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Evidence of line nodes in superconducting gap function in K$_2$Cr$_3$As$_3$ from specific-heat measurements

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Abstract – We present low-temperature specific-heat measurements of the quasi-one-dimensional superconductors K$_2$Cr$_3$As$_3$. Our result shows a sharp specific-heat jump around $T_c$ $\sim$ 6.1 K with $\Delta C/\gamma c T_c$ $\sim$ 2.5, which is much larger than the BCS prediction for a weak-coupling superconductor. It indicates that this superconductor is in the strong-coupling regime. After subtracting the lattice contribution and the Schottky anomaly from the total specific-heat data, the low-temperature electronic specific heat is proportional to $T^3$ at different fields and also proportional to $\sqrt{T}$ at different temperatures below 2.5 K. These results indicate that line nodes are present in the superconducting gap function of K$_2$Cr$_3$As$_3$.

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Introduction. – The superconductivity in Cr-based materials has raised great interest recently. CrAs becomes superconducting with $T_c$ $\sim$ 2.2 K by applying pressure of 0.7 GPa [1]. Then, quasi-one-dimensional superconductors A$_2$Cr$_3$As$_3$ ($A$ = K, Rb, Cs) were discovered with $T_c$ $\sim$ 6.1 K for K$_2$Cr$_3$As$_3$ [2], 4.8 K for Rb$_2$Cr$_3$As$_3$ [3] and 2.2 K for Cs$_2$Cr$_3$As$_3$ [4], respectively. The one-dimensional structure of A$_2$Cr$_3$As$_3$ consists of [(Cr$_3$As$_3$)$^n$]$_\infty$ linear chains. The chains are composed of outer As$_3$ twisted tubes and inner Cr$_3$ twisted tubes and separated by alkali-metal cations. The chains and the alkali-metal cations form a hexagonal lattice with the space group $P6m2$ [2]. The upper critical field $H_{c2}$ of K$_2$Cr$_3$As$_3$ is as about three times larger than the Pauli-paramagnetic limit [2,5], indicating that it is a candidate for a multiband triplet paring state. And the field-angle and temperature dependence of $H_{c2}$ mostly resemble those of heavy-fermion superconductor UPt$_3$, also indicating a dominant spin-triplet superconductivity with odd parity in K$_2$Cr$_3$As$_3$ [6].

Besides the very large upper critical field, a number of experiments show unusual properties both in normal and superconducting states. The $^{75}$As NMR measurements of K$_2$Cr$_3$As$_3$ indicate that there is strong enhancement of Cr spin fluctuations above $T_c$. The observed power-law temperature dependence of the spin-lattice relaxation rate above $T_c$ is consistent with the Tomonaga-Luttinger liquid. The absence of the Hebel-Slichter coherence peak at $T_c$ suggests unconventional superconductivity [7]. The signature of the Tomonaga-Luttinger liquid was also observed in the angle-resolved photoemission spectrum (ARPES) measurements [8]. The $^{75}$As NQR measurements of Rb$_2$Cr$_3$As$_3$ show that the spin-lattice relaxation rate divided by temperature has a Curie-Weiss–like temperature dependence. And the Knight shift increasing with decreasing temperature suggests ferromagnetic spin fluctuation. The Hebel-Slichter peak is also absent as observed for K$_2$Cr$_3$As$_3$. Interestingly, the spin-lattice relaxation rate follows a $T^5$ variation below 3 K, pointing to the presence of point nodes in superconducting gap function [9]. However, the temperature dependence of superfluid density from magnetization and muon-spin relaxation or rotation ($\mu$SR) measurements is more consistent with a $d$-wave model with line nodes [10]. And the penetration depth measurements of K$_2$Cr$_3$As$_3$ show a linear temperature dependence for $T \ll T_c$, which indicates the line nodes in the superconducting gap function [11]. Thus, it is of

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great interest to clarify whether there exist point nodes or line nodes in the superconducting gap function by other experiments.

The first-principle band calculations on K$_2$Cr$_3$As$_3$ showed that the Fermi surfaces consist of two quasi-1D sheets and one 3D sheet. The electron density of states near the Fermi surface is dominated by Cr-3d orbitals [12]. Several theoretical models were proposed to investigate the pairing symmetry of K$_2$Cr$_3$As$_3$ [13–16]. For example, Wu et al. [13,14] developed tight-binding effective models based on the $d_{x^2}$, $d_{xy}$ and $d_{z^2}$ orbitals of the Cr$_2$ sublattice. They found the triplet $p_z$-wave paring is the leading paring symmetry in both weak- and strong-coupling limits and the gap function of the paring state possesses line gap nodes on the $k_z=0$ plane on the Fermi surfaces. Zhou et al. [15] proposed a minimal model based on three molecular orbital states and found that the dominant paring channel was always a spin-triplet. At small Hubbard $U$ and moderate Hund’s coupling $J_H$, a spin-triplet state with line nodal gap, $f_{y(3x^2−y^2)}$, at the 3D gamma band will dominate.

Specific-heat measurement is a useful tool to study the superconducting condensate and paring symmetry. In this paper, we report comprehensive experimental data of low-temperature specific heat of K$_2$Cr$_3$As$_3$ with an applied magnetic field up to 9T. After subtracting the lattice contribution and the Schottky anomaly from the total specific-heat data, the low-temperature electronic specific heat is proportional to $T^2$ at different fields, and proportional to $\sqrt{H}$ at different temperatures below 2.5 K, which indicate that line nodes are present in the superconducting gap function of K$_2$Cr$_3$As$_3$.

**Experiments.** – The single crystals of K$_2$Cr$_3$As$_3$ were prepared by the self-flux method similar to that in Bao et al. [2]. The magnetic susceptibility was measured on a SQUID vibrating sample magnetometer (VSM) system. The specific heat was measured using the thermal relaxation method on a Quantum Design instrument physical property measurement system (PPMS). The low-temperature specific-heat measurements in the range from 0.4 to 10K were performed with a $^3$He heat-pulsed thermal relaxation calorimeter attached to the PPMS in the magnetic field up to 9T. The field dependence of thermometer and addenda was carefully calibrated before the specific heat was measured.

**Results and discussions.** – Figure 1 shows the temperature dependence of the dc magnetic susceptibility.

Figure 2 shows the temperature dependence of the total specific heat at zero magnetic field with a $C/T \sim T^2$ plot. The temperature range is between 0.4K and 10K. And the sharp jump of the specific heat occurs at $T_c \sim 6.1$K, which indicates the high quality of the crystal. The total specific heat contains the contribution from electrons, phonons and the magnetic impurities (called Schottky anomaly). According to the Debye model, the lattice specific heat at low temperatures can be expressed by $\beta T^3$ approximately, and $\beta$ is independent of both field and temperature. So the total specific heat of the sample can be expressed as

$$C(T) = C_e(T) + \beta T^3 + C_{Sch},$$

where $C_e(T)$ is the electronic specific heat and $C_{Sch}$ is the Schottky anomaly contribution of the specific heat. The electronic specific heat in the normal state is proportional to $\gamma_e(T)$. So the slope $\beta$ of the $C/T \sim T^2$ plot defines the contribution of the lattice specific heat, and the extrapolation to zero temperature $\gamma_e(T)$ yields the electronic specific-heat part. According to the data at zero field, we get $\gamma_e = 71 \text{ mJ/molK}^2$ and $\beta = 1.45 \text{ mJ/molK}^4$. Then the
Debye temperature can be calculated to be 221 K. These are consistent with previous reports [2,17]. As shown in the inset of fig. 2, the specific-heat jump $\Delta C/\gamma_n T_c \sim 2.5$ at the superconducting transition is significantly larger than the BCS prediction for a weak-coupling superconductor (1.43). The electron-bosonic coupling constant $\lambda$ can be estimated by [18–21]

$$\lambda = \frac{1.04 + \mu^* \ln(\omega_n/1.2 T_c)}{(1 - 0.62 \mu^*) \ln(\omega_n/1.2 T_c) - 1.04}. \quad (2)$$

The logarithmic averaged bosonic frequency $\omega_n$ can be determined by

$$\Delta C/\gamma_n T_c = 1.43[1 + 53(T_c/\omega_n)^2 \ln(\omega_n/3T_c)]. \quad (3)$$

Taking coulomb pseudopotential $\mu^* = 0.1$ and $T_c = 6.1$ K, we get $\omega_n = 53.0$ K and $\lambda = 1.5$. The large value of $\lambda$ confirms the strong-coupling nature of the superconducting pairing.

Below 1 K, we can observe a clear upturn, which is caused by the magnetic impurities contribution (Schottky anomaly). The upturn is suppressed at higher magnetic fields. In order to explore the intrinsic electronic specific-heat behavior under low temperature, we need to extract the electronic specific heat from the total specific heat by subtracting the lattice contribution and the Schottky anomaly.

Figure 3 shows the temperature dependence of the total specific heat at different fields up to 9 T ($H//ab$ plane). The superconducting transition temperature $T_c$ shifts to lower temperature with the increase of the applied magnetic fields. Using Werthammer–Helfand-Hohenberg formula [22], we obtain the $H_c(0) \approx 32.2$ T as shown in the inset of fig. 3, which is consistent with previous reports [2,5]. At low temperatures, the upturn of the specific heat is visible when the magnetic fields lower than 5 T and high fields ($H > 5$ T) suppress the upturn. The Schottky anomaly mainly comes from the Zeeman splitting of the paramagnetic impurities in the applied magnetic field. For a multilevel system, the change of the mean energy from Zeeman splitting can be expressed by

$$E_{Sch} = \sum_i E_i \exp(-E_i/k_B T)/\sum_i \exp(-E_i/k_B T), \quad E_i = M_J g \delta,$$

$$M_J = -S, -S + 1, \ldots, S - 1, S, \quad (4)$$

where $E_i$ is the energy of each level after the splitting. $g$ is the g-factor. $\delta$ is the energy of the level splitting. Taking the derivative with respect to the temperature on $E_{Sch}$ gives the Schottky anomaly contribution of the specific heat, as shown in

$$C_{Sch} = (3N_A \times n) dE_{Sch}/dT,$$

where $N_A$ is the Avogadro constant and $n$ is the concentration of paramagnetic centers per mole chromium. For $K_2Cr_3As_3$, we take $S = 3/2$ considering that the magnetic impurities may come from the $Cr^{3+}$. The parameter values of $n$ can be determined by the consideration of entropy conservation at $T_c$ for the second-order superconducting phase transition.

At zero field, the Schottky anomaly comes from the level splitting in the crystalline electric field [23]. We try to equivalently write the splitting of the energy level in the crystal field as $\delta = \delta_0$. The peak of the Schottky anomaly will shift to the higher temperature with the increase of $\delta_0$. We try to subtract the Schottky term with different parameter values of $\delta_0$ and $n$. Given a fixed $\delta_0$, the value of $n$ is determined by the equal entropy criteria. The temperature extrapolation below 0.4 K in $C_e/T \sim T$ plotting is done by the quadratic fitting of the data after subtracting the Schottky term in [0.4 K, 1.5 K]. After trying, we found that $\delta_0/k_BT = 0.5K$ and corresponding optimal $n = 4.6 \times 10^{-4}$ is consistent with the experimental results in zero field, otherwise the upturn cannot be subtracted under the entropy balance.

At non-zero applied magnetic field, our experiment data indicates that the energy of the level splitting is $\delta = \mu_B H$, where $\mu_B$ is the Bohr magneton. One possible reason might be due to the quench of the orbital angular momentum in $Cr^{3+}$ paramagnetic impurities. In applied magnetic field, the crystal field averages the orbital angular momentum $L_z$ to zero, so we only need to consider the spin contribution. Conducting the same way as zero field, the optimal values of $n$ are basically the same, which is self-consistent. So, we take $n = 4.6 \times 10^{-4}$ for all non-zero applied fields and zero field.

After subtracting the lattice contribution and the Schottky anomaly, we can get the temperature dependence of the electronic specific heat $C_e$ as shown in fig. 4(a). At low temperature, the data of electronic specific heat $C_e$ become smooth. Figure 4(b) shows the calculated Schottky anomaly at different fields ($H \leq 5$ T) and fig. 4(c) shows the temperature dependence of the entropy difference between the superconducting state and the normal state. We
can see that the conservation of entropy is maintained, which is an important criterion for the rationality of subtracting the Schottky anomaly.

Figure 5 shows the electronic specific heat of the sample at different fields from 0.4 K to 2.0 K. The solid lines are the linear fitting of $C_e/T$ with $T$. So we can conclude that $C_e(T)$ is proportional to $T^2$ at low temperatures ($T < 2.0$ K), which deviates from an s-wave fully gapped superconductor that should have an exponential temperature dependence. Assuming that the energy gap of a $p$-wave superconductor with line nodes can be written as $|\Delta(k)| = \Delta_0 |\cos \theta_k|$ [11], the density of states of quasiparticles $N(E)$ can be calculated by $N(E) = N_0 \frac{E}{\Delta_0} \frac{1}{\sqrt{E^2 - \Delta_0^2 \cos^2 \theta_k}}$. When $E \ll \Delta_0$, we can get $N(E) = \frac{\pi}{2} N_0 \frac{E}{\Delta_0}$. The total energy at $T \ll T_c$ is given by [24]

$$U(T) = \frac{3\gamma_n}{\pi k_B^2 \Delta_0} \int_0^\infty \frac{E^2}{\exp(E/\frac{\alpha}{T}) + 1} dE = 1.723 \frac{k_B \gamma_n T^3}{\Delta_0},$$

where $\gamma_n$ is the Sommerfeld constant. Then the specific heat $C_e$ at $T \ll T_c$ is $C_e = \frac{dT}{dT} = 5.17 \frac{k_B \gamma_n}{\Delta_0} T^2 = \alpha T^2$. So the temperature dependence of the electronic specific heat suggests that line nodes are present in the superconducting gap function of $K_2Cr_3As_3$. At zero field, the fitting of low-temperature data gives $\alpha \sim 7.8$. Then a ratio $\Delta_0/k_B T_c \sim 7.85$ can be obtained, which is significantly larger than that predicted for a $p$-wave superconductor in the weak-coupling limit. This fact implies that $K_2Cr_3As_3$ is a strong-coupling superconductor. The value of $\Delta_0/k_B T_c$ is larger than the penetration depth experiment results [11], which may be due to the neglect of anisotropy in our calculations [24].

Another typical behavior of the electronic specific heat for the superconductivity with line nodes is the $\sqrt{H}$ field dependence [25]. For a conventional $s$-wave superconductor, the low-energy density of states is dominated by the core bound states, which leads to the specific-heat scaling linearly with $H$. While for a superconductor with line nodes, Volovik pointed out that Doppler shift significantly influenced density of state and the low-energy density of states is dominated by extended quasiparticle states. The Volovik effect leads to the specific heat varying as $T \sqrt{H}$ in the limit $T \to 0$ [25]. Figure 6 shows the electronic specific heat of the sample at different low temperatures from 0 T to 9 T. The solid lines show the linear fitting of $C_e/T \sim T$.

![Figure 4](image1.png)

![Figure 5](image2.png)

![Figure 6](image3.png)
The presence of line nodes in the gap function of $K_2Cr_3As_3$ is consistent with both $p_z$-wave and $f$-wave spin-triplet pairing states proposed in theoretical calculations [13,15]. In the former case, the order parameter has a sign change along the $z$-direction; in the latter case, the sign change occurs in in-plane gap functions. These two states can be further distinguished by other experimental measurements. For example, the temperature dependences of the anisotropy of superfluid density in the two states are opposite [26]. The ARPES experiment below the superconductivity transition temperature with high-energy resolution can further determine the location of the nodal lines in momentum space.

Conclusions. – In summary, comprehensive low-temperature specific-heat data of $K_2Cr_3As_3$ have been measured at magnetic fields up to 9 T from 0.4 K to 10 K. We find that the temperature-dependent specific-heat coefficient scales linearly with $T$ at different fields after subtracting the Schottky anomaly and the field-dependent specific-heat coefficient scales with $\sqrt{H}$ at low temperatures. The detailed analysis of the specific-heat data indicates that line nodes are present in the superconducting gap function [14–16], and the exact paring symmetry of $K_2Cr_3As_3$ is a strong-coupling superconductor with nodal lines in the superconducting gap function. Our conclusion is consistent with the theoretical analysis of showing line nodes in the gap function [14–16], and the exact paring symmetry of $K_2Cr_3As_3$ needs to be validated by the ARPES study.

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