Superconducting State of the Organic Conductor $(TMTSF)_2ClO_4$

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$(TMTSF)_2ClO_4$ is a quasi-one-dimensional organic conductor and superconductor with $T_c = 1.4$ K, and one of at least two Bechgaard salts observed to have upper critical fields far exceeding the paramagnetic limit. Nevertheless, the ^{77}Se NMR Knight shift at low fields reveals a decrease in spin susceptibility χ_s consistent with singlet spin pairing. The field dependence of the spin-lattice relaxation rate at 100 mK exhibits a sharp crossover (or phase transition) at a field $H_s \sim 15$ kOe, to a regime where χ_s is close to the normal state value, even though $H_{c2} \gg H_s$.

Superconductivity in the Bechgaard salts $(TMTSF)_2X$ is distinctive for a number of reasons [1,2], but particularly for the very large upper critical fields H_{c2} relative to T_c [3,4]. When orbital suppression by magnetic fields is avoided, then singlet-paired superconductivity is still unstable beyond a paramagnetic pair-breaking field H_p [5] because of the difference in spin susceptibility χ_s between the normal and superconducting states. For *s*-wave superconductors in the weak-coupling limit, $H_p = (18 \text{ kOe/K})T_c$. H_{c2} has been reported greater than 90 kOe [6] for $(TMTSF)_2PF_6$, an enhancement of more than 4 times over $H_p = 22$ kOe for a $T_c = 1.4$ K. And for the isomorphic salt $(TMTSF)_2ClO_4$, superconductivity beyond 50 kOe was recently reported [4].

Layered superconductors can exhibit upper critical fields approaching H_p when the magnetic field lies in the plane of the layers. Commonly known examples include the high-T_c cuprates [7] and organic superconductors. Quasi-one-dimensional superconductors, as well as quasi-2D superconductors, offer an opportunity for decoupling the layers from field-induced confinement [8–10]. Evidently, *both* orbital suppression and spin pair breaking of superconductivity are weak for the Bechgaard salts.

Spin triplet pairing avoids paramagnetic limiting effects and is a possible explanation for the large H_{c2} [3,9,11]. Indeed, previous NMR Knight shift measurements in $(TMTSF)_2PF_6$ under pressure were interpreted as consistent with an equal-spin pairing triplet order parameter [12,13]. However, there are other circumstances under which the Pauli limit is exceeded. For example, the spatially inhomogeneous state described by Fulde and Ferrell, and independently by Larkin and Ovchinnikov (FFLO) [14,15], has $\chi_s \neq 0$, so it is not paramagnetically limited at H_p. Also, superconductors with strong spin-orbit scattering can exhibit large critical fields because there is a net spin magnetization in a magnetic field [16,17]. For the

Bechgaard salts, the proposal for triplet pairing is compelling for a number of reasons, including: a phase transition to an inhomogeneous FFLO state has not been identified, and, there is no evidence for significant spin-orbit scattering in either $(TMTSF)_2PF_6$ or in $(TMTSF)_2ClO_4$ [3]. And finally, the triplet pairing state is a known instability of one-dimensional [18] and quasi-1D electronic models [19,20].

The observation of large upper critical fields in $(TMTSF)_2ClO_4$ motivated us to investigate further with NMR techniques. In addition, we wanted to push our own measurements to lower fields and lower temperatures [21]. Here, we report on ^{77}Se NMR Knight shift experiments in $(TMTSF)_2ClO_4$, performed at smaller magnetic fields than the earlier work. The magnetic field was applied precisely in the crystallographic layers close to the **a** and **b**′ axes at a strength just less than $H_0 = O(10 \text{ kOe})$; this is well below the observed critical fields from transport experiments [4]. In both cases, a shift consistent with a decrease of χ_s in the superconducting state is observed. The experiments are interpreted to give evidence for spin-singlet pairing at low field. The existence of lines of nodes is indicated by the weak temperature dependence of the spin-lattice relaxation rate [13,22], though this aspect remains controversial [23]. However, the nature of the superconducting state at high fields remains a puzzle: as part of this study we made measurements of ^{77}Se longitudinal relaxation (T_1^{-1}) over a range of magnetic fields at $T = 100$ mK. We observed a significant and very sharply defined increase in the dynamical spin susceptibility within the superconducting state; the increase divides a low-field regime (LSC) from a high-field one (HSC). We discuss constraints imposed on the interpretation of the HSC by existing data.

Two single crystals of $(TMTSF)_2ClO_4$, with the approximate dimensions $6 \times 2 \times 0.4$ mm^3 (denoted hereafter *A*) and $4 \times 2 \times 1$ mm^3 (*B*), were placed into NMR coils. Tuning and matching elements of the NMR tank circuit

were made outside the cryostat ("top-tuning") so that a range of fields and frequencies could be accessed. Sample *B*, grown at the Ørsted Institute, Denmark, is 10% ^{13}C spin labeled on the bridge of the TMTSF dimer; it was configured for measurements with the magnetic field direction near **b′**. The other sample (*A*), grown at UCLA, was configured for magnetic field alignment near to **a**. The samples were mounted on the platform of a piezoelectric rotator with 0.5 millidegree increments, and the rotation angle was calibrated using two mutually orthogonal Hall sensors mounted to the platform. Electrical contacts were silver painted onto the sample surfaces normal to the **c***** direction. The samples were slow cooled at the rate of 7 mK/ min through the anion ordering transition ($T_{AO} = 24$ K) so as to reach the relaxed state and onset of superconductivity at $T_c = 1.4$ K. The superconducting transition was observed in the resistivity measurement and in reflected rf power measurements and alignment of the magnetic field direction to lie precisely within the layers was accomplished using the piezorotator while probing the angular dependence of the reflected power. NMR spectroscopic and relaxation measurements were performed on both ^{77}Se and ^{13}C nuclei.

In presenting the results, we start with the key observation: the ^{77}Se shifts in the superconducting state and normal state, and follow with complementary characterization data: spin-lattice relaxation rates and magnetoresistance. In Fig. 1(a), we show ^{77}Se spectra for the two samples, identified by the direction of the applied field. The spectroscopic experiments were performed at small tip angles (<3°) to avoid heating. More specifically, temperature rises were detected by time-synchronous resistivity measurements, and for both samples we were able to use sufficiently small tip angles and associated pulse energies so that temperature rises were undetectable. The local field decreases on entering the superconducting state for *A* (**H** ∥ **a**), and the opposite occurs for *B* (**H** ∥ **b′**). Note that the relative change is much smaller for *B*. Calibrations of the applied field were determined to better than 10 ppm (ppm) by measurements of the ^{63}Cu (in the coil) and ^{3}He (in the mixture in the vicinity of the coil) resonances. The demagnetization field, arising from screening currents in the superconducting state, was determined to be less than 100 ppm from ^{13}C spectroscopy in sample *B*. The effect of temperature and field is illustrated in Fig. 1(b). Note that no deviation from the normal state shift is seen for $H = 40$ kOe.

In Fig. 2, we show the temperature dependence of T_1^{-1} for both samples. The data collected at low field (open symbols, see caption) exhibit a change of slope associated with the superconductivity. No signature for superconductivity is apparent for the data collected with $H = 40$ kOe (closed symbols), which is close to the values for H_{c2} reported elsewhere [4]. Interpreting the change in slope as $T_c(H)$, we obtain values for the critical field lower than reported in Ref. [4] in both cases. We infer from the weak
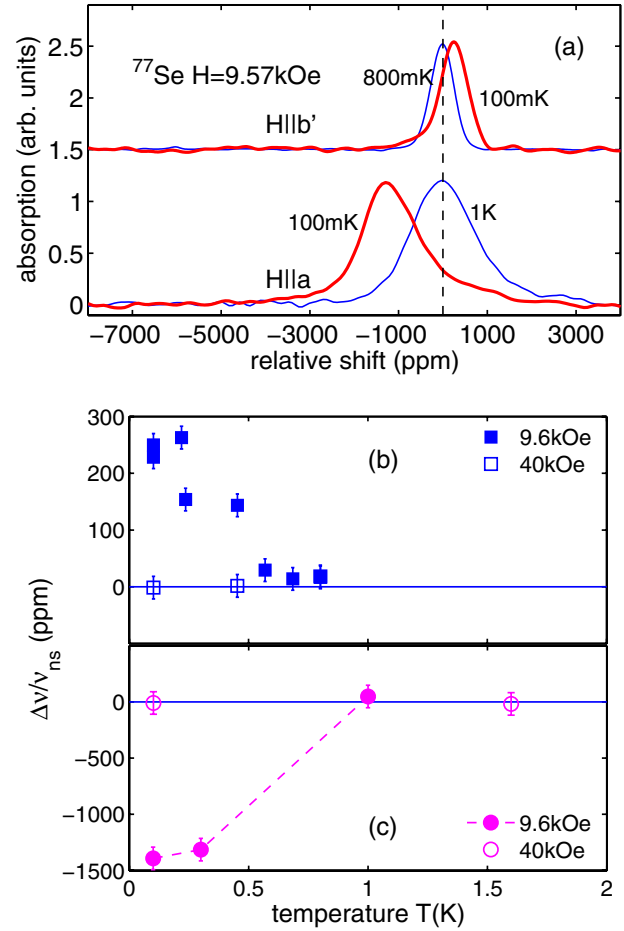

FIG. 1 (color online). (a) ^{77}Se spectra in the normal and superconducting states of $(TMTSF)_2ClO_4$ for two orthogonal field orientations within the crystallographic layers. (b), (c) Relative shifts vs temperature for **H** ∥ **b′**, **a**, respectively. At $H = 40$ kOe, there is no observable change from the normal state shifts at the lowest temperatures measured (100 mK). Zero shift is arbitrarily set to the normal state first moment.

temperature dependence of T_1^{-1} below $T \approx 200$ mK that there is a nonzero density of states at the Fermi level in at least part of both samples at the lowest temperatures measured. If we were to attribute the low temperature relaxation to a normal state fraction phase segregated from the part that is superconducting, then 30% is the assigned fraction in the normal state.

The hyperfine coupling is nearly uniaxial: the dominant contribution is a p_z orbital originating at the Se sites [24,25]. The normal state paramagnetic shift is given by

$$K = K_{iso} + K_{ax}(3\cos^2\theta - 1), \tag{1a}$$
$$K_{iso} = 3.9 \times 10^{-4}, \tag{1b}$$
$$K_{ax} = 10.5 \times 10^{-4}. \tag{1c}$$

Thus, in low fields and for $T \ll T_c(H \to 0)$, we expect a change for $\delta K_s \sim -700$ ppm ($\theta = \pi/2$, **H** ∥ **b′**) and $\delta K_s^a \sim +2500$ ppm ($\theta = 0$, **H** ∥ **a**) for a superconductor
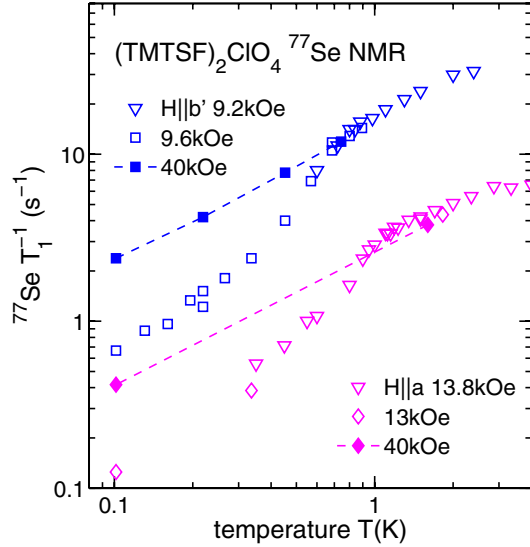
FIG. 2 (color online). T_1^{-1} vs T for $(TMTSF)_2ClO_4$, for $\mathbf{H} \parallel \mathbf{b}'$ and $\mathbf{H} \parallel \mathbf{a}$. Included are results from prior measurements using a single-shot ^{3}He cryostat ($\triangledown$) [21] and results from the current experiment.

with singlet spin pairing. From Fig. 1, we observe changes smaller than this using magnetic fields just less than 10 kOe: $\delta K_s^b = -275$ ppm and $\delta K_s^a = +1500$ ppm, respectively. In the first case, the observed value is a little less than half of what is expected for a singlet superconductor in the small field, zero temperature limit. In the second case, it is a little more. Unequivocally, χ_s is reduced in the superconducting state. Further, the opposing signs of the change are consistent with the known hyperfine couplings.

That χ_s does not completely vanish is not surprising when compared to the measurements of T_1^{-1}. And attributing the relaxation for $T \to 0$ to hyperfine fields is confirmed by comparing the rates at low temperatures in the ^{77}Se and ^{13}C nuclei. Still, the character of the hyperfine fields is unknown. For example, assuming that it arises from quasiparticles, it could originate from the existence of a volume fraction in the normal state, phase segregated from the superconducting portion. Another possibility is a field- or disorder-induced density of states at the Fermi energy. The observation of nearly single-exponential relaxation at low temperatures for both samples speaks against macroscopic phase segregation.

To explore further this issue we measured the ^{77}Se T_1^{-1} for varying magnetic fields at $T = 100$ mK. This is shown in Fig. 3 for both field directions, along $\mathbf{a}$ and along $\mathbf{b}'$. Shown also is the interlayer resistance, $R_{zz}(T = 100$ mK$)$ versus H ($\parallel \mathbf{a}$) for sample A. What is notable in the relaxation rate is the fairly sharp increase between 10 and 20 kOe. We will refer to the "crossover" field as H_s; it is much less than estimates of $H_{c2} \approx 50$ kOe or more [4]. The result here is no exception: *in situ* interlayer resistance measurements deviate from an undetectable resistance only for $H > 30$ kOe, and clearly the effects of superconductivity are evident to fields exceeding 50 kOe.
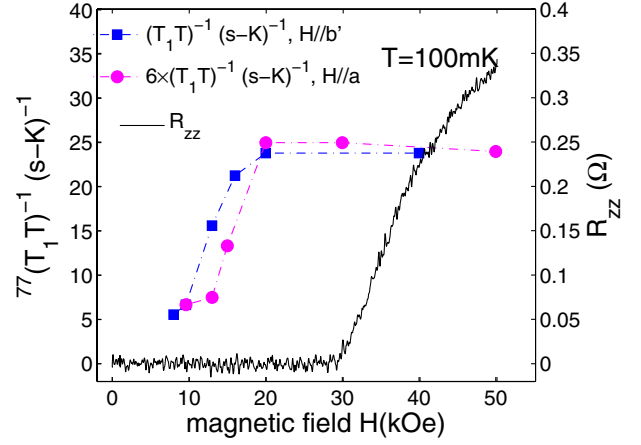

FIG. 3 (color online). ^{77}Se T_1^{-1} vs H at $T = 100$ mK (left axis). Also shown is the interlayer resistance $R_{zz}(\mathbf{H} \parallel \mathbf{a})$ over a similar range of fields (right-hand axis).

Unfortunately, a similar measurement for sample B was unreliable because of a missing contact.

As superconductivity persists for $H > H_s$, we label the two regimes as low-field SC ($H < H_s$, LSC) and high-field SC ($H > H_s$, HSC). In the HSC regime, the relaxation rate T_1^{-1} is close to the normal state value. The normal state behavior, shown in Fig. 4, is remarkably well described by the empirical form that is also characteristic of antiferromagnetic spin fluctuations in 2D,

$$T_1 T = C(T + \Theta), \qquad (2)$$

with C, Θ constants [26]. Relaxation in the HSC regime is similarly described and should also result primarily from hyperfine fields originating with quasiparticles.

The LSC regime exhibits a drop in χ_s that appears consistent with a singlet superconductor. Impurity studies [27] indicate a change in sign of the superconducting gap function over the Fermi surface. And although the existence of nodes is contradicted by thermal conductivity
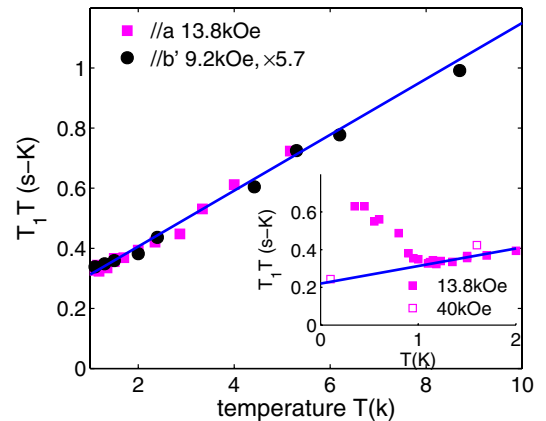

FIG. 4 (color online). ^{77}Se $T_1 T$ vs T, demonstrating that the normal state behavior follows closely to Eq. (2). Inset: an expanded scale for $T < 2$ K, $\mathbf{H} \parallel \mathbf{a}$.

experiments [23], zero-field NMR relaxation in the super-conducting state [22] provides evidence for the existence of nodes. Therefore, with the exception of the results for thermal conductivity, the LSC is consistent with a singlet state and nodes on the Fermi surface.

We are left to consider the nature of the HSC. We note that its existence could account for the temperature independence of $\chi_s(H = 14.3 \text{ kOe})$ reported in Ref. [12]. It is unlikely to be filamentary for a number of reasons, most notably that it is associated with a robust magnetic torque signal [4], and the zero resistance state is measured by many laboratories without controversy. In that case, we have to take into account the large H_{c2}. The suggestion that it may be triplet followed from this observation, and also because no phase transition to a FFLO state was identified. This study calls that into question because the apparent crossover at H_s and 100 mK seems quite sharp. Furthermore, there is evidence for a nonzero density of states at the Fermi surface in the HSC regime, which is qualitatively consistent with the FFLO. However, $H_{c2}(T \to 0)$ exceeds estimates for the paramagnetical limit of the FFLO state [11]. An alternative to the FFLO state is a transition to a triplet pairing state [28]; common to both cases is the increase in the spin susceptibility of the superconducting state, thus avoiding paramagnetic limiting. Nevertheless, in considering these possibilities, it is not clear why the spin-lattice relaxation should be so close to the normal state value as we observe. Consequently, a mapping of the phase diagram and more detailed NMR spectroscopy in the HSC regime [29,30] are necessary for a more definitive description of the superconductivity for $H > H_s$.

In summary, it is established that the Bechgaard salt superconductor $(TMTSF)_2ClO_4$ is in the singlet state, most likely with gap nodes, at low field. However, the H-T phase diagram remains puzzling: spin-lattice relaxation measurements give evidence for a sharp crossover or phase transition at a field H_s *within* the superconducting state. We note that for the sample aligned $H \parallel \mathbf{b}'$, assigning the steep increase in T_1^{-1} near $H = H_s$ to hyperfine field fluctuations is verified by comparing to the spin-lattice relaxation of ^{13}C in the same regime, whereas a similar check was not possible for the sample aligned $H \parallel \mathbf{a}$. The nature of the HSC regime is unknown and we consider the possibility that it is a transition to an inhomogeneous FFLO state or a triplet-paired state. Confirmation of the phase transition and the associated mapping of the phase diagram, together with NMR spectroscopic information in the high-field regime, is necessary to clarify which of these possibilities is the correct one or whether the large spin susceptibility in the HSC regime occurs for a different reason.

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