

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

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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 ($0 \leq x \leq 0.1$ and $0.25 \leq x \leq 0.55$) 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.

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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] BaFe₂As₂ (122 family),^[6] Na_{1- δ} 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 K₂Fe₄Se₅.^[9-11] Even in the stoichiometrically hole-type superconducting system CaKFe₄As₄ (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)_xFe₂As₂ 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 (μ 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 [Th₂N₂] and [Fe₂As₂] 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 ⁵⁷Fe Mössbauer spectroscopy, neutron powder diffraction, μ 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

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doping oxygen into the system, the superconductivity of $\text{ThFeAsN}_{1-x}\text{O}_x$ 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 $\text{LaFeAsO}_{1-x}\text{H}_x$, $\text{LaFeAsO}_{1-x}\text{F}_x$ and $\text{LaFeAs}_{1-x}\text{P}_x\text{O}$ 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 $\text{LaFeAs}_{1-x}\text{P}_x\text{O}$ is magnetically ordered.^[30–32] Thus it is essential to examine the possible magnetic order in the $\text{ThFeAsN}_{1-x}\text{O}_x$ system, especially for the non-superconducting dopings.

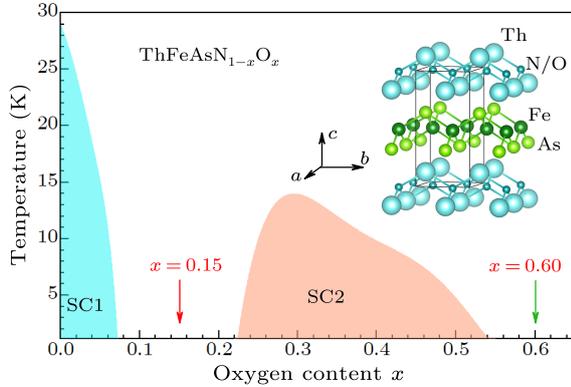


Fig. 1. Superconducting phase diagram and crystal structure of $\text{ThFeAsN}_{1-x}\text{O}_x$. The arrows mark two dopings in this study.

In this Letter, we report a neutron powder diffraction study on the non-superconducting phases of $\text{ThFeAsN}_{1-x}\text{O}_x$ 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 $\text{ThFeAsN}_{1-x}\text{O}_x$ ($x = 0.15, 0.6$) 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 $\lambda = 1.8846 \text{ \AA}$ for both the samples. The scattering data were collected at 4 K and 300 K by covering

the scattering angle 2θ of $10\text{--}145^\circ$. 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]

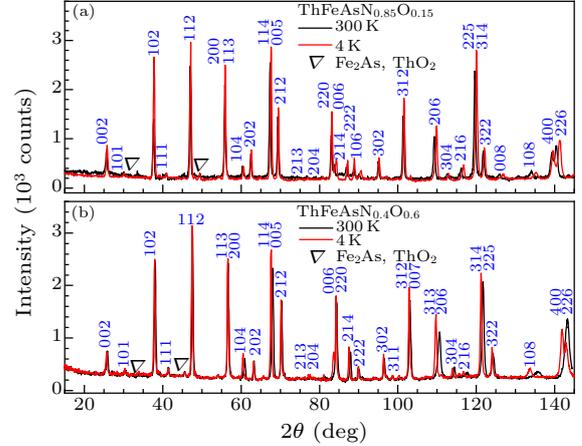


Fig. 2. Raw data of neutron powder diffraction for (a) $\text{ThFeAsN}_{0.85}\text{O}_{0.15}$ and (b) $\text{ThFeAsN}_{0.4}\text{O}_{0.6}$. All peaks are indexed by the tetragonal ZrCuSiAs -type structure.

The raw data of neutron diffraction patterns are presented in Fig. 2. For the $x = 0.15$ sample, the diffraction patterns almost overlap between $T = 4 \text{ K}$ and $T = 300 \text{ K}$. 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 $T = 4 \text{ K}$ and $T = 300 \text{ K}$ 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 pa-

rameters obtained from the refinements are listed in Tables 1 and 2.

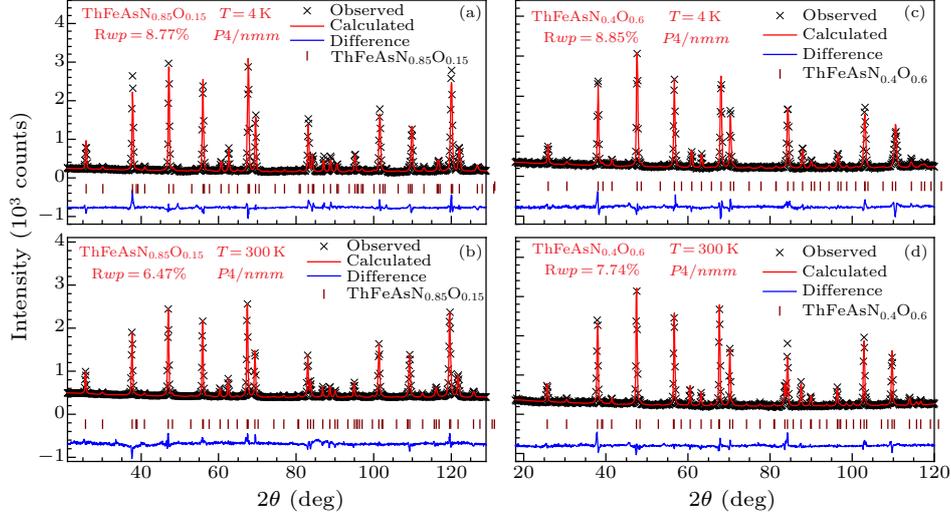


Fig. 3. Refinement results of neutron powder diffraction patterns for ThFeAsN_{0.85}O_{0.15} at (a) 4 K and (b) 300 K; and identical refinement results for ThFeAsN_{0.4}O_{0.6} at (c) 4 K and (d) 300 K.

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	2c	0.25	0.25	0.1415(1)	0.1232
Fe	2b	0.75	0.25	0.5	0.2542
As	2c	0.25	0.25	0.6564(8)	0.1495
N	2a	0.75	0.25	0	0.3374
O	2a	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	2c	0.25	0.25	0.1471(8)	1.0259
Fe	2b	0.75	0.25	0.5	0.8284
As	2c	0.25	0.25	0.6669(3)	0.0694
N	2a	0.75	0.25	0	0.8296
O	2a	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 [Th₂N₂] layer. By carefully comparing the results in Tables 1 and 2 with ThFeAsN data,^[38] a systematic distortion of the FeAs₄ 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]

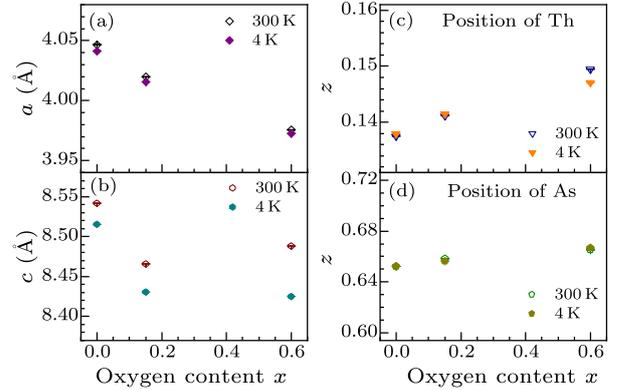


Fig. 4. Oxygen doping dependence of the lattice parameters [(a), (b)] and z position [(c), (d)] of Th and As in the ThFeAsN_{1-x}O_x system.

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.

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