NMR Investigation of the Quasi One-dimensional Superconductor K₂Cr₃As₃

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We report ⁷⁷As NMR measurements on the new quasi one-dimensional superconductor K₂Cr₃As₃ (Tc ∼ 6.1 K) [J. K. Bao et al., Phys. Rev. X 5, 011013 (2015)]. We found evidence for strong enhancement of Cr spin fluctuations above Tc in the [Cr₃As₃]∞ double-walled subnano-tubes based on the nuclear spin-lattice relaxation rate 1/T₁. The power law temperature dependence, 1/T₁ ∼ T⁻γ (γ ∼ 0.25), is consistent with the Tomonaga-Luttinger liquid. Moreover, absence of the Hebel-Slichter coherence peak of 1/T₁ just below Tc suggests unconventional nature of superconductivity.

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The surprising discovery of high Tc superconductivity in an iron-pnictide LaFeAsO₁₋ₓFx [1] led to frantic search for superconductivity in iron-based pnictides and chalcogenides [2]. The key building unit of these iron-based high Tc superconductors is the square lattice formed by Fe atoms. The mechanism of high Tc superconductivity in iron-pnictides remains as controversial as that in copper-oxides, which is also comprised of the square lattice of Cu atoms. The recent discovery of superconductivity in helimagnetic CrAs with Tc ∼ 2.2 K under modest applied pressure of ∼ 0.7 GPa [3,4] expanded the avenue of superconductivity research to Cr-pnictides.

Very recently, Bao et al. discovered superconductivity in K₂Cr₃As₃ with the onset of Tc = 6.1 K in ambient pressure [5]. Replacing K⁺ ions with larger Rb⁺ and Cs⁺ ions lowers the Tc to 4.8 K [6] and 2.2 K [7], respectively. In Fig. 1, we present the proposed crystal structure of K₂Cr₃As₃ with the most probable space group F̅6m2 (No. 187) [5]. The key building unit of K₂Cr₃As₃ is the one dimensional [(Cr₃As₃)²⁻]∞ double-walled subnano-tubes (DWSSTs) with the outer diameter of 0.58 nm separated by columns of K⁺ ions, in striking contrast with the two dimensional square lattice that forms iron-pnictides and copper-oxide high Tc superconductors. Assuming the standard ionic valence As³⁻ and ignoring vacancies in the lattice, the nominal valence of the transition metal element is Cr²⁺, and hence each Cr has 3.7 3d electrons on average. The short interatomic distance between Cr atoms, 2.61 to 2.69 Å, suggests that the Cr-Cr bonding is metallic, while the bonding of Cr with As³⁻ ions may be considered ionic [5]. The bulk physical property measurements on the critical field Hc₂ [5], the electronic specific [5,6], and the penetration depth [8] point toward the presence of a node(s) in the superconducting energy gap.

Besides the generic interest in the mechanism of exotic superconductors, the novel linear chain structure of

FIG. 1: (Color online) The crystal structure of quasi 1D superconductor K₂Cr₃As₃ [5]. (a) Top view of four unit cells. A complete [Cr₃As₃]∞ DWSST is in the middle. (b) Angled view of a unit cell, and (c)-(d) DWSST.

the [Cr₃As₃]∞ DWSSTs provides us with a unique opportunity to investigate the fundamental physics of a quasi one dimensional (1D) inorganic metal, and its relation with superconductivity [5]. Theoretically, it is well established that Fermions confined in 1D, commonly called the Tomonaga-Luttinger liquid (TLL), behave very differently from the two or three dimensional analogues, because electron-electron interactions completely alter the electronic properties near the Fermi energy no matter how weak the interactions are [9,11]. As a consequence, a simple Fermi liquid theory based on Landau’s quasiparticle picture breaks down. The peculiar influence of interactions between two particles in the TLL could be understood intuitively, if we realize that two particles must always meet each other head on in 1D; they cannot avoid each other by moving side ways. A fingerprint of the TLL is the power-law behavior arising from the singularity at the Fermi energy that manifest in various physical properties. Past explorations of the exotic properties of the TLL focused on organic conductors (see, for exam-
ple, discussions in [12,14] and references therein), semiconductor nanostructures [15], carbon nanotubes [16–20] and their superconductivity [21,22], or quasi-1D Heisenberg model systems [23,24]. Does the [Cr₃As₂]∞ DWST in K₂Cr₃As₃ indeed exhibit the signatures expected for the TLL above Tₖ? If so, is the superconducting state below Tₖ also exotic?

In this paper, we report the first microscopic 75As NMR investigation of K₂Cr₃As₃ by fully taking advantage of the versatile nature of the NMR techniques. We probed the electronic and superconducting properties at different 75As sites separately by measuring their nuclear spin-lattice relaxation rate 1/T₁. We found evidence for strong enhancement of Cr spin fluctuations toward Tₖ. The dynamical electron spin susceptibility χ” of the DWST obeys a characteristic temperature dependence, χ” ∝ 1/T₁T ∼ T⁻γ (γ = 0.25 ± 0.03). The observed power law behavior resembles that of the organic conductor TTF[Ni(dmit)₂] [13] and carbon nanotubes [17,20], and is consistent with the TLL. Moreover, we show that the Hebel-Slichter coherence peak of 1/T₁ [26], commonly observed for conventional BCS s-wave superconductors with isotropic energy gaps, is absent in the present case.

In view of the low symmetry of the 75As sites in K₂Cr₃As₃, the EFG (electric field gradient) at the 75As sites originating from K⁺, Cr²⁺3+, and As³⁻ ions in their vicinity must be large. Since the nuclear quadrupole interaction frequency νQ of the 75As nuclear spins (I = 3/2, nuclear gyromagnetic ratio γn/2π = 7.2919 MHz/T) is proportional to the EFG, we anticipated that νQ in K₂Cr₃As₃ should be much larger than νQ ∼ 2 MHz in the iron-pnictide high Tₖ superconductor Ba(Fe₁₋xCoₓ)₂As₂ [27]. The 75As site in Ba(Fe₁₋xCoₓ)₂As₂ is more symmetrical and surrounded by Ba²⁺ and Fe²⁺ ions. We first searched for the 75As NMR signals in our randomly oriented powder sample in high magnetic fields, and identified two distinct 75As NMR signals with νQ ∼ 40 MHz [28]. Such large values of νQ would readily allow us to detect 75As NQR (Nuclear Quadrupole Resonance) between the (nominal) Iₓ = ±3/2 and ±1/2 transitions in zero external magnetic field, B = 0. NQR is advantageous in probing the intrinsic superconducting properties, because we do not perturb the superconducting state with the applied magnetic field.

Armed with the preliminary knowledge of νQ, we searched for the 75As NQR signals between 33 and 55 MHz. We show representative 75As NQR spectra in Fig. 2. The lineshape observed at 200 K indicates the presence of two sets of sharp NQR peaks: the A line near 39 MHz and the B line near 44 MHz, both accompanied by smaller side peaks. Since the integrated intensity of the NQR signals below 43 MHz is equal to that above 43 MHz, these two sets of NQR signals must arise from As1 and As2 sites. Notice that the local arrangements of K⁺ ions near As1 and As2 sites are different, as readily seen in Fig.1(a,b). Therefore νQ should be somewhat different, too, between As1 and As2 sites. Unless we conduct single crystal NMR measurements, we are unable to determine which of the A and B lines arise from As1 and As2 sites, but none of our discussions below depend on the details of the site assignments.

The presence of smaller side peaks and broad continuum suggests the influence of K⁺ defects on νQ, as often observed in alloys and disordered materials. According to the energy-dispersive X-ray spectroscopy (EDS) analysis, the composition of the present material is actually close to K₁.₈₂±0.₁₉Cr₃As₂₉₉±0.₀₇ [25]. Generally, defects would locally alter the magnitude of νQ through the change of the EFG tensor (see [29] for a recent example of Cu substitution effects on νQ in the BaFe₂As₂ high Tₖ superconductor). Since the side peak of the B line is separately observable even at low temperatures, we distinguish the main and side peaks by calling them B₁ and B₂, respectively. The temperature dependence of the NQR frequency νQ is very similar at A, B₁ and B₂ sites as shown in the inset to Fig. 2. The decrease of νQ from 2 K to 295 K is anomalously large, 3 ~ 5%. The absence of a kink or jump in the temperature dependence of νQ, however, rules out the presence of Peierls instability.

Next, let us examine the electronic properties of the [(Cr₃As₂)²⁻]∞ DWSTs. In Fig. 3, we plot the temperature dependence of 1/T₁ measured by inversion recovery techniques [28] at 75As sites in a log-log scale. We also present 1/T₁T in Fig. 4. Quite generally, 1/T₁T probes the wave-vector q-integral in the first Brillouin zone of the imaginary part of the dynamical electron spin susceptibility, χ”(q, νQ), where νQ is the NQR frequency used to measure 1/T₁. In other words, 1/T₁T probes the low frequency spin dynamics of electrons integrated over the Brillouin zone. If the underlying electronic states of the DWSTs may be described by a simple Fermi liquid the-
FIG. 3: (Color online) $^{75}\text{As}$ nuclear spin-lattice relaxation rate $1/T_1$ measured by NQR techniques in $B = 0$ for A, B$_1$, and B$_2$ sites. The solid line above $T_c$ is the best fit for the A sites with a power-law, $1/T_1 \sim T^{1-\gamma}$ ($\gamma = 0.25 \pm 0.03$), while the dashed-dotted line below $T_c$ represents $1/T_1 \sim T^4$. The dotted line is the best linear fit of the normal state data for the B$_2$ peak, $1/T_1 = 0.27 \cdot T \cdot s^{-1}$.

The magnitude of $1/T_1 T$ in Fig. 4 is comparable to that of the iron-pnictide high $T_c$ superconductors such as Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [30–32]. If we assume that the hyperfine coupling of $^{75}\text{As}$ nuclear spins with Cr 3d electron spins in the present case is comparable to that with Fe 3d electron spins in iron-pnictides, our results in Fig. 4 imply that the dynamical spin susceptibility of Cr is enhanced near $T_c$ as much as the case of the superconducting Ba(Fe$_{0.92}$Co$_{0.08}$)$_2$As$_2$ near its $T_c \sim 25$ K [30]. At first glance, the gradual growth of $1/T_1 T$ (and hence $\chi''$) toward $T_c$ in the present case also seems similar to typical iron-pnictide high $T_c$ superconductors [30–32]. The growth of $\chi''$ near $T_c$ within the FeAs planes of iron-pnictides could be successfully fit with a Curie-Weiss law, $1/T_1 T \sim C/(T + \theta)$, where $C$ and $\theta$ are constants, in the temperature range where the electrical resistivity shows a linear temperature dependence [30–32]. The Curie-Weiss behavior is theoretically anticipated for two-dimensional electron gas systems with antiferromagnetic spin correlations [33–34].

In contrast with the case of quasi two-dimensional iron-pnictide high $T_c$ superconductors, the fundamental structural unit of quasi 1D K$_2$Cr$_3$As$_3$ is a metallic DWST formed by [Cr$_3$As$_3$]$_\infty$. Recent theoretical calculations predicted the existence of two quasi 1D bands and one three dimensional band [35–36], and very strong antiferromagnetic correlations along the DWST with the nearest-neighbor Cr-Cr exchange interaction as large as $\sim 1000$ K [30]. We also point out that the DWST’s form a triangular-lattice, as shown in Fig. 1(a). This means that three-dimensional antiferromagnetic couplings between the adjacent DWST’s are geometrically frustrated. The quasi 1D nature of spin correlations is therefore protected, suggesting the predominantly 1D character of Cr spin fluctuations enhanced near $T_c$.

As explained above, the 1D electron gas with electron-electron interactions forms a TLL that gives rise to a power law behavior in various physical observables. Earlier theoretical calculations showed that the TLL would show a power-law behavior, $1/T_1 T \sim T^{-\gamma}$, where the exponent $\gamma$ is a non-universal constant that depends on the details of the system, such as the band structure, nesting wave vector $2k_F$, and the strength of interactions [12–19]. Analogous power-law behavior was previously reported for TTF[Fe(dmit)$_2$] with $\gamma \sim 0.7$ [13] and for single-wall carbon nanotubes with $\gamma \sim 0.66$ [20].

Close examination of our $1/T_1$ data in Fig. 3 indeed reveals that all of our $1/T_1$ data points for the A (and
B₁) sites above $T_c$ are on a straight line in a log-log plot, implying a power-law, $1/T_1 \sim T^{1-\gamma}$, or equivalently, $\chi'' \propto 1/T_1 T \sim T^{-\gamma}$. The best fit yields $\gamma = 0.25 \pm 0.03$. We overlay a corresponding power-law fit with the same $\gamma$ in Fig. 4, which nicely reproduces the mysteriously strong divergent behavior of $\chi''$ near $T_c$. Our findings are similar to earlier reports on quasi 1D materials with the TLL behavior [12][15][18][20][24][25]. The observed value of $\gamma = 0.25$ in the present case suggests that the electron-electron interactions are repulsive, and the dominant channel of the spin correlations is antiferromagnetic for the wave vector $2k_F$ [12]. Our conclusion is consistent with the large antiferromagnetic exchange coupling $\sim 1000$ K expected for nearest-neighbor Cr-Cr spins along the DWST [36]. We call for additional experimental tests of the TLL behavior of the DWSTs in K₂Cr₃As₃ based on ARPES and other techniques.

Having established the characteristic quasi 1D behavior of Cr spin fluctuations above $T_c$, let us turn our attention to the superconducting state. In conventional isotropic BCS s-wave superconductors, $1/T_1$ exhibits a hump just below $T_c$ due to the sharp density of states at the edge of the energy gap, where the low energy quasi-particle excitations contribute constructively to $1/T_1$ due to the coherence factor predicted by the BCS theory [26][37]. The observation of such a Hebel-Slichter coherence peak of $1/T_1$ is a crucial test for the validity of the description of the superconducting state based on the conventional isotropic BCS s-wave model. In addition, $1/T_1$ decreases exponentially far below $T_c$, $1/T_1 \sim \exp(-\Delta/k_B T_c)$, in isotropic BCS s-wave superconductors, where $\Delta$ is the isotropic energy gap at the Fermi surface [37][38]. For contemporary examples of the conventional BCS s-wave superconductors, see [39][40].

In the present case, our $1/T_1$ data for the A and B₁ sites in Fig. 3 show a steep drop just below $T_c$ without exhibiting the coherence peak. Moreover, the temperature dependence of $1/T_1$ below $T_c$ is consistent with a power law, $1/T_1 \sim T^n$ with $n \sim 4$. These results below $T_c$ are similar to the case of unconventional superconductors, such as the high $T_c$ superconductor YBa₂Cu₃O₇−δ with d-wave pairing symmetry [41]. We are not aware of any theoretical prediction of $1/T_1$ below $T_c$ for the TLL; if we apply the conventional wisdom for exotic superconductivity in two- or three-dimensional correlated electron systems, our findings strongly suggest that the superconducting state is not an isotropic s-wave state. Instead, an unconventional superconducting ground state with a node in the energy gap seems realized in K₂Cr₃As₃. This conclusion is consistent with other reports of the possible presence of the nodes in the energy gap based on the measurements on the bulk properties [5][6][8].

Finally, we comment on the nature of the broad side peak B₂ in Fig. 2. $1/T_1 T$ at the B₂ sites is comparable to that of A and B₁ sites near room temperature, but remains constant, $1/T_1 T = 0.27$ s⁻¹K⁻¹, in the entire temperature range above $T_c$ with no signature of the TLL behavior. As shown in Fig. 3, all the $1/T_1$ data points of the B₂ sites in the superconducting state are below a naive extrapolation of the corresponding T-linear behavior. This is consistent with a viewpoint that the B₂ sites sense a small energy gap, suggesting the intrinsic nature of the B₂ sites. In this scenario, the broad line shape of the B₂ sites must be a consequence of the defects in their vicinity, which may explain why the TLL behavior is suppressed above $T_c$ and the energy gap is very small below $T_c$. We cannot rule out, however, an alternative possibility that the B₂ sites originate from a secondary phase with slightly different K concentration, and the B₂ peak is merely superposed on the broad tail of the B₁ sites accounting for $\sim 6$% of the overall intensity.

To summarize, we demonstrated strong enhancement of spin fluctuations in K₂Cr₃As₃ toward $T_c$, obeying a characteristic power-law predicted theoretically for the TLL. The absence of the Hebel-Slichter coherence peak of $1/T_1$ just below $T_c$ is followed by a steep decrease, in analogy with unconventional superconductors in higher dimensions with point or line nodes in the energy gap. K₂Cr₃As₃ exhibits unique quasi 1D properties and belongs to a league of its own, and deserves further attention both as a model system of the TLL and an exotic superconductor.

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