Absence of superconductivity in electron-doped chromium pnictides $ThCrAsN_{1-x}O_x$

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Theoretical studies predicted possible superconductivity in electron-doped chromium pnictides isostructural to their iron counterparts. Here, we report the synthesis and characterization of a ZrCuSiAs-type Cr-based compound ThCrAsN, as well as its oxygen-doped variants. All samples of ThCrAsN_{1-x}O_x show metallic conduction, but no superconductivity is observed above 30 mK even though the oxygen substitution reaches 75%. The magnetic structure of ThCrAsN is determined to be G-type antiferromagnetic by magnetization measurements and first-principles calculations jointly. The calculations also indicate that the in-plane Cr-Cr direct interaction of ThCrAsN is robust against the heavy electron doping. The calculated density of states of the orbital occupations of Cr for ThCrAs(N,O) is strongly spin polarized. Our results suggest the similarities between chromium pnictides and iron-based superconductors should not be overestimated.

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I. INTRODUCTION

Since the discovery of high- T_c superconductivity in Febased materials [1], tremendous efforts have been devoted to search for superconductivity in the Fe-free transitionmetal systems with the conducting layers isostructural to Fe₂ X_2 (X = As or Se) motifs [2,3]. Among them Cr₂As₂layer-based compounds are of particular interest because they exhibit antiferromagnetism with high Néel temperature [4–11], even though Cr-based superconductors are scarce due to the robustness of antiferromagnetism [12]. The exploration of superconductivity in Cr₂As₂-layer-based materials is not only inspired by the breakthrough in Cr-based superconductors in recent years [13–17], but also supported by the theoretical predictions [18–20].

Within the framework of the Mott scenario for the transition-metal arsenides [21], the d^4 case of Cr^{2+} is symmetrical to the d^6 case of Fe^{2+} with respect to half-filled d^5 configuration (Mn²⁺). In this context, Fe-based superconductors (FeSCs) are electron-doped systems compared to the Mott-type parent materials. Accordingly, Cr-based compounds are expected to show comparable electronic correlations with possible superconductivity as the hole-doped side to the d^5 system, when the $3d^n$ filling is between n = 4 and n = 5 [19,20]. That is to say, electron doping in the d^4

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configuration is likely to bring about superconductivity in Cr_2As_2 -based materials.

However, it is not easy to find a proper Cr_2As_2 -based compound to study the electron-doping effect systematically. With regard to LaCrAsO, the solid solubility limits F⁻ substitution for O²⁻ to 20% [4], while H⁻ doping results in the structural transformation [22]. In addition, the replacements of the Cr site by Mn and Fe lead to a metal-insulator transition in LaCrAsO and BaCr₂As₂, respectively [4,23].

In this work, we report a chromium pnictide, ThCrAsN, which is isostructural to LaCrAsO. The advantage of Th₂N₂ layers over La_2O_2 layers is the high solubility of O^{2-} in N^{3-} , making high electron doping possible [24–26]. A series of polycrystalline samples of ThCrAsN_{1-x}O_x were synthesized, and the actual O^{2-} doping concentration x could be as high as 75%. All the ThCrAsN_{1-x}O_x samples exhibit metallic electrical conduction. Nevertheless, none of the samples shows superconductivity above 30 mK, against the theoretical predictions [19,20]. Magnetic measurements and density functional theory (DFT) calculations indicate that ThCrAsN is G-type antiferromagnetic (AFM), the same as other reported Cr_2As_2 -based compounds [4,6,7,23]. And the magnetic structure of the hypothetical end member ThCrAsO, though unavailable, is also a G-type antiferromagnet within the DFT calculations, indicating the robustness of AFM order that hinder the appearance of superconductivity. From our results and analysis, the materials with Cr₂As₂ layers seem not to be a simple symmetry of FeSCs with respect to half 3d shell filling.

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FIG. 1. (a) Powder x-ray diffraction pattern and the corresponding Rietveld refinement for ThCrAsN, whose crystal structure is shown in the inset. (b) A series of XRD patterns from ThCrAsN_{1-x}O_x (x = 0-1) polycrystalline samples. The doping concentration x for each pattern increases from bottom to top. The triangles, crosses, diamonds, and circles below the curve of x = 0.4 mark the peaks from ThO₂, Th₃As₄, Cr₂As, and some unidentified impurities, respectively. The *hkl* indices in space group *P4/nmm* are shown with black tics below the curve of x = 0. Two green bars are sketched to show the shift of characteristic peaks of ThCrAsN_{1-x}O_x. Note that there is no phase in space group *P4/nmm* for the fully doped sample (the top curve, x = 1). (c) Cell parameters of ThCrAsN_{1-x}O_x as a function of the nominal doping concentration x ($0 \le x \le 0.9$). The errors of data points are of the order of 10^{-4} Å, which is invisible in comparison with the lattice parameters. So the error bars are not present. Two green bars are sketched based on the data points with $x \le 0.4$, and the green dashed line is at x = 0.75.

II. METHODS

Samples preparation. Polycrystalline samples of ThCrAsN_{1-x}O_x ($0 \le x \le 0.9$) were synthesized using powder of Th₃N₄, Th₃As₄, ThO₂, Cr, and CrAs as starting materials. CrAs was prepared with Cr powder (99.99%) and As pieces (99.999%) and at 750 °C in evacuated quartz tubes. ThO₂ was heated to 700 °C for 12 h in the furnace to remove absorbed water. Preparation of the thorium metal ingot, Th₃N₄ powder, and Th₃As₄ powder were described elsewhere [24,27,28]. A stoichiometric mixture of the starting materials was ground and cold-pressed into a pellet. The pellet was loaded in an alumina crucible, which was sealed in an evacuated quartz tube. Subsequently, the tube was heated to 1100 °C in a muffle furnace, holding for 50 h. The final product is dark gray and stable in air.

Powder x-ray diffraction. Powder x-ray diffraction (XRD) experiments were carried out at room temperature on a PANalytical x-ray diffractometer with Cu $K\alpha_1$ radiation. XRD data were collected in the range $20^\circ \le 2\theta \le 150^\circ$ with a step of 0.013°. The FULLPROF suite was used for the structural refinements [29]. *Resistivity and magnetization measurements.* A standard four-probe method was employed to collect the resistivity data. The data above 2 K were measured using a Quantum Design physical property measurement system Dynacool, while the measurements between 30 mK and 0.8 K were performed in a dilution refrigerator. The direct-current (dc) magnetization was measured on a Quantum Design magnetic property measurement system (MPMS3) equipped with the oven option.

First-principles calculations. The first-principles calculations were done within the generalized gradient approximation (GGA) by using the Vienna *Ab initio* Simulation Package (VASP) [30]. The experimental crystal structure was used for the calculations. The plane-wave basis energy cutoff was chosen to be 550 eV. A $15 \times 15 \times 7 \Gamma$ -centered *K* mesh was used for the density-of-states (DOS) calculations. The Coulomb and exchange parameters, *U* and *J*, were introduced by using the GGA + *U* calculations, where the parameters *U* and *J* are not independent and the difference ($U_{\text{eff}} = U - J$) is meaningful. We adopted a GGA + *U* ($U_{\text{eff}} = 11 \text{ eV}$) correction on the Th-*f* shell to prevent an unphysical 5*f* component at Fermi level [4,31]. And U_{eff} was chosen at 0 eV for Cr 3*d*.

III. RESULTS AND DISCUSSION

A. Crystal structure

The XRD patterns of ThCrAsN and its oxygen-doped variants are displayed in Figs. 1(a) and 1(b). The pattern of ThCrAsN can be indexed well using space group P4/nmm, indicating the successful preparation of the parent compound. Element substitutions of oxygen for nitrogen are carried out, ranging from 10% oxygen to 100% oxygen, and the doping step is equal to 10%. With increasing oxygen concentration, the impurity peaks emerge and become conspicuous. The impurities of Th₃As₄ (for $x \ge 0.1$), ThO₂ (for $x \ge 0.4$), and Cr₂As (for $x \ge 0.7$) can be identified, as well as some unknown impurity phase(s) (only for $0.2 \le x \le 0.4$). However, ThCrAsN_{1-x}O_x remains the main phase even though the nominal concentration of oxygen is as high as 80%. Even for the pattern of x = 0.9, the phase of 1111 is conspicuous enough to examine the existence of superconductivity. A simple estimation of the ratio between the 1111 phase and ThO₂ is presented in the Supplemental Material (SM) [32]. With regard to the wholly doped sample, i.e., ThCrAsO, no ZrCuSiAs-type phase can be identified. It is proper to believe ThCrAsO cannot be synthesized under the present synthesis conditions.

In Fig. 1(b), two tilted green bars are sketched to show the monotonic shift of the (111) peaks and (200) peaks, suggesting the unit cell of ThCrAsN $_{1-x}O_x$ decreases gradually with the increase of oxygen doping. By a least-squares fit for the XRD patterns, the lattice parameters of ThCrAsN_{1-x}O_x are determined and plotted as functions of nominal oxygen concentration x in Fig. 1(c). Both the a axis and the c axis decrease almost linearly with increasing x when $x \leq 0.4$, as indicated by the green bars on the data points. The dependences of cell parameters on x deviate from the green bars gradually when $x \ge 0.5$, indicating the real oxygen concentration is lower than the nominal doping x, in line with the increasing impurity of ThO_2 in panel (b). If we take the slopes of a(x) and c(x) ($x \le 0.4$) as reference, the real oxygen concentration for the sample of ThCrAsN $_{0.1}O_{0.9}$ is about 0.75, inferred from its cell parameters. It is worth noting that the change of the *c* axis is about 1.75% from x = 0 to 0.9, while the a axis only shrinks by 1.13%. That the c axis changes much faster than the *a* axis is consistent with the enhanced interlayer coupling by electron doping.

A Rietveld refinement was carried out using the collected XRD data shown in Fig. 1(a). The refinement yields a weighted reliable factor of $R_{wp} = 7.41\%$ and a goodness of fit of S = 1.54, indicating reliability of the refinement. The resulting crystallographic data were summarized in Table I, and compared with the selected structural parameters of LaCrAsO. The axial ratio c/a of ThCrAsN is smaller than that of LaCrAsO, implying ThCrAsN bears stronger internal chemical pressure along the *c* axis. Similar reduction of c/a was also observed in other siblings ThMAsN and LaMAsO (M = Mn, Fe, Ni, Co) [24,27,28,33]. Other structural parameters of ThCrAsN, such as the height of As from the Cr plane and As-Cr-As bond angle, are not distinct from those of LaCrAsO, which accounts for their close properties.

TABLE I. Crystallographic data of ThCrAsN at 300 K obtained by the Rietveld refinement shown in Fig. 1(a). The space group is P4/nmm (No. 129). The occupancy of each atom was fixed to be 1.0, and the temperature factors were fixed to avoid unphysical negative values. Selected structural parameters of LaCrAsO are also listed for comparison [4]. h_{As} in the table denotes the height of As from the Cr plane.

Atom	Wyckoff	x	У	z	$B_{\rm iso}$ (Å ⁻²)
Th	2c	0.25	0.25	0.1341(1)	0.1
Cr	2a	0.75	0.25	0.5	0.3
As	2c	0.25	0.25	0.6673(3)	0.3
N	2b	0.75	0.25	0	1
Compounds Lattice parameters		ThCrAsN		LaCrAsO [4]	
a (Å)		4.0290(1)		4.0412(3)	
c (Å)		8.8522(3)		8.9863(7)	
$V(Å^3)$		143.70(1)		146.76(2)	
c/a		2.197		2.224	
Selecte	d distances				
$h_{\rm As}$ (Å)		1.481(3)		1.460(2)	
d _{Th-N/La-O} (Å)		2.338(1)		2.364(1)	
d _{Cr-As} (Å)		2.500(2)		2.494(1)	
$d_{\text{Cr-Cr}}$ (Å)		2.8489(1)		2.8576(3)	
Bond a	ngle				
As-Cr-As (deg)		107.36(10)		108.26(8)	

B. Electrical resistivity

The resistivity data $[\rho(T)]$ for ThCrAsN_{1-x}O_x are plotted in Fig. 2. As seen in Fig. 2(a), $\rho(T)$ curves show a similar metallic behavior, regardless of the doping concentration. The magnitudes of resistivity are about $1 \text{ m}\Omega$ cm at room temperature, comparable to that of LaCrAsO [4]. Only the samples of x = 0.8 and 0.9 show a slightly higher resistivity due to the increased impurity proportion. Although the measured values of resistivity are affected by the contacts and impurity, the residual resistivity ratios for all samples are between 2 and 3. The data below 20 K for x = 0.2, 0.3, 0.4, 0.5, and 0.7 are enlarged in the inset of Fig. 2(a) so that the curves differentiate from each other. It is easily noticed that all curves but x = 0.9approach to constant values at 2 K. To examine the possibility that superconductivity emerges under lower temperatures, we measured $\rho(T)$ (30 mK < T < 0.8 K) of several selected compounds in the dilution refrigerator, which are displayed in Fig. 2(b). However, the data of $\rho(T)$ are almost constant below 0.8 K and show no signs for superconductivity. Hence, superconductivity cannot be induced in ThCrAsN $_{1-x}O_x$ even though the real electron-doping concentration is as high as 0.75 (n = 4.75), against the prediction of a superconductivity phase at n > 4.2 [20].

C. Magnetic properties

Figure 3(a) shows the $\chi(T)$ curve for the parent compound ThCrAsN under the magnetic field 1 T and there is no difference between zero-field-cooling and field-cooling data. Below 160 K, the susceptibility shows a Curie-Weiss-like



FIG. 2. Temperature dependences of resistivity (ρ) for ThCrAsN_{1-x}O_x. (a) $\rho(T)$ curves with T > 2 K. The inset zooms in the data between 2 and 20 K for x = 0.2, 0.3, 0.4, 0.5, and 0.7. (b) Data of $\rho(T)$ with 30 mK < T < 0.8 K collected in the dilution refrigerator. The specimens with the same composition exhibit different residual resistivity in panels (a) and (b), due to variations in contact resistance and electrode size across different measurements.

tail, which may be caused by trace amounts of paramagnetic impurity. Above 160 K, the susceptibility increases with the temperature monotonically and shows a gentle slope around 850 K, suggesting ThCrAsN is an antiferromagnet. The $\chi(T)$ behavior of ThCrAsN is reminiscent of the cases for polycrystalline SrCr₂As₂, which also shows no Curie-Weiss behavior below 900 K and no clear AFM transition [7]. In addition, LaCrAsO only shows a smooth maximum at 520-570 K [4]. The behaviors of $\chi(T)$ for these Cr₂As₂-based materials are considered as the character of a two-dimensional (2D) antiferromagnet, which means that strong 2D AFM correlations may set in well above the ordering temperature (T_N) [4]. Since the actual T_N could be notably lower than the maximum in the susceptibility for 2D AFM compounds, here we use the derivative $d(\chi T)/dT$ to extract T_N of ThCrAsN, as plotted in the inset [7,34,35]. $d(\chi T)/dT$ shows an AFM transition peak



FIG. 3. Temperature dependences of the magnetic susceptibility (χ) measured at 1 T for (a) ThCrAsN and (b) ThCrAsN_{0.9}O_{0.1}. The small kink around 50 K in panel (b) is due to the oxygen contamination. $d(\chi T)/dT$ is plotted as a function of T in the insets.

at about 630 K, indicating T_N of ThCrAsN is on the same level with most Cr₂As₂-based materials [4,7,23,36,37].

 $\chi(T)$ for ThCrAsN_{0.9}O_{0.1} under 1 T is displayed in Fig. 3(b), which is quite akin to that of ThCrAsN. Yet the AFM order was not suppressed by the oxygen doping. As shown in the inset of Fig. 3(b), T_N of ThCrAsN_{0.9}O_{0.1} is determined to be ~820 K from $d(\chi T)/dT$, even higher than the parent. In addition, the susceptibility maximum of ThCrAsN_{0.9}O_{0.1} appears at higher temperature than ThCrAsN, indicative of stronger 2D correlations. $\chi(T)$ curves for other ThCrAsN_{1-x}O_x samples are shown in Fig. S2 in the SM [32]. Unfortunately, the susceptibility data for other samples are not informative because of the strong background from the robust magnetic impurities. Nevertheless, we can still draw the conclusion that the susceptibility data show no sign of Meissner effect in ThCrAsN_{1-x}O_x.

D. Magnetic energies

To determine the magnetic structure of ThCrAsN and its oxygen-doped derivatives, we examined the magnetic energies (E_m) for several possible AFM structures by performing



FIG. 4. Calculated magnetic energies (black squares, left axis) and Cr spin moments (red circles, right axis) for (a) ThCrAsN and (b) ThCrAsO with different spin configurations. The notations for the magnetic structures are as follows: NM denotes nonmagnetic states; A denotes A-type AFM order (in-plane FM order and out-of-plane AFM coupling); C denotes C-type AFM order (in-plane checkerboard AFM order and out-of-plane FM coupling); G denotes G-type AFM order (in-plane checkerboard AFM order and out-of-plane AFM coupling); S denotes the structure with in-plane striped AFM order and out-of-plane FM coupling. The spin configurations are presented at the top of the figure.

DFT calculations. E_m is defined as the energy difference between the spin-polarized state and the nonmagnetic state. The selected spin configurations are presented in Fig. 4, as well as the corresponding E_m and Cr spin moments. E_m and Cr spin moments are calculated for both ThCrAsN and ThCrAsO, in spite of the failure of synthesis for the latter.

As shown in Fig. 4(a), all magnetic orders lower the total energy of ThCrAsN, compared to the nonmagnetic state. Among them G-type AFM order is the most stable magnetic structure, yet C-type spin configuration has a pretty close energy. The similar E_m values for G-type and C-type AFM orders demonstrate the interplane spin coupling for ThCrAsN is weak, consistent with the characteristic of 2D AFM order. Note that the calculated E_m of G-type and C-type AFM orders for LaCrAsO are also reported to be close [4]. And the spin structure of LaCrAsO is experimentally determined to be G type. Based on the comparable behaviors of χ -T and the results of E_m calculations, it is plausible to anticipate that ThCrAsN has a G-type order, like LaCrAsO. In addition, the G-type AFM order was found to be the ground state for Cr-based 122-type coumpounds like BaCr₂As₂, BaCr₂P₂, SrCr₂As₂, EuCr₂As₂, Sr₂Cr₃As₂O₂, and Sr₂Cr₂AsO₃ [6–8,11,23,38], which also supports our speculation of the magnetic structure of ThCrAsN.

To gain a deeper insight into the magnetic ordering of ThCrAsN, we calculate the exchange interactions between the Cr neighbors in light of a simple Heisenberg model [39]. The magnetic energies of C-type, G-type, and S-type AFM orderings can be expressed as

$$E_{\rm C} = (-2J_1 + 2J_2 + J_c)S^2, \tag{1}$$

$$E_{\rm G} = (-2J_1 + 2J_2 - J_c)S^2, \qquad (2)$$

$$E_{\rm S} = (-2J_2 + J_c)S^2, \tag{3}$$

where *S* is the local spin, and $J_1/J_2/J_c$ refer to the interactions of in-plane nearest neighbor, in-plane next-nearest neighbor, and out-of-plane nearest neighbor, respectively. The values of energies for ThCrAsN could be found in Table S2 in the SM [32]. Solutions of the equations are

$$J_1 = (-E_{\rm G} - E_{\rm S})/2S^2, \tag{4}$$

$$J_2 = (E_{\rm C} - E_{\rm G} - 2E_{\rm S})/4S^2,$$
 (5)

$$J_c = (E_{\rm C} - E_{\rm G})/2S^2.$$
 (6)

Assuming the Cr spin moment of ThCrAsN is $2.5\mu_B$ [S = 1.25, according to Fig. 4(a)], the resulting interactions are $J_1 = 187.9$ meV, $J_2 = 62.1$ meV, and $J_c = 0.66$ meV, consistent with the stability conditions of G-type AFM order that $J_1 > 0$, $J_1 > 2J_2$, and $J_c > 0$. The small positive J_c value confirms the AFM coupling between the adjacent Cr₂As₂ layers is weak, in good agreement with the $\chi(T)$ behavior. The large positive values of J_1 and J_1/J_2 indicate that in-plane Cr-Cr direct interaction is dominant, thus the high Néel temperature and robust G-type AFM order is explicit. We also notice that the calculated energies E_C , E_G , and E_S for ThCrAsN, as well as the Cr moment, are all close to the values for LaCrAsO [4]. Hence the resultant J_1 and J_2 are almost the same as the interactions for ThCrAsN.

 E_m and Cr spin moments of ThCrAsO (3 d^5 for Cr, one electron more compared to ThCrAsN) with the same magnetic structures as ThCrAsN are shown in Fig. 4(b). The calculation indicates that G-type order is still the ground state of ThCrAsO, although its E_m is significantly lower than ThCrAsN. And the corresponding Cr spin moment is reduced slightly to be 2.43 μ_B . That is to say, AFM order of ThCrAsN is to a certain extent suppressed by electron doping. However, the G-type magnetic order remains for the end member ThCrAsO.

Here we would like to point out that J_1 and J_2 values for LaFeAsO both are about 50 meV/ S^2 , which are close and conspicuously smaller than the values for ThCrAsN [40]. The competition of exchange interactions in FeSCs leads to the collinear (or bicollinear) AFM order, contrary to the case for ThCrAsN. And the next-nearest-neighbor interaction J_2 is generally believed to play an important role in the electron pairing mechanism of FeSCs [41,42].



FIG. 5. (a),(d) Total electronic density of states of G-type AFM ordered ThCrAsN and ThCrAsO, respectively. Insets of (a) and (d) zoom in on the DOS around the Fermi energy. (b),(c),(e),(f) Projected density of states of 3*d* orbitals of Cr in ThCrAsN and ThCrAsO, respectively. The contributions of d_{xz} and d_{yz} are combined because they are degenerate.

The magnetic structures and exchange interactions clearly point to the distinction between Cr_2As_2 -based materials and FeSCs.

E. Density of states

The total DOS of G-type AFM ordered ThCrAsN and ThCrAsO are calculated and plotted in Fig. 5, as well as their projected density of states (PDOS) of Cr 3*d* orbitals. Both ThCrAsN and ThCrAsO show a relatively large DOS at the Fermi energy (E_F), coinciding with the typical metallic behavior of ThCrAsN_{1-x}O_x. As shown in Fig. 5(a), the DOS of ThCrAsN around E_F is mainly contributed by Cr 3*d* and As 4*p* orbitals. And it is easy to recognize the modest hybridizations between Cr 3*d* and As 4*p* in the inset. The *d*-*p* hybridizations account for the itinerant magnetism and the reduced Cr 3*d* magnetic moment of ThCrAsN (theoretically 4 μ_B for Cr²⁺).

The DOS of ThCrAsO is shown in Fig. 5(d). DOSs for ThCrAsN and ThCrAsO are largely comparable, and the $E_{\rm F}$ of ThCrAsO shifts to a higher position due to its nominal Cr $3d^5$ electron configuration. The similarities of DOSs can be seen better in other panels about the PDOS of Cr. Cr 3d electrons still dominate the states around the $E_{\rm F}$ of ThCrAsO, but the hybridizations between Cr 3d and As 4p is negligible compared to ThCrAsN.

To compare the PDOS of Cr 3*d* orbitals for ThCrAsN and ThCrAsO more clearly, we divide the orbitals into two groups and present the curves in Figs. 5(b) and 5(e) $(d_{xy}, d_{yz} + d_{xz})$ and Figs. 5(c) and 5(f) $(d_{z^2}, d_{x^2-y^2})$, respectively. The itinerant magnetism of ThFeAsN and ThFeAsO is confirmed by the broad energy bands. We notice that the orbital occupations of

Cr for both ThCrAsN and ThCrAsO are highly spin polarized, indicating the crystal field splitting energy is small so that Hund's rule is followed. The high-spin state is also observed for LaCrAsO and LaMnAsO, while the spin polarization for LaFeAsO is much weaker [4,40]. For ThCrAsN, the PDOS at $E_{\rm F}$ comes from all five 3d orbitals, and the $d_{x^2-y^2}$ and $d_{yz} + d_{xz}$ contribute substantially. The heavy proportion of the $d_{r^2-v^2}$ orbital means enhanced direct exchange at $E_{\rm F}$, consistent with the G-type AFM order that is favored by the nearest Cr-Cr interactions. After the replacement of nitrogen by oxygen, the DOS of $d_{x^2-y^2}$ and d_{xy} decline sharply, meanwhile the contributions from d_{z^2} increase significantly, preceded only by $d_{vz} + d_{xz}$. Whether for ThCrAsN or ThCrAsO, there is a heavy mixing of the t_2 and e orbitals at E_F , which is deemed detrimental to high- T_c superconductivity in some theoretical work [43].

IV. CONCLUDING REMARKS

To summarize, we have successfully synthesized a new 1111-type material, ThCrAsN. Then we explored the possibility of superconductivity by electron doping in ThCrAsN through O^{2-} substitution for N³⁻. However, ThCrAsN_{1-x}O_x shows no sign of superconductivity with the oxygen concentration from 0 to 75%, inconsistent with the theoretical predictions. Magnetic susceptibility of ThCrAsN indicates its AFM ground states with an ordering temperature about 630 K, and DFT calculations imply the most probable spin structure for ThCrAsN and the doped variants is G type, the same as LaCrAsO and ACr_2As_2 (A = Sr, Ba, Eu), although

further examination of the magnetic structure with powder neutron scattering is still required. The analysis of the exchange interactions between Cr neighbors indicates in-plane direct interaction J_1 is dominant, resulting in the robust G-type AFM order of ThCrAs(N,O). Although the superconductivity could not be induced by electron doping in ThCrAsN, the AFM order is moderately suppressed, manifested by the reduced magnetic energy and Cr spin moment of ThCrAsO. In addition, the PDOSs of Cr show that the spin polarization for ThCrAsN and ThCrAsO is strong, which is a major difference from the DOS of LaFeAsO.

Since the pairing mechanism in FeSCs is still under debate, it is hard to elucidate the reasons for the absence of superconductivity in electron-doped ThCrAsN. Nevertheless, the distinctions between Cr2As2-based materials and FeSCs are explicit. In general, high- T_c superconductivity develops after a magnetic ordering is suppressed, suggesting the interplay between superconductivity and magnetism is crucial. G-type AFM order is usually found to be the ground state for Cr₂As₂-based compounds, which is apparently distinguished from collinear or bicollinear AFM orders for FeSCs. Essentially, the exchange interactions between Cr (or Fe) neighbors shape the magnetic structures and may be related to the superconducting pairing. And the different spin polarizations for FeSCs and Cr-based materials are also not inconsiderable. In addition, the electronic correlations may play an important role as well. In fact, an angle-resolved photoemission

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spectroscopy study shows that $BaCr_2As_2$ is much less correlated than $BaFe_2As_2$ [44]. The absence of superconductivity in Cr_2As_2 -based materials calls for an in-depth theoretical explanation.

Although the comparability of Cr-based compounds and Fe-based counterparts is highlighted in some theoretical works based on the doped-Mott scenario, their similarities should not be overestimated in respect to our work and other available experiments. Yet the possibility of superconductivity in Cr-based materials is not ruled out. We hope further experiments, such as high-pressure measurements and hole doping in the synthesis, will suppress the magnetic ordering and give rise to superconductivity in Cr_2As_2 -based materials.

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