

Ion-exchange synthesis and superconductivity at 8.6 K of $\text{Na}_2\text{Cr}_3\text{As}_3$ with quasi-one-dimensional crystal structure

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A Cr-based quasi-one-dimensional superconductor $\text{Na}_2\text{Cr}_3\text{As}_3$ was synthesized by an ion-exchange method in a sodium naphthalenide solution. The crystals are threadlike and the structure was analyzed by x-ray diffraction with a noncentrosymmetric hexagonal space group $P-6m2$ (No. 187), in which the $(\text{Cr}_3\text{As}_3)^{2-}$ linear chains are separated by Na^+ ions, and the refined lattice parameters are $a = 9.239(2) \text{ \AA}$ and $c = 4.209(6) \text{ \AA}$. The measurements for electrical resistivity, magnetic susceptibility, and heat capacity reveal a superconducting transition with unconventional characteristic at 8.6 K, which exceeds that of all previously reported Cr-based superconductors.

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I. INTRODUCTION

The discoveries of Cu-based and Fe-based high- T_c superconductors have vitalized extensive research interests in the unconventional superconductivity associated with magnetic instability especially among $3d$ transition metal compounds during the last 30 years [1–3]. Recently, the early transition metal Cr-based binary compound CrAs was found to undergo a superconducting transition at 2 K on the border of a helical antiferromagnetic order upon applying external pressure [4,5], which is significantly different from the several previously reported Cr-containing alloy superconductors [6–11]. Soon after, superconductivity was discovered at ambient pressure in new types of Cr-based ternary compounds $\text{A}_2\text{Cr}_3\text{As}_3$ and ACr_3As_3 ($A = \text{K}, \text{Rb}, \text{or Cs}$) which show very particular quasi-one-dimensional (Q1D) crystal structure and evidences for fascinating spin-triplet electron pairing [12–16]. This Cr-based superconducting family has attracted intense interests and is providing a platform for the understanding of unconventional superconductivity.

For the exploration of new superconductors, chemical pressure effect has been an effective tool to tune the crystal structure and the electronic properties for obtaining new superconductors or achieving higher T_c , which is usually realized by substituting part of the structural motif or ions with equivalent ones but different spacial sizes, and it causes a relative change of crystal lattice analogous to external physical pressure effect. This is typically illustrated in the iron-oxypnictide superconductors, as the superconducting T_c dramatically increases from 26 K of $\text{LaO}_{1-x}\text{F}_x\text{FeAs}$ to 55 K of $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$ by the substitution of $[\text{La}_2\text{O}_2]^{2+}$ with smaller $[\text{Sm}_2\text{O}_2]^{2+}$ [3,17,18]. For the superconductors $\text{A}_2\text{Cr}_3\text{As}_3$ ($A = \text{K}, \text{Rb}, \text{Cs}$), the crystal structure can be regarded as Q1D infinite $(\text{Cr}_3\text{As}_3)^{2-}$ linear chains which are separated by columns of alkali metal

cations A^+ within a noncentrosymmetric hexagonal crystal lattice with the space group $P-6m2$ (No. 187) [12–14]. The $(\text{Cr}_3\text{As}_3)^{2-}$ chain structure is regarded as the key unit to be responsible for the occurrence of superconductivity [19–21]. It was proved that replacing K^+ with larger Rb^+ or Cs^+ in $\text{K}_2\text{Cr}_3\text{As}_3$ results in decreasing T_c from 6.1 to 4.8 K and 2.2 K, which indicates a positive chemical pressure effect in the $\text{A}_2\text{Cr}_3\text{As}_3$ superconductors [12–14,22]. But contrarily, the superconducting T_c of $\text{K}_2\text{Cr}_3\text{As}_3$ decreases monotonically under external physical pressures revealed by several reports, which demonstrates a negative physical pressure effect on T_c [23–25]. This discrepancy possibly originated from the unique Q1D anisotropic crystal structure which has different electronic responses on the chain structure and interchain coupling to the chemical pressure and physical pressure, respectively [25]. Consequently, the only way to achieve higher T_c in this system might be replacing A^+ with much smaller monovalent ions of Na^+ or Li^+ , but all attempts to synthesize $\text{Na}_2\text{Cr}_3\text{As}_3$ or $\text{Li}_2\text{Cr}_3\text{As}_3$ by conventional high-temperature solid-state reaction method or single crystal growth failed in the past 3 years [26].

In this paper we report the successful synthesis of the metastable Q1D $\text{Na}_2\text{Cr}_3\text{As}_3$ compound using a soft chemistry method. The $\text{Na}_2\text{Cr}_3\text{As}_3$ is obtained by the spontaneous ion-exchange reaction that has been more widely utilized for layered materials previously [27–29]. We find superconductivity in this Cr-based compound by electrical resistivity, magnetic susceptibility, and heat capacity characterizations with a much enhanced T_c of 8.6 K.

II. EXPERIMENTAL DETAILS

The single crystals of $\text{Na}_2\text{Cr}_3\text{As}_3$ were prepared by ion-exchange method with sodium naphthalene solution (Naph.-Na) in tetrahydrofuran (THF) using $\text{K}_2\text{Cr}_3\text{As}_3$ crystals as the precursor. At first the high-quality $\text{K}_2\text{Cr}_3\text{As}_3$ crystals were grown by a high-temperature solution growth method as

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previously reported [12,30]. A 0.1 M Naph.-Na was prepared by dissolving an equimolar amount of naphthalene and sodium into THF which was dehydrated with molecular sieves (4A). Then, 10 mg as-grown rodlike $\text{K}_2\text{Cr}_3\text{As}_3$ crystals were immersed into 7.5 mL Naph.-Na in a Teflon liner and loaded into an autoclave, and the Naph.-Na was excessed to ensure the ion-exchange process was sufficient with K:Na molar ratio close to 1:17. The autoclave was tightly sealed, and heated in a muffle furnace at 373 K for 50–100 h. After cooling down to room temperature, the obtained samples were thoroughly washed with THF several times. All sample preparation procedures were carried out in a glove box (O_2 , H_2O < 0.1 ppm) filled with high-purity Ar gas.

The obtained $\text{Na}_2\text{Cr}_3\text{As}_3$ crystals are extremely unstable in air, and any exposure to air should be avoided when performing measurements on them. The crystal structure was characterized at room temperature by both powder x-ray diffraction (PXRD) using a PAN-analytical x-ray diffractometer and single-crystal x-ray diffraction (SXRD) using a Bruker single crystal x-ray diffractometer with $\text{Cu-K}\alpha$ radiation. The chemical composition was analyzed with both Phenom scanning electron microscopy (SEM) with an energy-dispersive spectrometer (EDS) and inductively coupled plasma-atomic emission spectroscopy (ICP). The resistivity and heat capacity were measured with a Quantum Design physical property measurement system by the standard four-probe method and relaxation method, respectively. The dc magnetic susceptibility measurement was performed with a Quantum Design magnetic property measurement system under zero-field-cooling (ZFC) and field-cooling (FC) modes from 2 to 10 K under a magnetic field of 10 Oe.

III. RESULTS AND DISCUSSION

The XRD patterns are shown in Fig. 1. Due to the Q1D crystal morphology of the sample, the grains are highly oriented after being powderized, hence the PXRD data only show the peaks of $(hk0)$ without the information associated with the c axis. On the other hand, the patterns collected by SXRD on a bundle of crystals show more complete diffraction

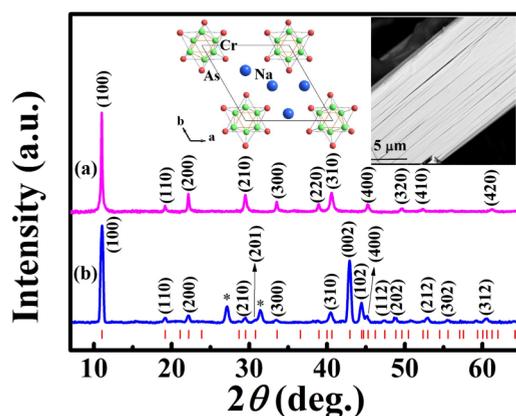


FIG. 1. The XRD patterns for $\text{Na}_2\text{Cr}_3\text{As}_3$ samples collected by (a) PXRD and (b) SXRD. The left inset is the hexagonal lattice structure of $\text{Na}_2\text{Cr}_3\text{As}_3$, and the right inset shows the SEM micrograph of $\text{Na}_2\text{Cr}_3\text{As}_3$ crystals.

peaks for the lattice planes. We note that our attempt to resolve the crystal structure by SXRD on a single piece of crystal all failed due to the split of all crystals during the ion exchange procedure. The XRD patterns are both well indexed with the hexagonal lattice structure with space group $P-6m2$ (No. 187) as that of $\text{K}_2\text{Cr}_3\text{As}_3$, except for two impurity peaks marked with asterisks [12,23]. The impurity is possibly Cr_2O_5 or some unknown phase which might be induced by oxidation during the experimental process due to the high activity of the $\text{Na}_2\text{Cr}_3\text{As}_3$ phase. The crystal lattice structure is also shown as the inset in Fig. 1. From the XRD patterns, the lattice parameters were refined to be $a = 9.239(2)$ Å and $c = 4.209(6)$ Å. The corresponding theoretical calculations for Bragg peaks are indicated by the vertical bars for a clear view. Comparing with $\text{K}_2\text{Cr}_3\text{As}_3$ [12,23], the interchain distance shrinks obviously along the a axis (about 7.6% from the $\text{K}_2\text{Cr}_3\text{As}_3$ precursor), while the Q1D chain structure shrinks very slightly along the c axis ($\sim 0.5\%$), which causes a primary chemical pressure perpendicular to the linear $(\text{Cr}_3\text{As}_3)^{2-}$ chain structure by the replacement of K^+ with much smaller Na^+ . The morphology of the Q1D threadlike crystals is shown by the SEM image as the inset in Fig. 1. The atomic ratio of Na:Cr:As measured by EDS on the sample surface is close to 2:3:3, which is also confirmed by the results of ICP with bulk measurements [30]. We note that no K^+ ion is detected, and the result proves that the $\text{K}_2\text{Cr}_3\text{As}_3$ precursors are fully converted to the $\text{Na}_2\text{Cr}_3\text{As}_3$ compound.

The temperature dependence of resistivity for the $\text{Na}_2\text{Cr}_3\text{As}_3$ crystal is characterized from 1.8 to 300 K at zero field with the electrical current along the c axis as illustrated in Fig. 2(a), which exhibits metallic behavior in the normal state, and a sudden superconducting transition is observed at low temperature. Notably, the onset superconducting T_c is 8.6 K as shown in the inset in Fig. 2(a), which is distinctly enhanced by 41% than that of the $\text{K}_2\text{Cr}_3\text{As}_3$ precursor (~ 6.1 K) and being the highest T_c in all previously reported Cr-based superconductors [4,5,12–16]. The width of the superconducting

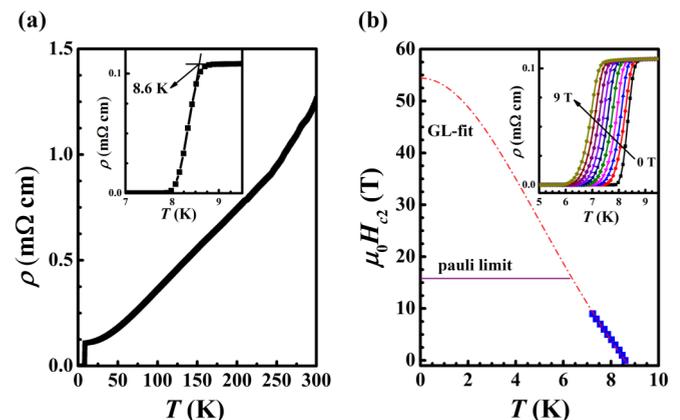


FIG. 2. (a) The temperature dependence of resistivity for $\text{Na}_2\text{Cr}_3\text{As}_3$ crystals, and the inset exhibits the enlarged view for the superconducting transition. (b) The derived upper critical field with GL theory and the Pauli paramagnetic limit for $\text{Na}_2\text{Cr}_3\text{As}_3$ crystals, and the inset represents the superconducting transition under different magnetic fields from 0 to 9 T.

transition is less than 1 K. The room temperature resistivity is about 1.3 m Ω cm, and the residual resistivity ratio (RRR) is about 12, which is much lower than that of K₂Cr₃As₃ single crystal (RRR \sim 60) [15,23]. The lower RRR value is possibly due to the increase of electron scattering by the crystal defects or lattice distortions induced during the ion-exchange process, as observed in impurity doped K₂Cr₃As₃ [31]. In the normal state the temperature dependence of resistivity deviates from linear behavior, which is similar with that of the single crystals of K₂Cr₃As₃ [23]. To further characterize the superconductivity under magnetic field, we measured the temperature dependence of resistivity under different magnetic fields from 0 to 9 T to study the upper critical field ($\mu_0 H_{c2}$) with the field perpendicular to the *c* axis and the electrical current along the *c* axis. The temperature dependence of resistivity at low temperature is shown in the inset in Fig. 2(b). Upon applying the magnetic field, the superconducting transition shifts to lower temperature slowly. The onset superconducting T_c under different magnetic fields is determined the same way as illustrated in the inset in Fig. 2(a), and the temperature dependence of $\mu_0 H_{c2}$ is depicted in Fig. 2(b). The $\mu_0 H_{c2}(T)$ data are fitted with the Ginzburg-Landau theory $\mu_0 H_{c2}(T) = \mu_0 H_{c2}(0)(1 - t^2)/(1 + t^2)$, here $t = T/T_c$, and the zero-temperature upper critical field $\mu_0 H_{c2}(0)$ is estimated to be 54 T. Considering Pauli paramagnetic limited $\mu_0 H_p = 1.84 T_c \approx 16$ T [32], the extrapolated $\mu_0 H_{c2}(0)$ is much higher than the Pauli paramagnetic limit for weak coupling conventional BCS superconductor. This gives a strong indication for the unconventional superconductivity in Na₂Cr₃As₃, which is also observed previously in A₂Cr₃As₃, ACr₃As₃, Li_{0.9}Mo₆O₁₇, and Sr₂RuO₄ superconductors [12–16,33,34].

To further confirm the superconductivity in Na₂Cr₃As₃, the temperature dependence of dc magnetization and heat capacity for the crystals were characterized and shown in Fig. 3. The dc magnetization data of Na₂Cr₃As₃ were collected under a magnetic field of 10 Oe which was perpendicular to the *c* axis. Both FC and ZFC data show the diamagnetic transition below an onset T_c of 8.1 K as shown in Fig. 3(a), which is consistent with the results of resistivity measurement. The

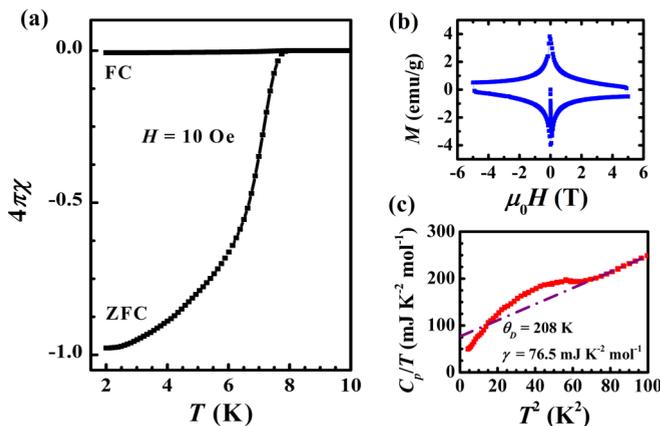


FIG. 3. (a) The temperature dependence of magnetic susceptibility for Na₂Cr₃As₃ crystals. (b) Isothermal magnetization at 2 K from -5 to 5 T. (c) The temperature dependence of heat capacity depicted as C_p/T vs T^2 with linear fitting in the normal state.

shielding volume fraction from ZFC data is nearly 100% at 2 K, suggesting bulk superconductivity in Na₂Cr₃As₃, while the much smaller value of FC susceptibility data indicates strong magnetic flux pinning effect caused by crystal defects. Figure 3(b) shows the isothermal magnetization data at 2 K with magnetic field from -5 to 5 T, and it reveals the behavior of a typical type-II superconductor for Na₂Cr₃As₃.

The temperature dependence of heat capacity is depicted as a relationship of C_p/T vs T^2 , which is shown in Fig. 3(c). The heat capacity of a common metal can be linearly fitted with $C_p/T = \gamma + \beta T^2$, which contains the contributions from electrons and phonons. When fitting the data with the above formula in the normal state, we obtained the Sommerfeld coefficient γ as 76.5 mJ K⁻² mol⁻¹, and Debye temperature θ_D as 208 K calculated from $\theta_D = [(12/5)NR\pi^4/\beta]^{1/3}$. Comparing with K₂Cr₃As₃, the close values of large γ indicate similar strong electron correlations in Na₂Cr₃As₃ [12], while the Debye temperature is a little lower. We note that there might be considerable experimental errors for these fitted parameters due to the difficulty in handling the very active Na₂Cr₃As₃ samples. The clear heat capacity anomaly is observed at about 8 K, suggesting the occurrence of a superconducting phase transition. This result further confirms the superconductivity observed in resistivity and magnetization measurements. However, the smaller value of electronic heat capacity jump $\Delta C_p/\gamma T_c$ (\sim 0.69) and the wider transition width compared with that of K₂Cr₃As₃ indicates the low sample quality with amounts of defects produced during the ion exchange process [12].

The lattice parameters upon the change of A⁺ ionic radius for all the existing A₂Cr₃As₃ (A = Na, K, Rb, or Cs) superconductors are summarized in Fig. 4(a) [12–14]. It shows that when decreasing the cation radius from Cs⁺ to Na⁺, the hexagonal crystal lattice shrinks very little along the Q1D (Cr₃As₃)²⁻ chain direction (the *c* axis), while it shrinks obviously along the *a* axis, which indicates enhanced interchain interactions and nearly unaltered inner-chain structure upon the chemical pressure from cation substitution [12–14,22]. This makes it much different with the hydrostatic physical pressure effect which is more isotropic [23–25]. Correspondingly, as shown in Fig. 4(b), the superconducting T_c increases dramatically from

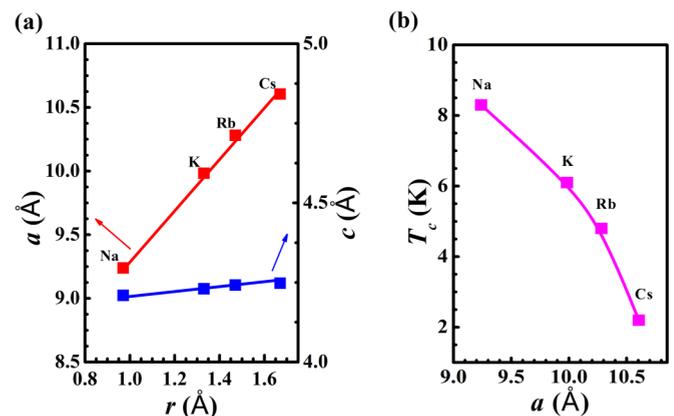


FIG. 4. (a) The variation of lattice parameters with the change of A⁺ ionic radius in A₂Cr₃As₃. (b) Superconducting T_c changes with the lattice parameter *a*.

2.2 to 8.6 K (about 4 times enhancement) by the replacement of alkali metal cation from Cs^+ to Na^+ , which shows very large positive chemical pressure effect on T_c in this Cr-233 superconducting family, and it also indicates the strong correlations between superconductivity and the interchain coupling. Hence it might be feasible to further increase the T_c in this family by reducing the interchain distance through chemical replacement with smaller cations like Li^+ . It is worth to point out that for the Cr-133 superconductors, the superconductivity shows a negative chemical pressure effect with the T_c decreasing from 7.3 K of RbCr_3As_3 to 5 K of KCr_3As_3 [15,16]. The discrepancy in these two series of superconductors is interesting and deserves more investigations.

In summary, we synthesized a Cr-based Q1D ternary compound $\text{Na}_2\text{Cr}_3\text{As}_3$ through the ion-exchange method, and superconductivity was discovered in this compound with

the transition temperature of 8.6 K, which is the highest T_c in all Cr-based superconductors. The characterizations of resistivity and heat capacity revealed unconventional superconductivity with strong electronic correlations in $\text{Na}_2\text{Cr}_3\text{As}_3$. The dramatic enhancement of T_c in this $\text{A}_2\text{Cr}_3\text{As}_3$ series indicates large chemical pressure effect on superconductivity.

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