Zeeman-Driven Phase Transition within the Superconducting State of κ-(BEDT-TTF)_{2}Cu(NCS)_{2}

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Zeeman-driven phase transition within the superconducting state of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

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^{13}C nuclear magnetic resonance measurements were performed on κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, with the external field placed parallel to the quasi 2D conducting layers. The absorption spectrum is used to determine the electronic spin polarization M_s as a function of external field H at a temperature T=0.35K. A discontinuity in the derivative dM_s/dH at an applied field of H_s=213±3kOe is taken as evidence for a Zeeman-driven transition within the superconducting state, and stabilization of inhomogeneous superconductivity.

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Magnetic fields tend to destabilize singlet superconductivity through coupling to both orbital and spin degrees of freedom. Typically, only the orbital degrees of freedom are relevant. In the event that orbital suppression of the superconducting state can be avoided, the Zeeman coupling to quasiparticles lowers the energy of the normal state relative to that of the superconducting (SC) state for fields exceeding the Pauli paramagnetic limit H_P [1]. Fulde and Ferrell [2], and independently Larkin and Ovchinnikov [3] showed that the direct, discontinuous, transition between the two phases is avoided under circumstances favorable to the formation of an intermediate, inhomogenous phase, which has become known as the FFLO state.

The requirements for FFLO formation are fairly stringent, and as a result, candidate systems are few. The Maki parameter $\alpha = H^0_{c2}/H_P$ provides a measure of the relative importance of orbital and Zeeman coupling to the magnetic fields. Calculations indicate that $\alpha > 1.8$ is necessary for an s-wave superconductor, thus generally favoring systems with large effective mass [4]. Moreover, the Cooper pairs in the FFLO state have finite momentum, and the associated characteristic length scale is of order the coherence length. Therefore, the superconductor must be in the clean limit [5, 6].

These conditions apply to some heavy fermion systems, and to layered materials such as the organic superconductors. In the first case, CeCoIn$_5$ is the best-known example. It is a Pauli-limited superconductor [7], and a field-induced phase transition within the superconducting state is known to occur at very low temperatures [8]. NMR and neutron scattering experiments demonstrated that the high field superconducting phase had a magnetic structure coexisting with superconductivity[9–11], and whether a magnetic component is compatible with the FFLO phase is a current topic of debate [12, 13].

Due to their remarkably anisotropic superconducting properties, the organic superconductors have also been proposed as candidates for inhomogeneous SC states [14–18], since for in-plane fields the flux penetrates between the layers in the form of Josephson vortices, thus limiting orbital suppression [19, 20]. As well, the in-plane mean free paths of the normal state are long, consistent with the clean limit. For κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ in particular, the temperature-magnetic field phase diagram has been established using dc transport [14], magnetic torque [21, 22], and thermodynamic [23] probes, with each providing evidence for bulk superconductivity in parallel fields significantly exceeding H_P.

Justification for this claim requires a knowledge of H_P, which can be estimated in a number of ways. If E_C is the condensation energy, then $H_P \equiv [E_c/2\mu_B]^{1/2}$. Using T_c=9.5K, and Clogston's well-known result for s-wave pairing in the weak coupling limit gives H_P=(18.4kOe/K)T_c = 180kOe [1]. A fully-gapped superconducting state was inferred from specific heat measurements, with $2\Delta_0/k_BT_c = 4.8$ giving a larger estimate $H_P \sim$230kOe [24]. On the other hand, NMR T_1 measurements were interpreted as evidence for gap nodes [25–27]. Then, for example, a weak-coupling $d_{x^2-y^2}$ superconductor and T_c=9.5K leads to H_P=214 kOe [28]. Even though uncertainties related to possible strong coupling effects and band structure details remain, extrapolation of the experimentally determined upper critical field in the limit $T \to 0$ is consistent with $H_P \sim$210kOe [22, 23].

The ^{13}C NMR results reported here were carried out to verify the existence of a line of transitions to a new, high-field superconducting (HSC) phase, and to characterize the HSC phase. The NMR absorption spectrum is directly sensitive to the distribution of hyperfine fields; hence its utility for studying inhomogeneous phases such as the FFLO state. From the observed evolution of the ^{13}C spectrum on varying the magnetic field with $T < T_c(H = 0)$, the existence of a line of Zeeman-driven phase transitions is established. It occurs at H_s =213kOe, and from the electronic spin polarization $M_s(H_0)$, we conclude that the system is a bulk superconductor on both sides. The high-field phase has significantly larger spin polarization, as would occur for a FFLO state. A specific model for the spin polarization distribution remains undetermined, but we propose the arrangement of zeroes in the real-space gap function is two-dimensional [29, 30], rather than the stripe structure originally proposed by Larkin and Ovchinnikov [3] for s-wave superconductors.

The crystals used in this study were grown at Argonne National Laboratory, and at RIKEN by standard electrolytic methods, following molecular synthesis including 100% ^{13}C (I=1/2, $^{13}\gamma$=1.0708kHz/G) spin labelling at the central carbon sites. The structure of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is quasi-2D (q2D), formed from conducting layers of the BEDT-TTF donors separated by Cu(NCS)$_2$- anion chains, with an interlayer spacing s=16Å. The crystal structure is monoclinic, with a=16.256Å, b=8.456Å, c=13.143Åand angles $\alpha = 90°$, $\beta = 110.3°$, $\gamma = 90°$ at 300K. The inset of Fig. 1 shows the angles θ, ϕ used to define the orientation of the applied magnetic field. With $\hat{n} \perp (bc)$ plane, $\theta = \angle(\hat{n}, H_0)$, and ϕ is the in-plane angle measured relative to c. A single-axis rotator for mounting the sample/coil assembly proved sufficient for aligning the sample to within $\delta\theta \leq 0.2°$ of the in-plane condition ($\theta = 90°$) necessary for minimizing orbital suppression of superconductivity. The azimuthal angle ϕ is fixed according to the sample orientation relative to the NMR coil. The measurements were carried out at UCLA (H_0=90kOe, $T \geq$1.5K), and in a resistive magnet at the National High Magnetic Field Laboratory (NHMFL, H_0=140-270kOe, $T \geq$0.3K).

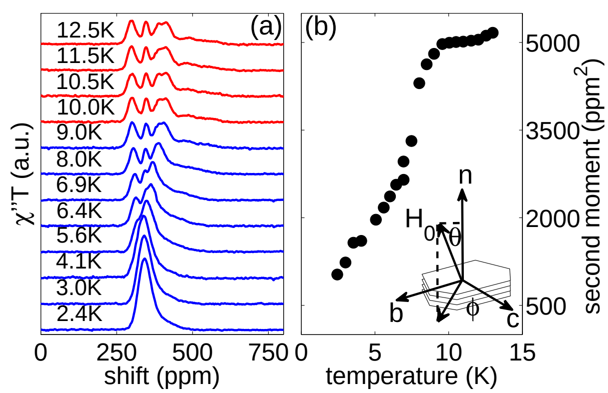

FIG. 1. (a) The ^{13}C spectrum is measured at various temperatures with the 90kOe magnetic field oriented parallel to the conducting layers and with $\phi \sim 15°$ from the c-axis. The shift is reported relative to the standard reference, (CH$_3$)$_4$Si (TMS). For $T > T_c$ (red spectra), a multi-peak spectrum results from hyperfine fields at inequivalent sites. For $T < T_c$, the decrease in M_s leads to unresolved features. (b) Second moment of the absorption spectrum, $S_2(T)$. The inset defines the angles θ, ϕ.

Figure 1(a) shows the ^{13}C NMR absorption spectrum at H_0=90kOe for various temperatures and measured using a standard Hahn echo rf pulse sequence, with $\theta = 90°$, $\phi \approx 15°$. For $T > T_c$=9.5K (spectra colored red in Fig. 1(a)), the ^{13}C spectrum displays multiple resonance peaks from inequivalent spin-labeled sites. Cooling through T_c, the spectrum narrows and distinct contributions become unresolved as M_s decreases. This demonstrates that the separation of peaks in the normal state are predominantly due to hyperfine fields, rather than from inequivalent orbital shifts or ^{13}C-^{13}C dipolar coupling. Therefore, the NMR linewidth can serve as a measure of M_s and the Knight shift K_s, as previously reported [26]. In Fig. 1(b) is plotted the second moment $S_2(T)$, showing very clearly the onset of superconductivity at T=9.5K. Note that with the weak interlayer coupling, no decrease of the spectrum intensity is observed for $T < T_c(H)$ and in-plane fields [17].

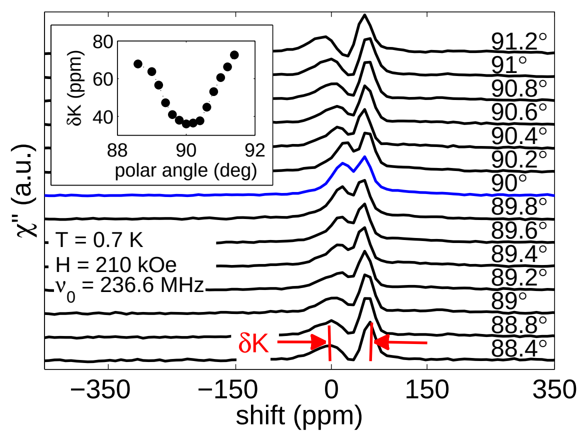

FIG. 2. The ^{13}C resonance spectrum measured at H_0=210kOe and T=0.7K is used to align the field to the bc plane. The spectrum broadens as the sample is rotated away from optimum alignment ($\theta = 90°$). The inset shows the separation (ppm) of the two resonance peaks observed, $\delta K(\theta)$.

The challenging working environment of the NHMFL required the adoption of an efficient alignment procedure. The sample was placed on a platform rotatable to $\delta\theta \sim$0.2deg. There exists a strong sensitivity of ^{13}C lineshape to orientation at fields 200-210kOe: as the sample is rotated away from optimal alignment ($\theta = 90°$), orbital effects cause the ^{13}C resonance spectrum to broaden. Figure 2 shows the resulting spectrum from the alignment procedure performed at H_0=210kOe and T=0.7K. Rotating so that $\theta > |\pm 3.5°|$ from the in-plane condition brings the sample to the normal state, as evidenced by a fully broadened multi-peak spectrum.

Once the crystal was oriented, the ^{13}C absorption was measured for a range of magnetic fields at T=0.35K. Figure 3 shows the results as the field is increased through H_P. Very slow temporal variations in the magnetic field caused the spectrum to move randomly in frequency by approximately 10ppm, so the frequencies are fixed relative to the sharp central resonance peak, which varies minimally with field and temperature. For the field range of 160-210kOe, the measurements were made using a single-pulse (free induction decay) rf excitation sequence. At higher fields, a two-pulse (spin-echo) sequence was used, while stepping the carrier frequency so as to cover the full absorption spectrum.

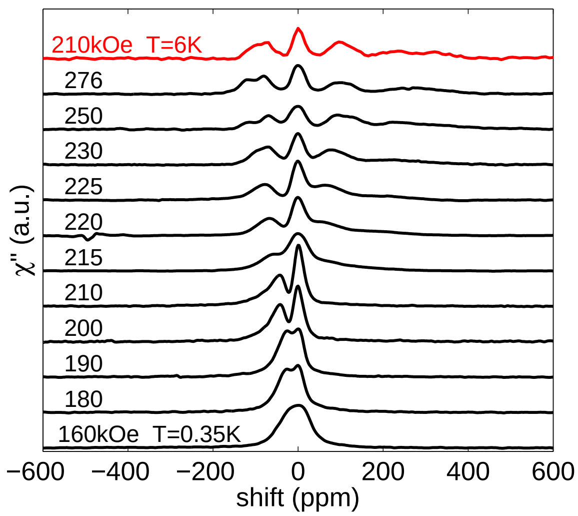

FIG. 3. The ^{13}C resonance spectrum measured at T=0.3K for the field range of 160 to 280 kOe. Spectrum have been aligned to the peak maximum, to compensate for very slow fluctuations in the field. A broadening of the resonance spectrum as a function of field is observed to onset at H=213kOe, indicating a turn on of the electronic spin susceptibility. The normal state resonance spectrum, measured at H=210kOe and T=6K is included for comparison.

For fields less than 213kOe, the spectrum gradually broadens with increasing H_0. Beyond 213kOe, the spectral evolution changes abruptly, with multiple peaks detected at higher and lower frequency than the sharp central resonance feature; this peak splitting continuously increases as the external field is increased. For comparison, the normal state spectrum was measured at H_0=210kOe and T=6K, outside the superconducting region of the phase diagram, and the resulting spectrum is included in Fig. 3. It is consistent with $\theta = 90°, \phi = 45°$.

In Fig. 4 is shown the second moment $S_{2n}(H, T = 0.35\text{K})$ normalized to the normal state, which serves as a measure of the ^{13}C line-broadening. For $H_0 < 210$kOe, the electronic polarization shows minimal field dependence, reaching approximately 20% of the normal state value at H_0=210kOe. As the field is increased and exceeds H_s, the rate of increase changes abruptly. Finally, for magnetic fields $H_0 \geq$250kOe, the linewidth is indistinguishable from that of the normal state. The behavior of $S_{2n}(H, T = 0.35\text{K})$, as well as the smooth evolution

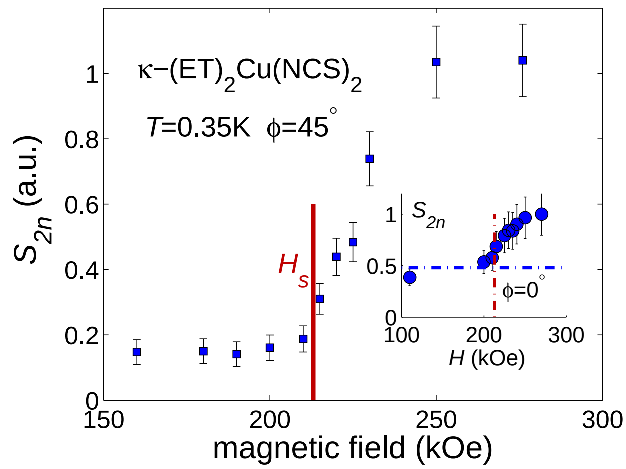

FIG. 4. The second moment of the ^{13}C spectrum measured at T=0.35K is plotted as a function of applied magnetic field. The values have been normalized to the second moment of the normal state spectrum. At H=213kOe, the second moment is observed to increase from its low-field value and increases as a function of applied field, indicating a transition from within the superconducting state associated with an increase in electronic spin polarization. The inset shows the results of an identical measurement with $\phi = 0°$; the dashed line again marks H_s=213kOe.

of the absorption lineshape for the range of fields greater than $H_s \sim$ 210kOe, is consistent with a bulk superconductor, but one with monotonically increasing average spin polarization relative to what is observed for smaller magnetic fields. Specifically, the spectrum at fields just greater than H_s cannot be constructed by simply including a volume fraction in the normal state. The results of spin-lattice relaxation measurements are interpreted consistently and will be presented elsewhere. We take the change of behavior at H_s as evidence for a phase transition directly connected to the spin polarization, separating two superconducting phases. To within experimental uncertainties, a similar onset for the high-field phase was observed also for $\phi \sim 0°, 90°$. That H_s appears independent of ϕ is further suggestive of a Zeeman-driven phase transition.

Next, we comment on the compatibility of the present measurements with an FFLO scenario, which has been extensively studied theoretically; manifestations evidently may depend on dimensionality, gap structure, temperature, field, and material parameters [29, 31, 32]. Central to the discussion is the real space gap structure in the FFLO state, which may have 1d modulations, or 2d modulations [29, 30]. Not unrelated is the nature of the transition separating uniform and inhomogeneous phases, which may depend on microscopic details and in this context both continuous [28, 30, 33] and discontinuous [32] transitions are proposed.

The possibility of the high field phase exhibiting the 1d modulated order parameter, as for an s-wave superconductor in the FFLO state, seems excluded by these measurements. In that case and in the absence of other significant line broadening effects, the absorption is dominated by large edge singularities that are not apparent in Fig. 3. However, the edge divergences become steps for the 2d case, and moreover are expected less pronounced after other line-broadening effects are taken into account. Regarding the boundary separating low-field and high-field SC phases, results from torque measurements indicate it is discontinuous [22]. The relatively smooth increase in M_s, shown in Fig. 4, suggests that if it is first order, then it is only weakly so. No indications for a transition into the normal state were detected for fields up to the maximum field applied, 270kOe.

In conclusion, we have characterized the microscopic electronic properties of a superconductor which is Pauli limited, yet superconductivity persists for fields in excess of H_P. The electronic spin polarization was locally measured as a function of field through the hyperfine interaction, and provided evidence for a phase transition at a field $H_s = 213$kOe within the SC state. The independence of this transition to in-plane field orientation, as well as the structure of the NMR spectrum measured, indicates that the transition is not associated with vortex dynamics, and may be evidence for a 2D spatially inhomogeneous superconductor at high fields.

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