Probing Triplet Superconductivity in $(TMTSF)_2ClO_4$ with ^{77}Se Knight shift measurements

Colin Parker*
Harvey Mudd College, Claremont, CA, 91711
(Dated: August 27, 2004)

Following Knight shift measurements suggesting triplet superconductivity in $(TMTSF)_2PF_6$, we perform similar measurements on $(TMTSF)_2ClO_4$. We measure the change in the Knight shift along a axis between the superconducting and normal state. Currently the results are inconclusive, but we hope to show that this molecule, like its PF_6 cousin, exhibits triplet superconductivity.

Introduction

The spin pairing in the superconducting state in the family of organic superconductors $(TMTSF)_2X$ has been the subject of controversy. Historically, most superconductors are described by the BCS theory, where the ground state has s-wave symmetry and singlet pairing[7]. Recently, superconductors not fitting this model have been discovered. For example, the high-temperature cuprate superconductors are known to exhibit d-wave symmetry. More elusive is p-wave triplet pairing, which has been proposed for UPt_3, $SrRuO_3$, and $(TMTSF)_2X$, but not yet proven. In both of the compounds $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$, superconductivity has been shown to exist above the Pauli limit[1][2][3]. This suggests that the spin pairing is not singlet. Previous Knight shift (K) measurements performed on the PF_6 compound show that there is no significant change in the susceptibility between the normal and superconducting states, providing strong evidence for spin triplet pairing[4][5]. The TMTSF molecules form conducting chains, and these chains form into planes in the crystal. These planes are layered, with alternating layers of TMTSF and counterions. The spectrum was measured with the primary field along both the a axis, parallel to the conducting chains, and the b axis, perpendicular to the chains but in the plane of the layers, with the same result.

Following these results for both alignments, and the recent measurements of the upper critical field in the ClO_4 compound[2], we present Knight shift measurements along the a axis in $(TMTSF)_2ClO_4$. Based on the data taken so far, we do not have enough evidence to argue on either side for triplet superconductivity.

Experiment

A sample of dimension 2mm x 1mm x 1mm with the longest axis along a was placed inside a coil of radius 1mm and length 2mm (see figure 1). The sample was connected to four gold wires using silver paint, in order

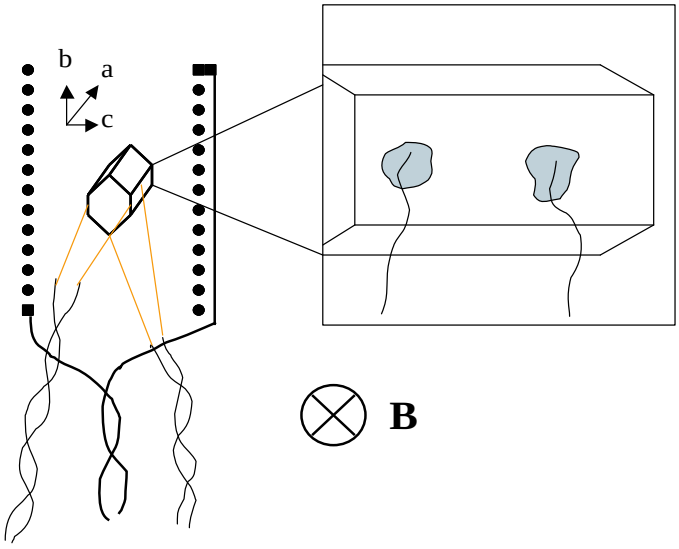

FIG. 1: Sample Mounting

to perform resistance measurements. The resistance measurements were taken between the layers, where the highest normal state resistance is found, and could be performed under the same conditions as the NMR measurements. The radio frequency magnetic field was aligned along the b axis. The sample and coil were put into a pressure cell turned hand tight ($\sim$1 atm), and placed in a cryostat, with the b axis vertical. The primary magnetic field was across the cryostat and perpendicular to the vertical. This field could be rotated anywhere in the plane of the a and c axises by rotation of the entire magnet assembly. The sample was cooled from room temperature down to liquid ^{4}He temperature, going no faster than 0.1 K/min in the range 30K to 20K, to avoid freezing in a disordered anion state[6]. Figure 2 shows the resistance as the sample was cooled. The kink around 25K shows the anion ordering temperature. The anion ordering is a first order phase transition which must be crossed slowly. If the transition is crossed quickly, anions quench in a disordered state and the cooled sample becomes an insulating anti-ferromagnet. If the transition is crossed slowly, the anions order and the sample cools to the superconducting state. Spectra were obtained at 4.2K and 0.4K. The thermometer used to measure temperature was on the outside

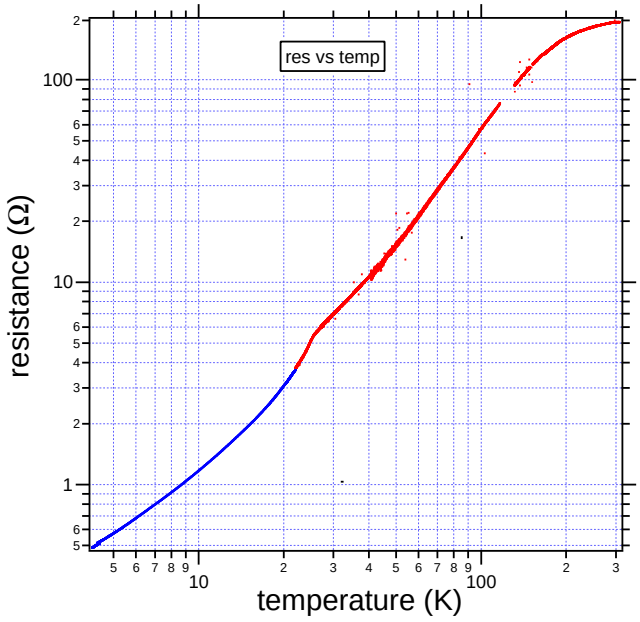

FIG. 2: Cooling Curve

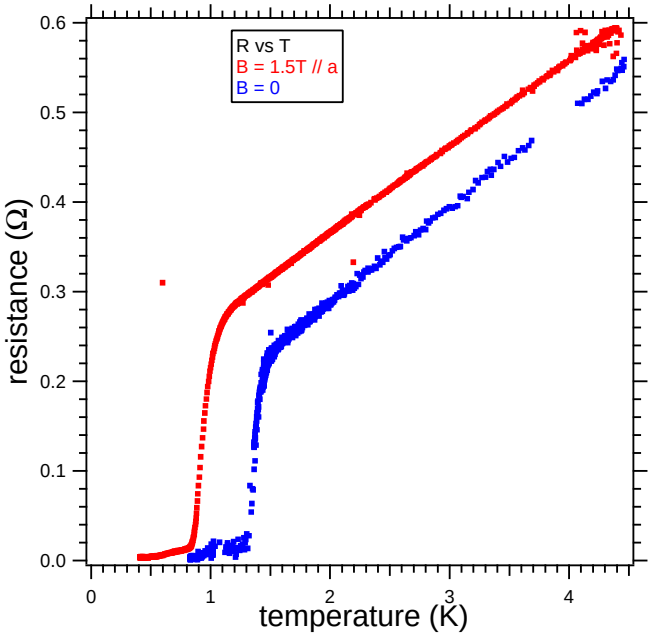

FIG. 3: Superconducting Transitions

of the pressure cell. The thermometer has non-negligible magnetoresistance in the range of interest, which causes artificial temperature shifts. Unfortunately, we are not entirely confident of the calibration of this thermometer even at zero field. New results should be calculated when the thermometer is calibrated correctly, taking into account the magnetoresistance.

Sample Heating

Because it is critical to the validity of these measurements that the sample is in the superconducting state, we must evaluate the possibility that the RF pulse used to obtain the spectrum could heat the sample out of the superconducting state. To do this we used the superconducting transition in the sample as a temperature reference point. We first applied a magnetic field along the a axis and and observed the superconducting transition (see figure 3). We selected 0.1Ω as the threshold for the transition, then cooled to 0.6K. We rotated the field until 0.6K corresponded with 0.1Ω, then cooled to a ^{3}He base temperature of 0.3K. At this point we applied 2 μs pulses of varying amplitude. Simultaneously, we measured the sample resistance using a four-wire AC lock-in amplifier. For large pulses, the resistance rose to a peak due to heating and decayed (see figure 4). The decay is not a pure exponential, because although the temperature may decay exponentially, the dependence of resistance on temperature is linear only for a short space in the superconducting transition. The time constant of the lock-in was adjusted low compared with the resistance decay time. From the heating curve, we could evaluate whether or

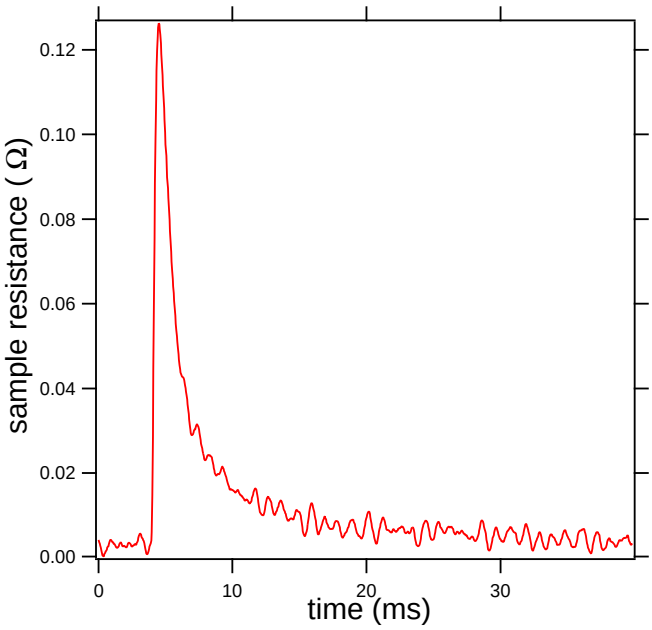

FIG. 4: Sample Response to Pulse

not the sample exceeded 0.6K. From this data we chose pulses such that the sample is definitely superconducting for the entire pulse sequence.

Conclusion

Figure 5 is a plot of two spectra, one in the normal phase and one in the superconducting phase. Figure 6 is a plot of the spectra at varius angles, with a at around

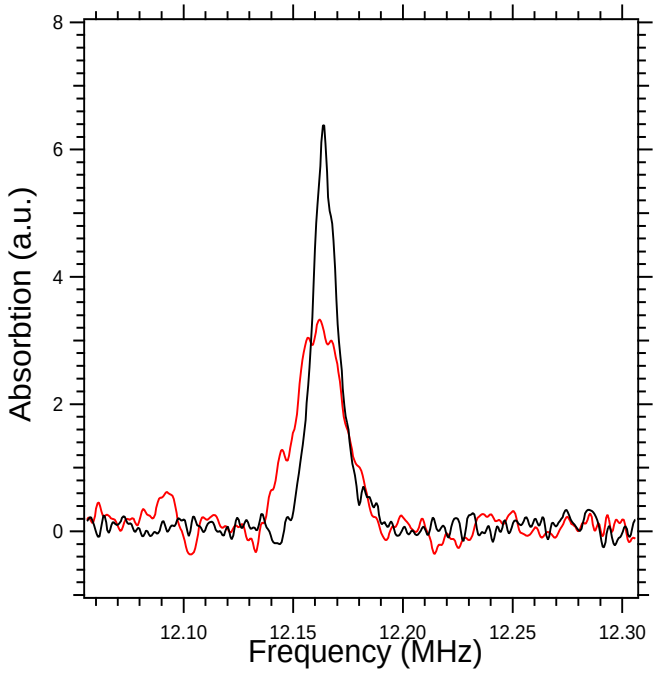

FIG. 5: ^{77}Se NMR Spectra
The black line shows B = 15.015T T = 4.18K
The red line shows B = 14.995T T = 0.34K

75°. The dipole coupling takes the form

$$\hbar\gamma\vec{I}\cdot\sum_i\int\frac{\mu_0}{4\pi r^3}\vec{m}(3\cos^2\theta-1)|\Psi_i(\vec{r})|^2d^3\vec{r},$$

where $\vec{I}$ is the nuclear spin, $\vec{m}$ is the dipole moment of an electron, and Ψ_i is the wavefunction of the i^{th} electron. Therefore, we expect the Knight shift to be on the order of two thirds the change in frequency between a and c, or about 20 kHz. Unfortunately, there is not sufficient evidence to support a claim of triplet superconductivity in $(TMTSF)_2ClO_4$. We have taken spectra in both the superconducting and normal states. Preliminary data indicates that there is some broadening and shifting of the spectrum in the superconducting state as compared with the normal state. As data with better signal to noise is evaluated, we will determined whether or not this shift is significant.

* cvparker@hmc.edu

[1] I. J. Lee, M. J. Naughton, G. M. Danner, and P. M. Chaikin, Phys. Rev. Lett. **78**, 3555 (1997).
[2] J. I. Oh and M. J. Naughton Phys. Rev. Lett. **92**, 067001 (2004).
[3] A. Clogston, Phys. Rev. Lett. **9**, 266 (1962).
[4] I. J. Lee et al., Phys. Rev. Lett. **88**, 017004 (2002).
[5] I. J. Lee et al., Phys. Rev. B **68**, 092510 (2003).
[6] H. Schwenk, K. Andres, and F. Wudl, Phys. Rev. B. **29**, 500 (1984).

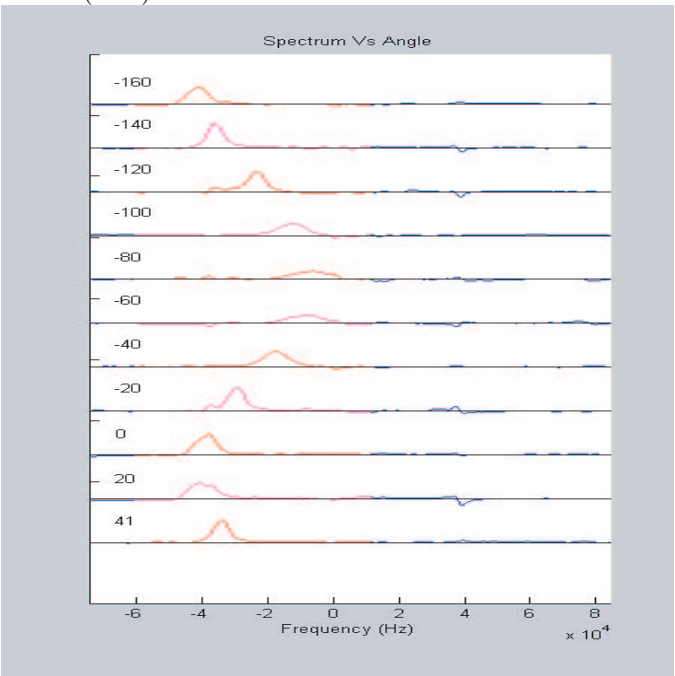

FIG. 6: ^{77}Se NMR Spectra Showing Anisotropy
B = 1.4910T ν_0 = 12.098 MHz T = ∼4.8K

[7] J. Bardeen, L. N. Cooper, and J. R. Schrieffer Phys. Rev. **108**, 1175-1204 (1957)