LETTER

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Superconductivity at 7.3 K in the 133-type Cr-based $RbCr_3As_3$ single crystals

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Abstract – Here we report the preparation and superconductivity of the 133-type Cr-based quasi–one-dimensional (Q1D) $RbCr_3As_3$ single crystals. The samples were prepared by the deintercalation of Rb^+ ions from the 233-type $Rb_2Cr_3As_3$ crystals which were grown from a high-temperature solution growth method. The $RbCr_3As_3$ compound crystallizes in a centrosymmetric structure with the space group $P6_3/m$ (No. 176) different from its non-centrosymmetric $Rb_2Cr_3As_3$ superconducting precursor, and the refined lattice parameters are $a = 9.373(3)$ Å and $c = 4.203(7)$ Å. Electrical resistivity and magnetic susceptibility characterizations reveal the occurrence of superconductivity with an interestingly higher onset T_c of 7.3 K than other Cr-based superconductors, and an estimated high upper critical field $H_{c2}(0)$ about 72.4 T in this 133-type $RbCr_3As_3$ crystals.

Recently a new family of Cr-based superconductors $A_2Cr_3As_3$ (A = K, Rb, Cs) was reported and attracted a lot of interest for the study of unconventional superconductivity in more 3d-transition-metal compounds [1–6]. These $A_2Cr_3As_3$ compounds have a particular quasi–one-dimensional (Q1D) hexagonal crystal lattice with non-centrosymmetric symmetry, which is formed with infinite Q1D $(Cr_3As_3)^{2-}$ linear chains separated by alkali-metal cations. By replacing the K^+ ions with larger Rb^+ or Cs^+ ions, the superconducting T_c decreases dramatically from 6.1 K to 4.8 K and 2.2 K, respectively, which indicates a distinct positive chemical pressure effect on its superconductivity upon lattice changing similar to the iron-based superconductors [7–9], although characterizations under external physical pressure on $K_2Cr_3As_3$ give a monotonically reduced T_c with increasing pressure [10,11]. More interestingly, previous experimental and theoretical researches revealed rich physics in these $A_2Cr_3As_3$ superconductors but inconsistent results about spin-triplet or singlet paring superconductivity [4,12–17]. Nevertheless, these $A_2Cr_3As_3$ compounds are extremely reactive when exposed in air and easily oxidized during most experimental procedures, which hinders many further studies for its intrinsic physical characteristics. Lately, by deintercalating half of the A^+ ions using ethanol from the $A_2Cr_3As_3$ lattice, another type of Q1D compounds ACr_3As_3 (A = K, Rb, Cs) with similar crystal structure but centrosymmetric lattice was obtained, while physical studies on these 133-type polycrystalline samples reported a spin-glass ground state at low temperatures [18,19]. However, by preparing single-crystalline samples of KCr_3As_3 and employing a delicate annealing process to improve the crystal quality, we recently found superconductivity with an onset T_c of 5 K in this air-stable 133-type KCr_3As_3 [20].

In this letter we report the preparation and characterization of the 133-type Cr-based $RbCr_3As_3$ single crystal, which has an interestingly enhanced onset superconducting T_c at 7.3 K.

The single crystals of $RbCr_3As_3$ were prepared by the deintercalation of Rb^+ ions from $Rb_2Cr_3As_3$ precursors, similar to our previous report of KCr_3As_3 [20].

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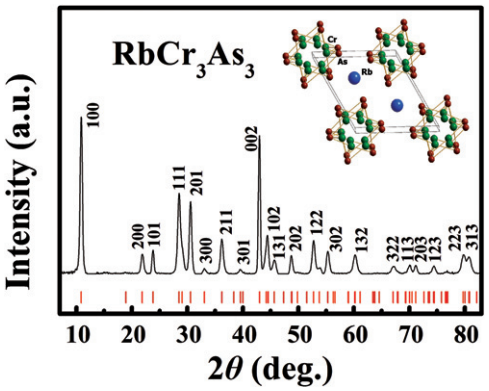

Fig. 1: (Colour online) The XRD patterns for the $RbCr_3As_3$ samples, and the vertical bars represent the position of calculated Bragg peaks. The insert depicts the crystal structure of $RbCr_3As_3$.

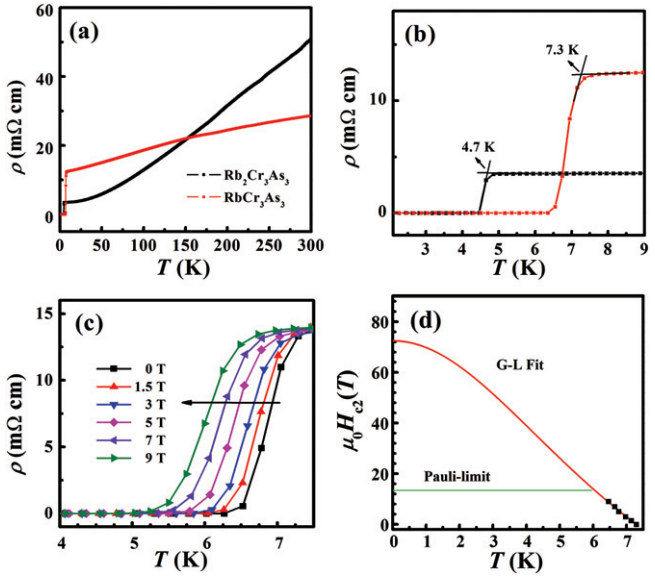

Fig. 2: (Colour online) (a) Temperature dependence of electrical resistivity for single crystals of $Rb_2Cr_3As_3$ and $RbCr_3As_3$. (b) Enlarged view for the resistive superconducting transitions. (c) The resistive transitions under different magnetic fields for $RbCr_3As_3$ from 0 T to 9 T. (d) Derived upper critical field and the Pauli paramagnetic limit for $RbCr_3As_3$.

At first, high-quality single crystals of $Rb_2Cr_3As_3$ were grown out of the RbAs and CrAs mixture using a high-temperature solution growth method [1]. Secondly, the as-grown $Rb_2Cr_3As_3$ single crystals were immersed in pure dehydrated ethanol and kept for one week for the fully deintercalation of Rb^+ ions at room temperature. The obtained samples were washed by ethanol thoroughly. To further improve the sample quality, the as-prepared crystals were annealed in an evacuated quartz tube at 373 K for 10 h [20]. All the experimental procedures were performed in a glove box filled with high-purity Ar gas to avoid introducing impurities. The obtained $RbCr_3As_3$ crystals are quite stable in air at room temperature.

The crystal structure of the $RbCr_3As_3$ single crystals was characterized at room temperature by a Bruker single-crystal X-ray diffractometer (SXRD) using Cu-K_α radiation. The electrical resistivity was measured in a Quantum Design physical property measurement system (PPMS) by the standard four-probe method, and the dc magnetization was measured by a Vibrating Sample Magnetometer (VSM) system under zero-field-cooling (ZFC) and field-cooling (FC) modes, respectively.

The XRD patterns collected from the $RbCr_3As_3$ samples at room temperature are presented in fig. 1. We note that the data were collected by SXRD on a bundle of crystals, and our efforts to resolve the crystal structure on a single piece of crystal all failed due to the difficulty to separate the crystals. All the diffraction peaks are well indexed with the hexagonal space group $P6_3/m$ (No. 176) as well as the previously reported 133-type compounds [19], and no other impurity phase is detected in the diffraction peaks. The vertical bars represent the theoretical calculations for Bragg peak positions of the Rb-133 phase. The crystal structure was refined by the least-square fit method, which gave the lattice parameters $a = 9.373(3)$ Å and $c = 4.203(7)$ Å. Compared with the $Rb_2Cr_3As_3$ precursor, the crystal lattice of $RbCr_3As_3$ shows an obvious shrinkage along the a-axis while little change along the c-axis by the ion deintercalation process. The schematic crystal structure of the Q1D hexagonal $RbCr_3As_3$ lattice is depicted as an inset in fig. 1. We note that the energy-dispersive X-ray spectroscopy (EDS) measurements on the crystal surface of $RbCr_3As_3$ crystals give the atomic ratio of Rb:Cr:As close to 1:3:3, which also verifies the chemical composition of the obtained samples.

The temperature dependence of electrical resistivity was characterized from 1.8 K to 300 K and the data are shown in fig. 2. Both resistivity curves of the $Rb_2Cr_3As_3$ and $RbCr_3As_3$ show a metallic behavior at the measured temperature range, and superconducting transitions are observed in both samples at low temperatures, which is in contrast with a previous report of spin-glass ground state for the polycrystalline Rb-133 sample [18]. The residual resistance ratio (RRR) of the $RbCr_3As_3$ (∼2.3) is much smaller than that of $Rb_2Cr_3As_3$ (∼15), indicating the still poor crystalline quality of the 133-type crystals mainly caused by the deintercalation process. Unexpectedly, for this 133-type $RbCr_3As_3$, the onset superconducting T_c is enhanced up to 7.3 K, which is much higher than that of the 233-type $Rb_2Cr_3As_3$ (∼4.7 K), and even higher than all other known Cr-based superconductors. We note that the crystals before annealing usually have much lower T_c with wider transitions which is caused by the poor sample quality. The higher T_c of Rb-133 than K-133 indicates a negative chemical pressure effect on T_c in these 133-type superconductors which is opposite to that of the 233-type superconductors. The superconducting transition width is less than 1 K for both samples. To estimate the upper critical field, we performed resistivity measurements with sweeping temperature under constant

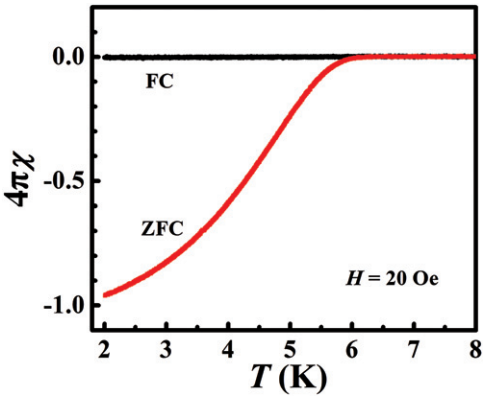

Fig. 3: (Colour online) Temperature dependence of magnetic susceptibility for the $RbCr_3As_3$ single crystals.

magnetic fields from 0 T to 9 T (with the field perpendicular to the c-axis and electrical current along the c-axis), and the data are shown in fig. 2(c). With magnetic field increasing, the superconducting transitions shift to lower temperatures systematically. The upper critical field $\mu_0 H_{c2}$ was depicted as a function of temperature in fig. 2(d), in which the $\mu_0 H_{c2}$ stands for each of the applied field and the temperature stands for the onset T_c. Considering the Ginzburg-Landau (GL) theory, $\mu_0 H_{c2}(\mathrm{T}) = \mu_0 H_{c2}(0)(1-t^2)/(1+t^2)$, here $t = T/T_c$, the zero-temperature upper critical field $\mu_0 H_{c2}(0)$ is estimated to be 72.4 T. We note that the orbital limited upper critical field from the Werthammer-Helfand-Hohenberg model is also estimated to be about 57.3 T. These values are much higher than the Pauli paramagnetic limited upper critical field $\mu_0 H_p = 1.84 T_c = 13.4\,\mathrm{T}$ [21], which gives an evidence for unconventional superconductivity in this $RbCr_3As_3$, and the quite large $\mu_0 H_{c2}$ also indicates possible potentials for future high field applications.

The temperature dependence of magnetic susceptibility for the $RbCr_3As_3$ single-crystal samples was characterized by a magnetic field of 20 Oe (perpendicular to the c-axis) and shown in fig. 3. The results indicate clear diamagnetic superconducting transitions with an onset T_c ~6.2 K. The shielding volume fraction at 2 K from the ZFC data is close to 100%, while the Meissner volume fraction from the FC data is quite small possibly due to the extremely strong flux pinning effect by remaining atomic defects inside the crystal lattice produced during the Rb^+ ions deintercalation process.

In conclusion, we successfully prepared the 133-type $RbCr_3As_3$ single crystals, and the resistivity and magnetization measurements show clear superconducting transitions with a higher onset temperature of T_c ~7.3 K than all other Cr-based superconductors, and a high upper critical field $H_{c2}(0)$ of about 72.4 T estimated by the GL fit. These 133-type superconductors also show a negative chemical pressure effect on T_c in contrast to the 233-type superconductors.

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