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Unconventional superconductivity in quasi-one-dimensional Rb₂Cr₃As₃

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(Received 8 December 2014; revised manuscript received 20 January 2015; published 30 January 2015)

Following the discovery of superconductivity in quasi-one-dimensional $K_2Cr_3As_3$ containing $[(Cr_3As_3)^{2-}]_{\infty}$ chains (J. K. Bao *et al.*, arXiv:1412.0067), we succeeded in synthesizing an analogous compound, Rb₂Cr₃As₃, which also crystallizes in a hexagonal lattice. The replacement of K by Rb results in an expansion of the *a* axis by 3%, indicating a weaker interchain coupling in Rb₂Cr₃As₃. Bulk superconductivity emerges at 4.8 K, above which the normal-state resistivity shows a linear temperature dependence up to 35 K. The estimated upper critical field at zero temperature exceeds the Pauli paramagnetic limit by a factor of 2. Furthermore, the electronic specific-heat coefficient extrapolated to zero temperature in the mixed state increases with \sqrt{H} , suggesting the existence of nodes in the superconductor in the Cr₃As₃-chain based system.

DOI: 10.1103/PhysRevB.91.020506

Superconductivity (SC) infrequently appears in quasi-onedimensional (O1D) crystalline materials primarily because of the Peierls instability towards a state of the charge-density wave [1,2]. An additional disadvantage of Q1D systems for SC may come from the possible realization of a Luttinger liquid, as well as the reduced density of states when the Fermi level $(E_{\rm F})$ does not incidentally locate at the van Hove singularities. Nevertheless, 1D systems have long been studied theoretically [3] owing to their inherent simplicity and, the discovery of SC in Q1D Bechgaard salts [4] has attracted sustained research interest [5]. Examples of inorganic Q1D superconductors include $Li_{0.9}Mo_6O_{17}$ [6] and $Tl_2Mo_6Se_6$ [7], in which the Mo 4d electrons bear relatively weak electron correlations. Nevertheless, peculiar properties were revealed in $Li_{0.9}Mo_6O_{17}$ [8–10], and a possible triplet SC was proposed [11].

Very recently, we discovered bulk SC at 6.1 K in a Q1D pnictide $K_2Cr_3As_3$ in which correlated Cr 3d electrons are involved [12]. The crystal structure is characterized by $[(Cr_3As_3)^{2-}]_{\infty}$ double-walled subnanotubes in which $Cr_{6/2}(As_{6/2})$ face-sharing octahedron chains constitute the inner (outer) wall. The intrachain Cr-Cr bond distances (2.6-2.7 Å) are close to those in Cr metal, indicating a dominant metallic bonding along the chain direction. In comparison, the shortest interchain Cr-Cr distance is as large as 7.3 Å, and a much weaker (if not negligible) interchain overlap of Cr 3d orbitals is expected. Thus, the material is really Q1D, at least in the sense of chemical bonding as well as crystal structure. This material hosts a series of peculiar physical properties including a large Sommerfeld coefficient of 70–75 mJ K^{-2} mol⁻¹, a linear temperature dependence of resistivity from 7 to 300 K, and high upper critical fields exceeding the Pauli limit by a factor over 3. The first-principles calculations [13] indicate that the electrons around $E_{\rm F}$ are PACS number(s): 74.70.-b, 74.62.Bf, 74.25.Bt

dominated by the Cr 3*d* states, which form two Q1D Fermi surface (FS) sheets and one three-dimensional (3D) FS pocket. The calculated "bare" density of state (DOS) at E_F is less than 1/3 of the experimental value from the specific-heat measurement, confirming the electron correlation effect. In addition, ferromagnetic instability and/or ferromagnetic spin fluctuations are revealed, which favor spin-triplet Cooper pairing. These experimental and theoretical-calculation results suggest unconventional SC in K₂Cr₃As₃.

In Q1D systems, the interchain coupling plays a crucial role in the competition between SC and the charge- or spin-density wave. For example, unlike Tl₂Mo₆Se₆, which remains metallic and superconducts at 4.2 K [14], Rb₂Mo₆Se₆ undergoes a metal-insulator transition at ~170 K, which is explained in terms of a dynamical charge-density wave owing to the reduced interchain hopping [14]. Thus, the appearance of SC in K₂Cr₃As₃ suggests a significant interchain coupling, as revealed by the existence of 3D FSs. Therefore, it is of considerable interest to investigate the effect of interchain coupling by the elemental replacement (e.g., Rb for K) in the spacer columns. Furthermore, it is important to check whether the unconventional SC is a common feature in Q1D Cr-based pnictides.

In this Rapid Communication, we report the synthesis, structural characterization, and physical property measurement of an analogous material, $Rb_2Cr_3As_3$. Indeed, a weaker interchain coupling is signatured by the obviously expanded interchain distance. Nevertheless, bulk superconductivity at a little lowered temperature of 4.8 K was observed, accompanied with a mildly reduced Sommerfeld coefficient of 55 mJ K⁻² mol⁻¹. Remarkably, unconventional SC is evidenced by the electrical transport and the thermodynamic properties.

The Rb₂Cr₃As₃ polycrystalline sample was synthesized by solid-state reactions in a sealed vacuum. First, the starting materials (Rb piece, Cr powder, and As piece), all of high purity (\geq 99.9%, Alfa Aesar), were weighed in a nearly stoichiometric ratio (with 3% excess of Rb in order to compensate for the loss of Rb in the process of the solid-state

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reaction), and the mixture was loaded in a quartz ampoule. The quartz ampoule was evacuated $(<10^{-2}$ Pa) and sealed, followed by slowly heating in a muffle furnace to 523 K for 15 h. After the first stage reaction, the mixture was homogenized by grinding, pressed into pellets, and put into an alumina tube which was then sealed by arc welding in argon atmosphere in a Ta tube. The sealed Ta tube, jacketed by an evacuated quartz ampoule, was then sintered at 973 K for 24 h. This procedure was repeated to allow a full solid-state reaction. The obtained sample was sensitive to air, and it should not be exposed to air as much as possible. Note that all the operations of weighing, mixing, grinding, pelletizing, etc., were carried out in an argon-filled glove box with a water and oxygen contents of less than 0.1 ppm.

Powder x-ray diffraction (XRD) was carried out at room temperature on a PANalytical x-ray diffractometer (Model EMPYREAN) with monochromatic Cu $K\alpha_1$ radiation. To avoid exposure to air, the sample powder was mixed with a small amount of Apiezon N grease before putting on the sample holder, and the sample was in vacuum during the XRD data collection. The crystal structure parameters were refined based on the K₂Cr₃As₃-type structure [12] by a Rietveld analysis with the code RIETAN-FP [15]. Note that the XRD data of $2\theta = 8^{\circ}-25^{\circ}$ were not included for the refinement to avoid the extrinsic influence from the N grease.

We conducted the electrical, magnetic, and heat capacity measurements on a physical property measurement system (Quantum Design, PPMS-9) and a magnetic property measurement system (Quantum Design, MPMS-5). The electrical resistivity was measured using a standard four-electrode method. The as-prepared $Rb_2Cr_3As_3$ pellet was cut into a thin rectangular bar, and gold wires were attached onto the sample's surface with silver paint. The heat capacity was measured by a thermal relaxation method using a squareshaped sample plate (9.0 mg). The temperature dependence of dc magnetic susceptibility was measured in the protocols of zero-field cooling (ZFC) and field cooling (FC) under a field of 10 Oe. The dc magnetization was also measured as a function of magnetic field at 2 K.

Figure 1 shows the XRD profile of the Rb₂Cr₃As₃ sample. The reflections can be well indexed by a hexagonal unit cell whose size is slightly larger than that of K₂Cr₃As₃, and no obvious impurity phase can be identified. The Rietveld refinement was successful, and the resulting structural parameters are listed in Table I. Compared with $K_2Cr_3As_3$, the *a* axis is 3.0% larger, while the c axis is expanded by only 0.28%. Since the a axis just measures the interchain distance [see the inset of Fig. 1(b)], one may expect a weaker interchain interaction in Rb₂Cr₃As₃. This is further revealed by the enlargement of the interchain Cr-Cr distance (from 7.30 Å in K₂Cr₃As₃ to 7.63 Å in Rb₂Cr₃As₃), while the average Cr-Cr bond distance remains almost unchanged. Also, the $[(Cr_3As_3)^{2-}]_{\infty}$ column itself suffers significant modifications. The Cr2-Cr2 bond distance of the Cr2 triangle in the z = 0 plane *decreases* by 4.5%, and the Cr1-Cr1 bond distance in the z = 0.5 plane *expands* by 1.5%, as compared with those in $K_2Cr_3As_3$. Consequently, the geometry of the Cr octahedron becomes inverse.

Figure 2(a) shows the temperature dependence of resistivity $\rho(T)$ for the Rb₂Cr₃As₃ polycrystalline sample. The $\rho(T)$ shows metallic conduction and, similar to that in K₂Cr₃As₃,



FIG. 1. (Color online) (a) Powder x-ray diffraction of the Rb₂Cr₃As₃ polycrystalline sample protected by the Apiezon *N* grease, which is indexed by a hexagonal unit cell. (b) Rietveld refinement profile for the powder x-ray diffraction with $25^{\circ} \leq 2\theta \leq 120^{\circ}$. $R_{\rm wp}$ and *S* denote the weighted profile reliable factor and "goodness-of-fit" parameter, respectively. The inset shows the crystal structure projected along the **c** axis.

a T-linear resistivity can also be seen, albeit in a narrower temperature range from 5 to 35 K. This indicates a non-Fermi-liquid (NFL) behavior, if it is not an accidental phenomenon due to a "polycrystal effect" [16]. The origin of the NFL behavior could be related to a Tomonaga-Luttinger liquid state [17], which is characteristic of a 1D fermion system [3,18]. Nonetheless, superconductivity emerges below 4.8 K with a transition width $\Delta T_{\rm c} = 0.44$ K [$\Delta T_{\rm c} = T(90\%\rho_{\rm n}) T(10\%\rho_n)$, where ρ_n refers to the extrapolated normalstate resistivity at the superconducting transition midpoint]. This ΔT_c value is obviously larger than that (0.24 K) of $K_2Cr_3As_3$, which seems to be related to the relatively weak interchain coupling in Rb₂Cr₃As₃. Other explanations of the broadening of superconducting transition include less inhomogeneity and/or larger stresses in the present polycrystalline sample.

Upon applying magnetic field, T_c decreases monotonically, as shown in Fig. 2(b), from which the upper critical field H_{c2} can be determined using the conventional criteria of $90\%\rho_n$. The resulting H_{c2} is plotted as a function of temperature in

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TABLE I. Comparison of crystallographic data and some physical parameters of A_2 Cr₃As₃ [A = K [12] and Rb (present work)]. The atomic coordinates are as follows: As1 (x, -x,0); As2 (x, -x,0.5); Cr1 (x, -x,0.5); Cr2 (x, -x,0); A1 (x, -x,0.5); A2 (1/3,2/3,0). T_c , ΔT_c , H_{c2} , γ_n , θ_D , and ΔC denote the superconducting critical temperature, transition width, upper critical field, electronic specificheat coefficient, Debye temperature, and dimensionless specific-heat jump, respectively.

Space group	$\frac{K_2Cr_3As_3}{P\overline{6}m2}$	$\begin{array}{c} \operatorname{Rb}_2\operatorname{Cr}_3\operatorname{As}_3\\ P\overline{6}m2 \end{array}$
a (Å)	9.9832(9)	10.281(1)
<i>c</i> (Å)	4.2304(4)	4.2421(3)
V (Å ³)	365.13(6)	388.32(5)
Coordinates (x)		
As1 (3 <i>j</i>)	0.8339(2)	0.8382(2)
As2 (3k)	0.6649(4)	0.6727(2)
Cr1 (3 <i>k</i>)	0.9127(3)	0.9140(2)
Cr2 (3 <i>j</i>)	0.8203(6)	0.8333(3)
A1 (3k)	0.5387(4)	0.5372(1)
A2 (1c)	0.3333	0.3333
Bond distances		
Cr1-Cr1 (Å)	2.614(9)	2.654(4)
Cr1-Cr2 (Å)	2.612(2)	2.603(2)
Cr2-Cr2 (Å)	2.69(1)	2.570(3)
Physical property parameters		
$T_{\rm c}$ (K)	6.1	4.8
$\Delta T_{\rm c}$ (K)	0.24	0.44
$\mu_0 (dH_{c2}/dT)_{T_c}$ (T/K)	-7.43	-5.08
$\gamma_n (mJ/K^2/mol)$	70–75	55
$\theta_{\rm D}$ (K)	215-218	175
$\Delta C/(\gamma_{\rm n}T_{\rm c})$	2.0-2.4	1.8

Fig. 2(c). The initial slope $\mu_0 (dH_{c2}/dT)_{T_c}$ is -5.08 T/K. If using the empirical Ginzburg-Landau relation [19], $H_{c2}(T) = H_{c2}(0)(1-t^2)/(1+t^2)$, where t denotes a reduced temperature T/T_c , the upper critical field at zero temperature $[\mu_0 H_{c2}(0)]$ is estimated to be ~20 T. Alternatively, the orbital limited upper critical field $\mu_0 H_{c2}^{orb}(0)$ can be estimated by the Werthammer-Helfand-Hohenberg model [20,21], which yields $\mu_0 H_{c2}^{\text{orb}}(0) = -0.693T_c (d\mu_0 H_{c2}/dT)_{T_c} \approx 17 \text{ T for an}$ isotropic full superconducting gap in the dirty limit and without spin-orbit coupling. Both the $\mu_0 H_{c2}(0)$ values exceed the Pauli paramagnetic limited upper critical field of $\mu_0 H_{\rm P} = 1.84 T_{\rm c} \approx$ 9.0 T (also for an isotropic full superconducting gap without spin-orbit coupling) [22,23]. Note that the $H_{c2}(T)$ data were measured on the polycrystalline sample, and one may expect a higher $H_{c2}(0)$ for **H** $\parallel c$. A similar phenomenon of large $H_{c2}(0)$ beyond the Pauli limit was reported in Q1D Li_{0.9}Mo₆O₁₇ [10], which was regarded as evidence of spin-triplet SC [11]. For the Q1D superconductor $Tl_2Mo_6Se_6$ ($T_c = 4.2$ K), in comparison, the measured $\mu_0 H_{c2}(0)$ values are 5.8 and 0.47 T, respectively, for magnetic fields parallel and perpendicular to the c axis [14], both of which are less than the Pauli-limited upper critical field.

In order to verify whether the observed SC is of a bulk nature, we performed dc magnetic susceptibility measurements in both ZFC and FC modes under a 10 Oe magnetic field. Indeed, a superconducting diamagnetic transition can be seen

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FIG. 2. (Color online) (a) Temperature dependence of the electrical resistivity for Rb₂Cr₃As₃. The inset show the linear temperature dependence from 5 to 35 K. (b) Superconducting transitions under magnetic fields up to 8 T. (c) The upper critical field as a function of temperature. The dashed line denotes a Ginzburg-Landau (GL) fit. The Pauli-limit field ($\mu_0 H_P = 1.84T_c$) is labeled by the horizontal line.

at $T_c = 4.8$ K in Fig. 3(a). The volume fraction of magnetic shielding scaled by $4\pi \chi_{ZFC}$ is 91% at 2 K after the correction of the demagnetization effect, suggesting bulk SC. In contrast, the volume fraction of magnetic repulsion ($4\pi \chi_{FC}$) is merely 1.6%. This could be due to the magnetic flux pinning in the process of cooling down under magnetic fields. It is also noted that the diamagnetic transition width is significantly broadened, compared with K₂Cr₃As₃ [12], consistent with the above resistivity measurement result. Figure 3(b) shows the field dependence of magnetization at 2 K, indicating an extreme type-II SC with a very small lower critical field (below 40 Oe). The magnetic flux pinning effect is evident from the magnetic hysteresis loop.

Figure 4 shows the temperature dependence of specific heat [C(T)] in the low-*T* regime, plotted in a C/T vs T^2 scale. In a short temperature range from 4.8 to 6 K, the C/T vs T^2 is essentially linear, and the linear fit with a formula $C/T = \gamma_n + \beta T^2$ yields an intersect of $\gamma_n = 55.1$ mJ K⁻² mol⁻¹ and a slope of $\beta = 2.9$ mJ K⁻⁴ mol⁻¹. The γ_n value refers to the normal-state Sommerfeld coefficient, which is lower but comparable to that of K₂Cr₃As₃ (70–75 mJ K⁻² mol⁻¹) [12]. With the fitted β value, and using the formula $\theta_D = [(12/5)NR\pi^4/\beta]^{1/3}$, the Debye temperature can be calculated to be 175 K, which is reasonably smaller than that in K₂Cr₃As₃ (215–218 K).

Bulk SC is further confirmed by the characteristic specificheat jump $[\Delta(C)]$ below 4.8 K. In general, the phonon contribution to the specific heat in the superconducting state



FIG. 3. (a) Temperature dependence of magnetic susceptibility (scaled by $4\pi\chi$) for the Rb₂Cr₃As₃ polycrystals. The inset zooms in the superconducting transition in the field-cooling (FC) mode. (b) Field dependence of magnetization at 2 K. The magnetic field was applied in the order of $0 \rightarrow 5 \text{ T} \rightarrow -5 \text{ T} \rightarrow 5 \text{ T}$.

follows the relation fitted from the normal-state C(T) data. Hence the electronic specific heat $[C_e(T)]$ can be obtained by the deduction of βT^3 from the total C(T) [24]. The inset of Fig. 4(a) shows the obtained $C_e(T)$ (normalized by $\gamma_n T$) as a function of temperature. By the entropy conserving construction, the thermodynamic transition temperature is determined to be 4.4 K. The dimensionless specific-heat jump at $T_c [\Delta C/(\gamma_n T_c)]$ is about 1.8, substantially lower than that (2.0–2.4) in K₂Cr₃As₃, which seems to be related to the reduced interchain coupling. Here we are unable to make a reasonable fit for the $C_e(T)$ dependence because of the limitation of the temperature range (only down to $0.43T_c$).

To examine whether the superconducting gap has nodes, we investigated the magnetic field dependence of the electronic specific heat $C_e(T,H)$ which gives the information about the low-energy excitations in the superconducting state. For a conventional fully gapped type-II superconductor, the excited states are basically the "normal-state quasiparticles" in the vortex cores. This generates an additional Sommerfeld coefficient of $\gamma(H) \approx \frac{H}{H_2(0)}\gamma_n$ at zero temperature in the superconducting mixed state [25]. At zero field, the linear extrapolation of C/T vs T^2 gives a "residual" Sommerfeld coefficient of $\gamma_0 = 5.3$ mJ K⁻² mol⁻¹, which could be either due to the existence of a small fraction (~10%) of the nonsuperconducting phase, or because of the existence of quasiparticles from impurity scattering in the case of nodal superconductivity. With increasing magnetic fields, $\gamma(H)$ increases faster than the full-gap prediction, especially at

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FIG. 4. (Color online) Low-temperature specific-heat data for Rb₂Cr₃As₃, plotted with C/T vs T^2 . The inset of (a) shows the normalized electronic specific heat $C_e(T)/(\gamma_n T)$ as a function of temperature. (b) presents the C(T) data under magnetic fields, from which the zero-temperature Sommerfeld coefficients in the superconducting mixed state $\gamma(H)$ can be extrapolated. The inset displays the $\gamma(H)$ dependence, in which the theoretical prediction for a nodal (full) superconducting gap is shown by the solid (dotted) line.

lower fields. Further, $[\gamma(H) - \gamma_0]$ basically obeys the Volovik relation (i.e., $\propto \sqrt{H}$) [26], suggesting the presence of nodes in the superconducting gap.

It is informative to compare the two the Cr₃As₃-chain based superconductors, K₂Cr₃As₃ and Rb₂Cr₃As₃, whose structural and physical parameters are listed in Table I. The "anisotropic" expansion of the *a* axis suggests a weaker interchain coupling in Rb₂Cr₃As₃, which could account for the broadening of the superconducting transition and a reduced $\Delta C/(\gamma_{\rm n}T_{\rm c})$ value. Nevertheless, superconductivity emerges at a comparable temperature, and the variation of $T_{\rm c}$ (decreased by 21%) basically scales with the change in γ_n (decreased by 22%) which measures the DOS at $E_{\rm F}$. If this is not an incidental phenomenon, one may expect higher T_c for a larger γ_n value. The estimated upper critical field exceeding the Pauli limit by a factor of 2 can be a hint for spin-triplet Cooper pairing. In addition, the existence of nodes in the superconducting order parameter, as suggested by the thermodynamic analysis, does not contradict with the spin-triplet scenario. Although much work needs to be done for the details of the superconducting order parameter, the fact that the only two existing members [27] in the Q1D Cr-based family so far both show evidence of unconventional SC suggests that the unconventionality should be a common phenomenon in the Cr_3As_3 -chain based system.

This work was supported by the National Basic Research Program of China (Grant No. 2011CBA00103), the NSFC (Grant No. 11190023), and the Fundamental Research Funds for the Central Universities of China.

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