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Penetration depth measurements of $K_2Cr_3As_3$ and $Rb_2Cr_3As_3$

G.M. Pang [a], M. Smidman [a], W.B. Jiang [a], Y.G. Shi [c], J.K. Bao [a], Z.T. Tang [a], Z.F. Weng [a], Y.F. Wang [a], L. Jiao [a], J.L. Zhang [a], J.L. Luo [c], G.H. Cao [a,b], H.Q. Yuan [a,b,*]

[a] Center for Correlated Matter and Department of Physics, Zhejiang University, Hangzhou 310058, China
[b] Collaborative Innovation Center of Advanced Microstructures, Nanjing 210093, China
[c] Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Science, Beijing 100190, China

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ABSTRACT

The newly discovered superconductors $A_2Cr_3As_3$ (A=K, Rb, Cs), with a quasi-one-dimensional crystal structure have attracted considerable interest. The crystal structure consists of double-walled tubes of $[Cr_3As_3]^{2-}$ that extend along the c-axis. Previously we reported measurements of the change in London penetration depth of polycrystalline samples of $K_2Cr_3As_3$ using a tunnel diode oscillator based technique, which show a linear temperature dependence at low temperatures, giving evidence for line nodes in the superconducting gap. Here we report similar measurements of the penetration depth for polycrystalline $Rb_2Cr_3As_3$ and several single crystals of $K_2Cr_3As_3$, prepared by two different research groups. The single crystal measurements show similar behavior to polycrystalline samples down to 0.9–1.2 K, where a downturn is observed in the frequency shift for all single crystal samples. These results give further evidence for nodal superconductivity in $K_2Cr_3As_3$, which indicates that the superconducting pairing state is unconventional. The different low temperature behavior, observed in samples which have deteriorated after being exposed to air, emphasizes that it is necessary to properly handle the samples prior to being measured because the $A_2Cr_3As_3$ compounds are extremely air sensitive and evidence for nodal superconductivity from penetration depth measurements is only observed in the samples which display a sharp superconducting transition. Therefore further work is required to improve the quality of single crystals and to identify the origin of the downturn.

1. Introduction

Superconductivity in Cr-based compounds has recently attracted attention after the discovery that CrAs becomes superconducting with $T_c \approx 2$ K under an applied pressure of $p_c \approx 0.8$ GPa, where antiferromagnetism is suppressed [1]. Subsequently, a family of related superconductors $A_2Cr_3As_3$ (A=K, Rb, Cs) were also discovered, with a highest transition temperature of $T_c = 6.1$ K for $K_2Cr_3As_3$ [2–4]. The crystal structure of $A_2Cr_3As_3$ shown in Fig. 1 displays quasi-one-dimensional (q1D) structural features, namely $[(Cr_3As_3)^{2-}]^{\infty}$ double-walled tubes which extend along the c-axis, separated by alkaline metal cations. The structure of the tubes is shown in Fig. 1(b), where the inner tube consists of Cr atoms, surrounded by a tube of As atoms. Evidence for unconventional superconductivity in $K_2Cr_3As_3$ arises from the absence of a Hebel Slichter coherence peak in NMR measurements [5] and measurements of the London penetration depth [6]. We reported measurements of the London penetration depth on polycrystalline samples of $K_2Cr_3As_3$, where the samples with the sharpest superconducting transitions display linear behavior below about 1.4 K [6], which is a strong evidence for the presence of line nodes in the superconducting gap. The samples are also extremely air sensitive and measurements of samples with broadened superconducting transitions show $\Delta\lambda(T) \sim T^n$ dependence with $n > 1$, which emphasizes the necessity of studying high quality samples which have not partially decomposed.

A number of interesting properties of the normal state of $K_2Cr_3As_3$ have been reported such as a linear temperature dependence of the electrical resistivity between 7 and 300 K [2], and a temperature dependence of the spin relaxation rate from NMR measurements consistent with that of a Tomonaga–Luttinger liquid [5]. The specific heat shows a bulk superconducting transition and gives a large value of the Sommerfeld coefficient γ of around 70–75 mJ/mol K^2 [2], which indicates enhanced electronic correlations. Upon increasing the size of the alkaline metal cation A, there is a significant increase in the lattice parameter a and a reduction of T_c. This would suggest that increasing the interchain distance suppresses superconductivity, but seemingly the opposite result is obtained from measurements under pressure, where

* Corresponding author at: Center for Correlated Matter and Department of Physics, Zhejiang University, Hangzhou 310058, China.
E-mail address: hqyuan@zju.edu.cn (H.Q. Yuan).

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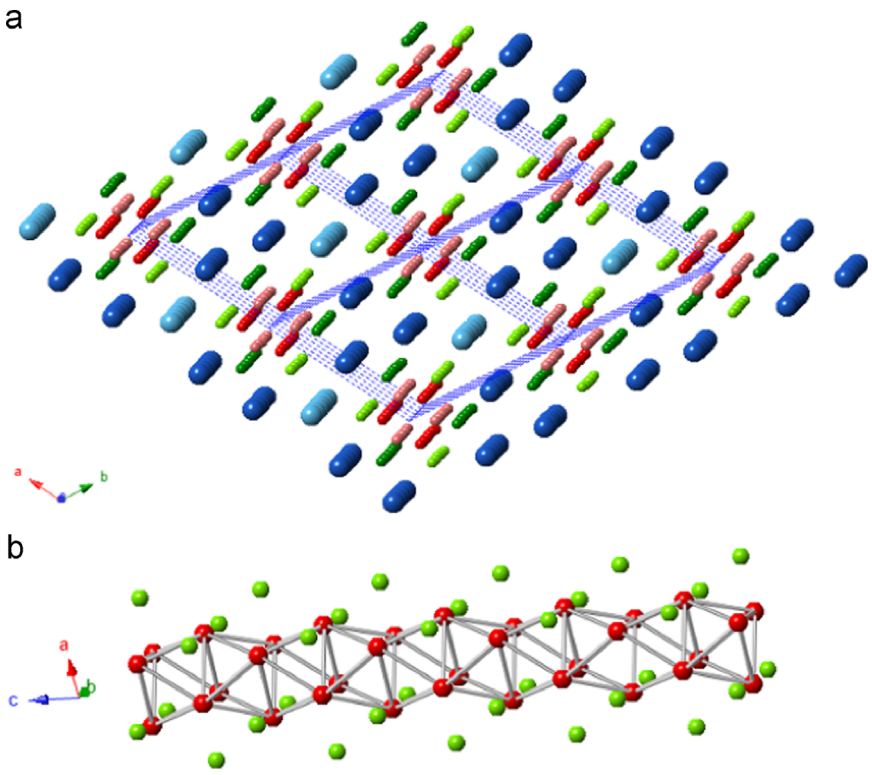

Fig. 1. (a) Crystal structure of $A_2Cr_3As_3$ (A=K, Rb, Cs), with the Cr atoms shown in red, As in green and A in blue. The two different colors for each element indicate the two inequivalent sites. The dashed lines mark the boundaries of the unit cell and the double walled nanotubes are located at the corners of four cells. (b) A sideways view of one of the nanotubes, showing both the Cr atoms on the inside and the As on the outside. The solid lines show how the atoms form face-sharing octahedra. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

increasing the pressure causes a decrease in the T_c of $K_2Cr_3As_3$ and $Rb_2Cr_3As_3$ [7]. This suggests that the superconductivity in $A_2Cr_3As_3$ is sensitive to distortions of the $[(Cr_3As_3)^{2-}]^{\infty}$ tubes [8].

It is therefore of interest to establish to what extent the superconductivity can be regarded as q1D and what is the nature of the pairing state in these compounds. The calculated electronic structure of $K_2Cr_3As_3$ is complex, with two one-dimensional Fermi surface sheets (α and β) and one anisotropic three dimensional sheet (γ) [9]. Theoretical studies using a three-band tight-binding model predict the dominant pairing states to be spin triplet, namely the p_z pairing state for small J/U and an f-wave state for large J/U [10,11], where U is the intra-orbital Coulomb repulsion and J is the Hunds coupling. The p_z state has a nodal plane at k_z=0, although the pairing amplitude is strongest on one of the q1D sheets, which are at fixed values of k_z and the gap is fully open and isotropic on these surfaces. The f-wave pairing is strongest on the 3D γ sheet, where there are line nodes in the ab plane. Initial measurements of the upper critical field (H_{c2}) showed large values with a small anisotropy [12]. The extrapolated value of $H_{c2}(0)$ was estimated to be about 31.2 T, which is much greater than the Pauli limiting value for weak coupling BCS superconductors of $1.84T_c \sim 11.2$ T, which was taken as evidence for triplet superconductivity. However, recent experiments performed at higher applied magnetic fields [13] demonstrate that a larger anisotropy develops at lower temperatures, which may indicate that contrary to the predictions of spin triplet superconductivity, paramagnetic limiting is present for fields applied along the chains but is absent for fields applied perpendicularly.

Linear behavior of the penetration has also been predicted to occur in measurements of polycrystalline superconductors as a result of Josephson coupling between different grains [14]. Muon spin rotation measurements of $K_2Cr_3As_3$ were unable to discriminate between nodal superconductivity and a fully gapped model with a smaller gap than the BCS value [15]. Therefore to confirm the intrinsic nature of the behavior of the London penetration depth, in this work we report measurements of single crystals using a tunnel diode oscillator (TDO) based technique. A downturn in the frequency shift (Δf) is consistently observed in all measured samples at around 0.9–1.2 K. However, above the downturn there is good agreement with the polycrystalline data and linear behavior extends from about 1.4 K to the onset of the downturn. Although further work is required to improve the quality of single crystal samples and to determine the origin of the downturn, these results indicate that the linear behavior observed in polycrystalline samples is not due to Josephson coupling between grains, but is an intrinsic property of the compound.

2. Experimental details

Polycrystalline samples of $K_2Cr_3As_3$ and $Rb_2Cr_3As_3$ were prepared by a solid state reaction described in Refs. [2,3]. Single crystals of $K_2Cr_3As_3$ were synthesized by spontaneous nucleation using a self-flux of As–K [2]. The London penetration depth was precisely measured using a self-induced tunnel diode oscillator based method down to about 0.4 K in a ^{3}He cryostat. Since the samples are very air sensitive and decompose very quickly upon being exposed, they were always handled in an argon glove box and were kept in Apiezon N grease when being measured. During the measurements, a very small alternating field of about 20 mOe is applied, which is much smaller than the lower critical field. As a result, the sample is always in the Meissner state so that the measured frequency shift Δf is proportional to the London penetration depth, which is given by $\Delta\lambda(T) = G\Delta f(T)$, where the calibration constant G is solely dependent on the sample and coil geometry [16].