.05.F− DOI: 10.1088/0256-307X/36/10/107403

Understanding the magnetic ground state is one of the major task in the mechanism research of iron-based superconductors, where the magnetic interactions are generally believed to be involved in the superconducting pair process.[1–3] In most families of iron pnictide or chalcogenide superconductors, a long-range antiferromagnetic order always emerges in the undoped parent compounds,[4] such as the collinear order in LaFeAsO (1111 family),[5] $BaFe_2As_2$ (122 family),[6] $Na_{1-\delta}FeAs$ (111 family),[7] the bi-collinear order in $Fe_{1+x}Te$ (11 family),[8] and the $\sqrt{5}\times\sqrt{5}$ block order in $K_2Fe_4Se_5$.[9–11] Even in the stoichiometrically hole-type superconducting system $CaKFe_4As_4$ (1144 family), compensating electron doping by Ni or Co can induce a spin-vortex phase (hedgehog order) with $C_4$ rotation symmetry.[12,13] Another $C_4$ magnetic order can be found in the hole-doped $Ba_{1-x}(K, Na)_xFe_2As_2$ systems near the optimal doping.[14,15] Specifically for the 1111 family (e.g., LaFeAsO),[16,17] superconductivity can be induced by doping fluorine,[17–21] hydrogen[22–25] and phosphorus[26–31] into the parent compound, where they all result in a two-superconducting-dome structure with slightly different optimal $T_c$. Antiferromagnetic parent compounds for both sides are discovered by neutron diffraction, muon spin relaxation ($\mu$SR) and nuclear magnetic resonance (NMR) experiments.[24,25,32,33]

Recently, a new nitride iron pnictide superconductor ThFeAsN has been discovered with intrinsic $T_c = 30$ K.[34] The layered tetragonal ZrCuSiAs-type structure consisting of $[Th_2N_2]$ and $[Fe_2As_2]$ blocks is classified as a 1111-type iron-based superconducting family (inset of Fig. 1). Although the first-principles calculations of ThFeAsN indicate that the lowest-energy magnetic ground state is the collinear stripe-type antiferromagnetic state,[35,36] the normal-state resistivity/magnetization do not show any magnetic anomaly above $T_c$,[34] further $^{57}$Fe Mössbauer spectroscopy, neutron powder diffraction, $\mu$SR and NMR experiments have not found any magnetic order down to 2 K,[37–40] either. Possible extra electrons from nitrogen deficiency or oxygen occupancy at the nitrogen site make the compound approximate to the optimal doping level.[38] Indeed, by

*Supported by the Strategic Priority Research Program of Chinese Academy of Sciences under Grant Nos XDB07020300 and XDB25000000, the National Key Research and Development Program of China under Grant Nos 2017YFA0303103, 2017YFA0302903 and 2016YFA0300502, the National Natural Science Foundation of China under Grant Nos 11374011, 11504347, 11304183, 11674406 and 11822411, the Youth Innovation Promotion Association of Chinese Academy of Sciences under Grant No 2016004, the Key Laboratory of Neutron Physics of CAEP under Grant No 2015AB03, and the Science Challenge Project under Grant No TZ2016004.

**Corresponding author. Email: hqluo@iphy.ac.cn; hbf@caep.cn

© 2019 Chinese Physical Society and IOP Publishing Ltd

doping oxygen into the system, the superconductivity of $ThFeAsN_{1-x}O_x$ is quickly suppressed until $x = 0.1$.[41] Surprisingly, a second superconducting dome emerges from $x = 0.25$ to $x = 0.55$ with maximum $T_c$ about 15 K (Fig. 1),[41] which closely resembles the two superconducting domes in the phase diagrams of $LaFeAsO_{1-x}H_x$, $LaFeAsO_{1-x}F_x$ and $LaFeAs_{1-x}P_xO$ systems.[19,22–29,31] It should be noticed that the hydrogen doped 1111 systems always have double parent compounds with different magnetic structures and ordered moments adjacent to each superconducting dome,[24,25,33] and the intermediate non-superconducting phase of $LaFeAs_{1-x}P_xO$ is magnetically ordered.[30–32] Thus it is essential to examine the possible magnetic order in the $ThFeAsN_{1-x}O_x$ system, especially for the non-superconducting dopings.

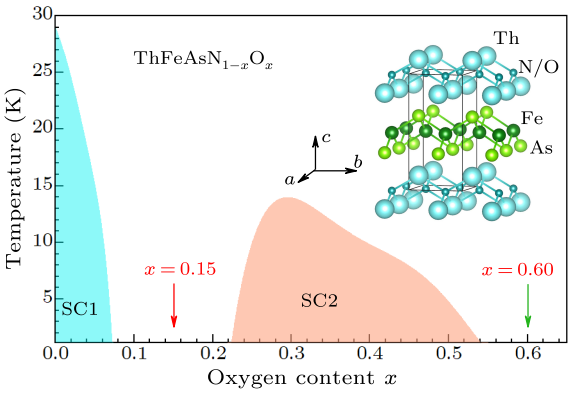


**Fig. 1.** Superconducting phase diagram and crystal structure of $ThFeAsN_{1-x}O_x$. The arrows mark two dopings in this study.

In this Letter, we report a neutron powder diffraction study on the non-superconducting phases of $ThFeAsN_{1-x}O_x$ with $x = 0.15$, 0.6. By cooling down from 300 K to 4 K, no magnetic order is found within the instrument resolution. The refinement shows a slight compression of the unit cell volume and a lift of the Th position upon oxygen doping. Together with our previous results on the undoped compound ThFeAsN, we conclude that no magnetic parent compound exists in this nitride family. The two separated superconducting regions may come from a combination effect of electron doping and uniaxial chemical pressure from oxygen substitutions.

Polycrystalline samples of $ThFeAsN_{1-x}O_x$ ($x = 0.15$, 0.6) were synthesized by the solid-state reaction method as described elsewhere.[34,41] About 5 g high pure powders were prepared for each doping, and sealed in a vanadium can. Neutron powder diffraction experiments were carried out on a high resolution neutron diffractometer (HRND) at the Key Laboratory of Neutron Physics, Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics. The wavelength of neutron was selected to be $\lambda = 1.8846$ Å for both the samples. The scattering data were collected at 4 K and 300 K by covering the scattering angle $2\theta$ of 10–145°. All these diffraction patterns were refined with the Rietveld method within the program FullProf,[42] and the structural parameters were obtained by assuming the occupancy is the same as chemical composition.[38]

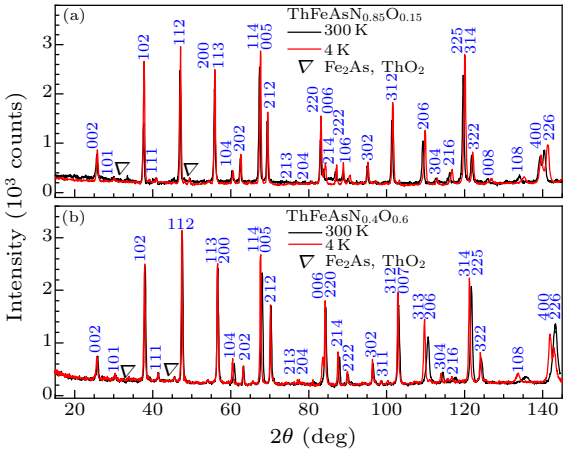


**Fig. 2.** Raw data of neutron powder diffraction for (a) $ThFeAsN_{0.85}O_{0.15}$ and (b) $ThFeAsN_{0.4}O_{0.6}$. All peaks are indexed by the tetragonal ZrCuSiAs-type structure.

The raw data of neutron diffraction patterns are presented in Fig. 2. For the $x = 0.15$ sample, the diffraction patterns almost overlap between $T = 4$ K and $T = 300$ K. All reflections can be indexed by a tetragonal phase in ZrCuSiAs-type structure[43] with the space group $P4/nmm$, except for two tiny peaks (marked by inverted triangles) from $Fe_2As$ or $ThO_2$ impurity phases (Fig. 2(a)). Similar results are obtained on the $x = 0.6$ sample, as shown in Fig. 2(b). As both data sets at base temperature and room temperature can be fully identified as nuclear peaks, and no additional peaks emerge at low temperature, we tend to consider no magnetic order in both the compounds within the measurement resolution of HRND. Here the slight difference between the $T = 4$ K and $T = 300$ K patterns can be attributed to the background change, and the peak shift at high angles is due to thermal expansion of the lattice.

To quantitatively compare the neutron diffraction results, we have performed the Rietveld refinement for four data sets by assuming the occupancy is the same as chemical composition, as shown in Fig. 3. The weighted profile factor $R_{wp}$ without the background is slightly higher than the previous results on ThFeAsN,[38] which may be attributed to the much lower neutron flux of this high resolution diffractometer in comparison with WOMBAT high-intensity diffractometer at the Australian Centre for Neutron Scattering (ACNS). Again, four sets of the diffraction patterns can be refined quite well by the space group $P4/nmm$ without any magnetic scattering, suggesting no static magnetic order in both the samples. This is consistent with the magnetic susceptibility measurements, where no anomaly related to magnetic transition can be observed in $\chi(T)$, and

only Pauli paramagnetic behavior shows up instead of the Curie–Weiss behavior. All crystallographic parameters obtained from the refinements are listed in Tables 1 and 2.

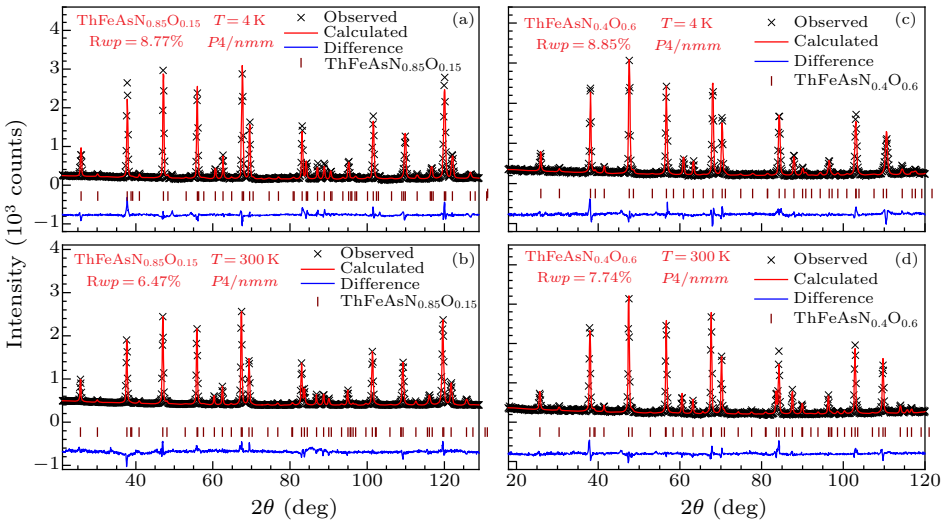


**Fig. 3.** Refinement results of neutron powder diffraction patterns for $ThFeAsN_{0.85}O_{0.15}$ at (a) 4 K and (b) 300 K; and identical refinement results for $ThFeAsN_{0.4}O_{0.6}$ at (c) 4 K and (d) 300 K.

**Table 1.** Crystallographic data of $ThFeAsN_{0.85}O_{0.15}$ at 4 K.

| | | | | | |
|---|---|---|---|---|---|
| Space group | $P4/nmm$ | | $R_{wp}$(%) | | 8.77(3) |
| $a$ (Å) | 4.0156(3) | | $h_{Th-As}$ (Å) | | 1.7037(8) |
| $c$ (Å) | 8.4305(1) | | $h_{Fe-As}$ (Å) | | 1.3185(1) |
| $\alpha_{As-Fe-As}$ | 113.4° | | $d_{Th-As}$ (Å) | | 3.311(4) |
| $\beta_{As-Fe-As}$ | 107.55° | | $d_{Fe-As}$ (Å) | | 2.403(3) |
| Atom | Wyckoff | $x$ | $y$ | $z$ | $U_{iso}$ |
| Th | 2$c$ | 0.25 | 0.25 | 0.1415(1) | 0.1232 |
| Fe | 2$b$ | 0.75 | 0.25 | 0.5 | 0.2542 |
| As | 2$c$ | 0.25 | 0.25 | 0.6564(8) | 0.1495 |
| N | 2$a$ | 0.75 | 0.25 | 0 | 0.3374 |
| O | 2$a$ | 0.75 | 0.25 | 0 | 0.3374 |

**Table 2.** Crystallographic data of $ThFeAsN_{0.4}O_{0.6}$ at 4 K.

| | | | | | |
|---|---|---|---|---|---|
| Space group | $P4/nmm$ | | $R_{wp}$(%) | | 8.85(1) |
| $a$(Å) | 3.9727(9) | | $h_{Th-As}$ (Å) | | 1.5671(1) |
| $c$(Å) | 8.4253(1) | | $h_{Fe-As}$ (Å) | | 1.4061(8) |
| $\alpha_{As-Fe-As}$ | 109.4° | | $d_{Th-As}$ (Å) | | 3.216(3) |
| $\beta_{As-Fe-As}$ | 109.5° | | $d_{Fe-As}$ (Å) | | 2.434(3) |
| Atom | Wyckoff | $x$ | $y$ | $z$ | $U_{iso}$ |
| Th | 2$c$ | 0.25 | 0.25 | 0.1471(8) | 1.0259 |
| Fe | 2$b$ | 0.75 | 0.25 | 0.5 | 0.8284 |
| As | 2$c$ | 0.25 | 0.25 | 0.6669(3) | 0.0694 |
| N | 2$a$ | 0.75 | 0.25 | 0 | 0.8296 |
| O | 2$a$ | 0.75 | 0.25 | 0 | 0.8296 |

We finally compare the structural parameters for all the three compounds measured by neutron scattering: ThFeAsN, $ThFeAsN_{0.85}O_{0.15}$ and $ThFeAsN_{0.4}O_{0.6}$. Figure 4 summarizes the oxygen doping dependence of the lattice parameters and $z$ position of Th and As. Both $a$ and $c$ decrease upon oxygen doping at low temperature, while $c$ recovers a little for $x = 0.6$ at room temperature (Figs. 4(a) and 4(b)), suggesting that the volume of unit cell is compressed by chemical doping. The $z$ position of As are almost the same for all the three compounds, but the $z$ position of Th obviously increases upon oxygen doping, suggesting the substitution of nitrogen by oxygen mainly affects the $[Th_2N_2]$ layer. By carefully comparing the results in Tables 1 and 2 with ThFeAsN data,[38] a systematic distortion of the $FeAs_4$ tetrahedron is also found, where $\alpha_{As-Fe-As}$ and $\beta_{As-Fe-As}$ show different behaviors when increasing oxygen doping. The microscopic distortion of the lattice structure rather than the phase transition can be explained by uniaxial chemical pressure, which may give the result in the two separated superconducting regions in combination from the doping effect.[41]

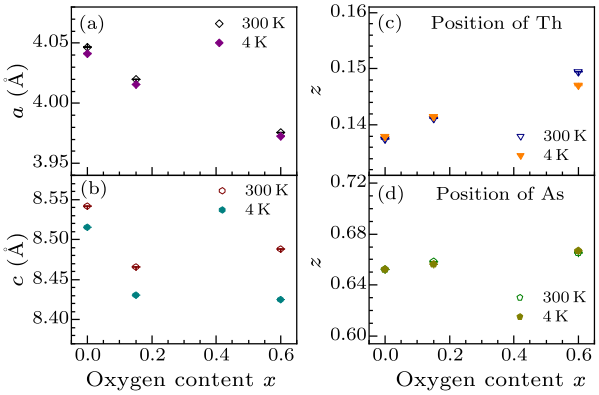


**Fig. 4.** Oxygen doping dependence of the lattice parameters [(a), (b)] and $z$ position [(c), (d)] of Th and As in the $ThFeAsN_{1-x}O_x$ system.

In summary, we have carried out neutron diffraction experiments on non-superconducting phases of $ThFeAsN_{1-x}O_x$ with $x = 0.15$, 0.6. None of them shows any magnetic order down to 4 K. Therefore, despite the two superconducting phases with different optimal $T_c$ similar to other 1111-type iron-based superconductors, this oxygen doped nitride iron-based superconductor may not have magnetically ordered parent compounds. Further inelastic neutron scattering experiments are highly desired to measure the spin

dynamics and check whether it interplays with superconductivity in this nitride family.

The authors are grateful to Qingzhen Huang at NIST, USA for the help on data analysis.

## References

[1] Dai P C 2015 *Rev. Mod. Phys.* **87** 855
[2] Si Q, Yu R and Abrahams E 2016 *Nat. Rev. Mater.* **1** 16017
[3] Inosov D S 2016 *C. R. Phys.* **17** 60
[4] Stewart G R 2011 *Rev. Mod. Phys.* **83** 1589
[5] de la Cruz C et al 2008 *Nature* **453** 899
[6] Huang Q Z et al 2008 *Phys. Rev. Lett.* **101** 257003
[7] Li S L et al 2009 *Phys. Rev. B* **80** 020504(R)
[8] Li S L et al 2009 *Phys. Rev. B* **79** 054503
[9] Bao W, Huang Q Z , Chen G F, Green M A, Wang D M , He J B and Qiu Y M 2011 *Chin. Phys. Lett.* **28** 086104
[10] Ye F, Chi S, Bao W, Wang X F, Ying J J, Chen X H, Wang H D, Dong C H and Fang M H 2011 *Phys. Rev. Lett.* **107** 137003
[11] Wang M et al 2011 *Phys. Rev. B* **84** 094504
[12] Meier W R et al 2018 *npj Quantum Mater.* **3** 5
[13] Kreyssig A et al 2018 *Phys. Rev. B* **97** 224521
[14] Böhmer A E, Hardy F, Wang L, Wolf T, Schweiss P and Meingast C 2015 *Nat. Commun.* **6** 7911
[15] Avci S et al 2014 *Nat. Commun.* **5** 3845
[16] Hosono H et al 2015 *Sci. Technol. Adv. Mater.* **16** 033503
[17] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 *J. Am. Chem. Soc.* **130** 3296
[18] Luetkens H et al 2009 *Nat. Mater.* **8** 305
[19] Yang J et al 2015 *Chin. Phys. Lett.* **32** 107401
[20] Yang J, Oka T, Li Z, Yang H X, Li J Q, Chen G F and Zheng G Q 2018 *Sci. Chin.-Phys. Mech. Astron.* **61** 117411
[21] Xiao Y, Su Y, Mittal R, Chatterji T, Hansen T, Kumar C M N, Matsuishi S, Hosono H and Brueckel T 2009 *Phys. Rev. B* **79** 060504(R)
[22] Matsuishi Set al 2012 *Phys. Rev. B* **85** 014514
[23] Iimura S, Matuishi S, Sato H, Hanna T, Muraba Y, Kim S W, Kim J E, Takata M and Hosono H 2012 *Nat. Commun.* **3** 943
[24] Fujiwara N, Tsutsumi S, Iimura S, Matsuishi S, Hosono H, Yamakawa Y and Kontani H 2013 *Phys. Rev. Lett.* **111** 097002
[25] Hosono H and Matsuishi S 2013 *Curr. Opin. Solid State Mater. Sci.* **17** 49
[26] Wang C et al 2009 *Europhys. Lett.* **86** 47002
[27] Kitagawa S, Iye T, Nakia Y, Ishida K, Wang C, Cao G H and Xu Z A 2014 *J. Phys. Soc. Jpn.* **83** 023707
[28] Miyasaka S, Takemori A, Kobayashi T, Suzuki S, Saijo S and Tajima S 2013 *J. Phys. Soc. Jpn.* **82** 124706
[29] Lai K T, Takemori A, Miyasaka S, Engetsu F, Mukuda H and Tajima S 2014 *Phys. Rev. B* **90** 064504
[30] Shen C, Si B, Cao C, Yang X, Bao J, Tao Q, Li Y, Cao G and Xu Z A 2016 *J. Appl. Phys.* **119** 083903
[31] Miyasaka S et al 2017 *Phys. Rev. B* **95** 214515
[32] Mukuda H, Engetsu F, Shiota T, Lai K T, Yashima M, Kitaoka Y, Miyasaka S and Tajima S 2014 *J. Phys. Soc. Jpn.* **83** 083702
[33] Hiraishi M et al 2014 *Nat. Phys.* **10** 300
[34] Wang C et al 2016 *J. Am. Chem. Soc.* **138** 2170
[35] Singh D J 2016 *J. Alloys Compd.* **687** 786
[36] Wang G and Shi X 2016 *Europhys. Lett.* **113** 67006
[37] Albedah M A et al 2017 *J. Alloys Compd.* **695** 1128
[38] Mao H C, Wang C, Maynard-Casely H E, Huang Q Z, Wang Z C, Cao G H, Li S L and Luo H Q 2017 *Europhys. Lett.* **117** 57005
[39] Shiroka T, Shang T, Wang C, Cao G H, Eremin I, Ott H R and Mesot J 2017 *Nat. Commun.* **8** 156
[40] Adroja D et al 2017 *Phys. Rev. B* **96** 144502
[41] Li B Z et al 2018 *J. Phys.: Condens. Matter* **30** 255602
[42] Rodríguez-Carvajal J 1993 *Physica B* **192** 55
[43] Muir S and Subramanian M A 2012 *Prog. Solid State Chem.* **40** 41