Field Dependence of the Ground State in the Exotic Superconductor CeCoIn$_5$: A Nuclear Magnetic Resonance Investigation

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We report ^{115}In nuclear magnetic resonance (NMR) measurements in CeCoIn$_5$ at low temperature ($T \approx 70$ mK) as a function of the magnetic field (H_0) from 2 to 13.5 T applied perpendicular to the $\hat{c}$ axis. A NMR line shift reveals that below 10 T the spin susceptibility increases as $\sqrt{H_0}$. We associate this with an increase of the density of states due to the Zeeman and Doppler-shifted quasiparticles extended outside the vortex cores in a d-wave superconductor. Above 10 T a new superconducting state is stabilized, possibly the modulated phase predicted by Fulde, Ferrell, Larkin, and Ovchinnikov. This phase is clearly identified by a strong and linear increase of the NMR shift with the field, before a jump at the first order transition to the normal state.

Applying a magnetic field to a superconductor is a powerful way of revealing the complexity of this macroscopic quantum state of matter. Even though the effects of the field in conventional type-II superconductors are well established, in a wide range of systems the consequences are far from being understood. One possibility is that the magnetic field may affect the competition between superconductivity and antiferromagnetism (or other competing orders), as suggested by several experiments and theories in high-T_c superconductors [1,2]. Particularly, in the case of a d-wave superconductor, study of the low energy excitations in the vortex state can provide useful information about the nature of the underlying ground states. The local density of states (DOS) of these excitations can be effectively probed by measuring the magnetic field dependence of the NMR shift as presented here. Single crystals of heavy-fermion superconductor CeCoIn$_5$ are an ideal material for such a study owing to their high purity, most likely d-wave gap symmetry [3,4], and entirely accessible magnetic field-temperature (T) phase diagram.

Furthermore, an applied magnetic field (H_0) may induce a novel superconducting (SC) state in which the momentum of the Cooper pairs is not equal to zero, but becomes finite and proportional to H_0, as predicted by Fulde, Ferrell, Larkin, and Ovchinnikov (FFLO) [5]. In this state the SC order parameter oscillates in real space. The FFLO phase is expected to occur in the vicinity of H_{c2} when Pauli pair breaking dominates over orbital effects. The search for this exotic SC phase has attracted much of current interest [6–9], and there is experimental evidence that it is realized in CeCoIn$_5$ [6,7,10,11]. Moreover, CeCoIn$_5$ is close to an antiferromagnetic (AF) instability, offering thus a unique possibility to study the competition between FFLO and AF instabilities. It was recently shown that a substitution of 10% of Cd for In could generate AF droplets [12]. Even in pure CeCoIn$_5$, NMR has revealed the existence of some form of magnetism within the possible FFLO phase [13].

Here we report detailed ^{115}In NMR measurements as a function of H_0 from 2 to 13.5 T at $T = 73$ mK. We establish that the shape of the NMR spectra is determined by the inhomogeneous field distribution of a vortex lattice (VL) for $H_0 \lesssim 10$ T. For fields above 10 T, where a possible FFLO state (henceforth referred to as "modulated" or mSC state) is stabilized, the NMR spectra broaden well beyond what is expected on the basis of the VL distribution. Magnetic field dependence of the shift reveals explicit effects of the Zeeman energy on quasiparticles in this Pauli-limited superconductor. Below 10 T, the spin susceptibility increases as $\sqrt{H_0}$. This increase is related to the excess DOS due to the Zeeman and Doppler-shifted nodal quasiparticles, confirming the presence of gap nodes in the SC state of CeCoIn$_5$. Above 10 T, the spin susceptibility is strongly enhanced and increases linearly with H_0, as expected in the FFLO state [14]. If instead this enhancement is ascribed to field induced magnetism, our data place a lower bound on the spatial extent of the magnetic regions.

We have used high quality single crystals of CeCoIn$_5$ grown by a flux method [15]. Here, the spectra of the axially symmetric In(1) site in $H_0 \parallel [100]$ (aligned to better than 2°) are reported. They were recorded using a custom built NMR spectrometer and obtained, at each given value of H_0, from the sum of spin-echo Fourier transforms recorded at constant frequency intervals. The magnetic shift was determined by the diagonalization of the full nuclear spin Hamiltonian and by subtracting the orbital contribution of $\simeq 0.13\%$. The rf coil was mounted into the mixing chamber of a ^{3}He/^{4}He dilution refrigerator while a variable tuning delay line and matching capacitor were mounted outside the NMR probe to allow for a wide frequency or field coverage. The ^{63}Cu NMR on copper nuclei from the rf coil was used to determine the exact value of H_0. The sample was both zero-field and field-cooled and no visible influence of the sample's cooling history on the NMR spectra was detected. To avoid heating

of the sample by rf pulses we used very weak rf excitation power [16] and repetition times of the order of 10 sec.

In the Abrikosov SC state (henceforth referred to as the "uniform" uSC state), at low T, vortices tend to form a solid lattice [17] resulting in a spatial distribution of magnetic fields. This distribution is reflected in the NMR line shape, as shown in Fig. 1(a), and can be calculated by solving the Ginzburg-Landau (GL) equations [17,18]. We calculated the spectra employing Brandt's method [18], valid at any value of H_0 between the lower and upper critical fields. The input parameters for the calculation are the H_0, coherence length (ξ), penetration depth (λ), and VL geometry (the angle α). For a given value of H_0, a χ^2 minimization of the difference between the calculated and measured spectra, normalized to their corresponding areas, was performed with ξ, λ, and α as variational parameters. As the result is not very sensitive to the variation of α parameter, its value was set to $\alpha = 90°$, i.e., a square vortex lattice. At $H_0 = 4$ T the minimum χ^2 was achieved for $\xi = 34 \pm 10$ Å and $\lambda = 1580 \pm 120$ Å, values consistent with earlier reports [19]. The spectra were then simulated for all field values 2 T $< H_0 <$ 11.6 T using this *single* set of parameters. In order to make a quantitative comparison, the full width at half maximum (FWHM) and the square root of the second moment ($\sqrt{\sigma^2}$) of the simulated and measured spectra are plotted in Fig. 1(b) as a function of H_0. The agreement between the simulation and the experiment in the uSC state for $H_0 \lesssim 10$ T is excellent. To our knowledge this is the first time that the comparison is performed over such a wide field range. Within the sensitivity of our measurements, these results indicate that for $H_0 \parallel [100]$, ranging from 2 to 10 T, the GL model provides an adequate description of the vortex state even for this Pauli-limited superconductor, contrary to the results of neutron scattering study for H_0 perpendicular to the planes [20]. This discrepancy might

stem, besides H_0 orientation, from the fact that the probability distribution, i.e., NMR spectrum, is insensitive to the Pauli effects which are enhanced near the vortex cores [21].

For fields above 10 T, the measured spectra broaden beyond what is expected from the calculated VL distribution in the GL model. We have found that it is impossible to account for the high-field linewidth broadening regardless of the ξ and λ values used. An appreciable discrepancy begins at $H_0 = H^*$ that corresponds to the transition field from the uSC to the mSC state [6,16]. Therefore, we demonstrate that at low T the transition to the mSC state is identified by the onset of the additional asymmetric NMR linewidth broadening. This implies the presence of an additional modulation of the internal field in the mSC state. The line shape contains a *single* peak, which is consistent with an incommensurate modulation of the internal field along *two* spatial directions [22], as expected for an FFLO state in a *d*-wave SC [23,24].

We now proceed to the discussion of the main result, the H_0 dependence of the low T shift data illustrated in Fig. 2. Two phase transitions are clearly discerned. The first order phase transition from the normal to the mSC state at $H_0 = H_{c2}$ is characterized by the sizable discontinuity of the shift. The continuous second order phase transition from the uSC to mSC state occurs at $H_0 = H^*$. Presented data provide the first clear NMR signature of this phase transition [13,16]. In both SC states, the shift increases with increasing H_0. However, above H^* the field dependence of the shift is significantly enhanced. In the following, we will first address variation of the shift in the uSC.
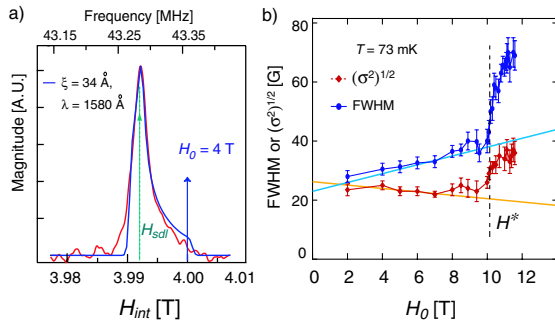

FIG. 1 (color online). (a) In(1), $\langle -1/2 \leftrightarrow -3/2 \rangle$ transition, spectra (red) at $T = 73$ mK and $H_0 = 4$ T compared to calculated VL line shape (blue), as described in the text, as a function of the internal magnetic field (H_{int}). The arrows indicate H_{int} corresponding to the saddle point (H_{sdl}) and H_0 fields, respectively. (b) FWHM and $\sqrt{\sigma^2}$ of the measured In(1) spectra (closed symbols) as a function of H_0. Solid lines are the calculated values obtained as described in the text. The dashed line denotes the field H^*.
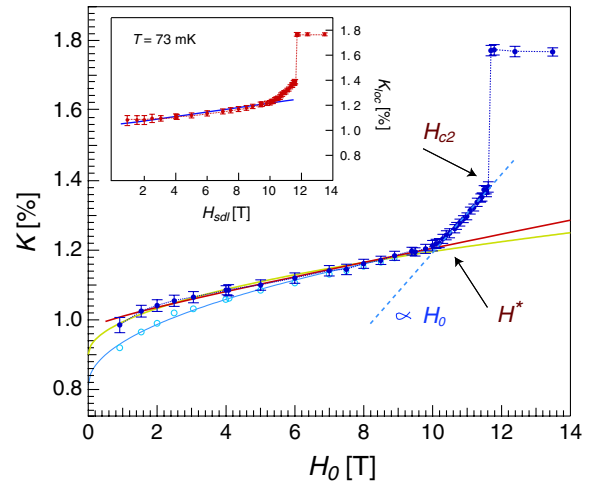

FIG. 2 (color online). In(1) magnetic shift (open circles) as a function of H_0 at $T = 73$ mK. The solid circles are the shift corrected for diamagnetic contribution, i.e., shift with respect to the average magnetic field in the VL unit cell. The dotted lines are guide to the eye. The darker (red) solid line is the calculated shift, as described in the text. The lighter solid lines are a fit of the data, for $H_0 < 10$ T, to Eq. (2). The dashed line is a linear fit to the data for $H_0 > 10$ T. Inset: Magnetic field dependence of the local In(1) shift K_{loc} at the saddle point field. The solid line is calculated shift, $K = 1.04\% + 77.1(\epsilon + E_Z + E_{Dsdl})\% \text{eV}^{-1}$.

In a SC with the *d*-wave gap symmetry in the excitation spectrum, at low T the quasiparticle excitations are restricted to nodal regions [25]. These low energy quasiparticles can be probed with NMR shift measurements. Specifically, the shift is proportional to the DOS [$N(E)$] averaged over energy E in a range of the order of $k_B T$ around the Fermi energy, E_F [26]. Thus, at sufficiently low T the shift is proportional to the DOS at the Fermi level, i.e, $K \sim \langle N(E) \rangle \equiv N_F$. This implies that in the SC state only the DOS in the regions around the nodes of the gap contributes to K. Near the nodes the DOS depends linearly on quasiparticle excitation energy, for energies less than half of the gap magnitude. Therefore, the low T shift is given by,

$$K \sim \langle N_F \rangle \propto \langle |\epsilon + E_Z + E_D| \rangle, \quad (1)$$

where $\langle \ldots \rangle$ denote the average over four nodes in the k space, and $\epsilon \approx k_B T$, $E_Z = \mu_{\text{eff}} H_0$, and $E_D = \mathbf{v}_F \cdot \mathbf{p}_s$ are the thermal, Zeeman, and Doppler energy terms, respectively. The Doppler term originates from the shift of the excitation energies of the nodal quasiparticles, with Fermi velocity $\mathbf{v}_F$, moving in the superflow field with momentum $\mathbf{p}_s$. Both E_Z and E_D depend on H_0. The H_0 dependence of the local $\mathbf{p}_s$, and thus E_D at any point in the real space of the VL, can be calculated exploiting Brandt's algorithm [18]. The same algorithm is then used to directly calculate the H_0 dependence of the shift averaged over the real space of a VL unit cell from $K = K_0 + K_e(\langle |\epsilon + E_Z + E_D| \rangle)$. The following input parameters were used: $\mathbf{v}_F \hbar = 49.1$ meV Å [27], $E_Z = 0.5\mu_B H_0$, $K_0 = 0.97\%$, and $K_e = 85.24\%$eV^{-1}, determined so that K at H_{c2}^{orb}, the orbital $H_{c2} = 38.6$ T, equals the normal state shift. Excellent agreement with the data for $H_0 < 10$ T is obtained with this simple model, as illustrated in Fig. 2.

We point out that the shift has been determined from the frequency corresponding to the first moment, that is the average frequency, of the spectra and thus reflects the real space average of K over a VL unit cell. In Fig. 2 we have thus presented both the shift data with respect to the applied field H_0, as well as the same data calculated with respect to the field averaged over the VL unit cell as obtained from the Brandt's algorithm. In our calculation of the average K in the uSC state, we neglected the Pauli paramagnetic effects and their variation across the VL. This is justified by the fact that these effects are insignificant outside and are enhanced only near the vortex cores. Thus, mainly due to the large volume contribution from the outside of the cores, the average DOS is not notably affected by the Pauli paramagnetism [21]. The field dependence of the data is fully explained by the increase in the dominant Zeeman and average Doppler energy of the quasiparticles. Note that this behavior is in sharp contrast with that in a conventional SC without nodes, where the Doppler term has a negligible effect. Thus, our results indicate that CeCoIn$_5$ is a SC with nodes in the gap, which is most likely of *d*-wave ($d_{x^2-y^2}$) symmetry.

The observed field dependence is also consistent with Volovik's prediction [25] for a *d*-wave SC that the average DOS $\propto \sqrt{H_0/H_{c2}}$. As shown in Fig. 2, $H_0 < 10$ T data are well fitted to

$$K = K_0 + \beta K_n \sqrt{H_0/H_{c2}^{\text{orb}}}, \quad (2)$$

where H_{c2}^{orb} is fixed to 38.6 T and $K_n = 1.77\%$ is the normal state shift. The fit parameters are $K_0 = 0.90 \pm 0.01\%$ and $\beta = 0.33 \pm 0.02$. In the limit $H_0 \to 0$, K remains finite, at nearly half of the normal state shift. The finite shift, that is the field independent constant contribution K_0, may be attributed to the multiband nature of SC in CeCoIn$_5$. The contribution K_0 would then originate from *normal* quasiparticles in the small gap band [28].

In order to verify the significance of the contribution of E_D to the quasiparticle energy, we have also extracted the *local* shift from the peak of the spectra which corresponds to the nuclei positioned at the saddle point of the field distribution, that is at the point in real space midway between two vortices. At this point where $H = H_{sdl}$, the local $\mathbf{p}_s$, and thus E_D, increases very slightly with increasing H_0 (for $H_0 \ll H_{c2}^{\text{orb}}$) since it is not influenced by geometry effects such as the change in the vortex number with varying H_0. Thus, the local shift at the saddle point should exhibit weaker field dependence than the shift averaged over the entire VL. This is indeed the case as shown in the inset to Fig. 2, where the local shift at H_{sdl} is displayed. This shift corresponds to that of the peak of the spectrum calculated with respect to the H_{sdl}, obtained from Brandt's algorithm. Here the observed field dependence arises solely from the increase of the quasiparticles' Zeeman energy.

We next consider the field dependence of the shift in 10 T $< H_0 < H_{c2}$. As apparent in Fig. 2, in this regime K increases linearly with H_0. Contrary to [7], no evidence of discontinuous jump in K, indicating the transitions between different Landau levels within the FFLO state, is observed. Our data can be well described by

$$K = K_0^h + \beta_h K_n(H_0/H_{c2}), \quad (3)$$

where H_{c2} is fixed to 11.7 T, $K_n = 1.77\%$ is the normal state shift, $\beta_h = 0.77 \pm 0.02$, and $K_0^h = 0.03 \pm 0.01$. The latter parameter shows that as $H_0 \to 0$, K extrapolates to zero. The rate of increase of the shift ($\Delta K/\Delta H_0$) is 5 times higher than that in the uSC for $H_0 < H^*$. After careful consideration of all the possibilities regarding the values of K_0^h and the Doppler term, we conclude that this large increase can be ascribed to an enhancement of E_Z and its dominance over E_D in the entire VL unit cell. For several reasons the fulfillment of the $E_Z > E_D$ condition is very likely in the FFLO state. First, the internal field, due to paramagnetic effects, can be large enough in the FFLO state to exceed the E_D term everywhere in the VL unit cell. Second, it is possible that E_D is suppressed by either the opening of a subdominant gap, or a change in the gap

structure so that $\mathbf{v_F}$ and $\mathbf{p_S}$ become nearly orthogonal. The gap opening scenario is very unlikely since K increases in the FFLO state contrary to expectations in the presence of a gap [23,24]. On the other hand, changes in the gap structure are expected in the FFLO state. The observed $\Delta K/\Delta H_0$ could reflect the fact that the DOS is no longer simply proportional to E. That is, the DOS dispersion relation changes and/or an extra structure, such as bound states, is induced by H_0. This is consistent with the FFLO scenario [23] but further calculations are required for a quantitative comparison.

Nonetheless, a magnetic origin of the mSC phase or coexistence of some magnetic order with the FFLO state cannot be excluded [11,13]. Given the *a priori* antagonistic relationship between SC and magnetism, it is likely that magnetism appears in the spatial regions where SC is suppressed as is the case in the vortex cores [1,13]. However, it was shown that the existence of the local moment magnetism requires pair coherence [11]. The absence of magnetism in the normal state could be attributed to the Kondo screening, acting on a short length scale, of Ce local moments. In the SC state the Kondo screening becomes ineffective, since quasiparticles have very small momentum inhibiting short range screening, giving rise to magnetism. Besides, a magnetic phase could be stabilized only in high fields when there is a sufficient overlap between vortex cores, so that the correlations between magnetic regions can be established. In field of 10 T, the distance between neighboring vortices is ≈ 140 Å. Thus, the long range magnetic order could be established in fields above 10 T if the radius of the magnetic cores is larger than $2\xi \approx 70$ Å. In this case, the field enhancement of the shift would be a consequence of the canting of local Ce moments. Varying H_0 from 10.2 to 11.7 T increases the shift from 1.22% to 1.38%. With a hyperfine coupling between In(1) nucleus and its 4 Ce neighboring atoms of $A \approx 1.2 T/\mu_B$ [29], the increase of the average local magnetic moment is $\Delta\mu_{\text{eff}} = \Delta(KH_0)/4A \approx 0.0075\mu_B/\text{Ce}$. This corresponds to 7.5% of a typical normal state local Ce moment ($\simeq 0.1\mu_B$), implying that for $H^* < H_0 < H_{c2}$, the increase of H_0 induces a canting of $\simeq 7.5\%$ of the normal state local Ce moment.

In conclusion, our essentially zero-T limit data provide the clearest NMR evidence of two phase transitions in the vicinity of H_{c2} thus far. In the uSC phase, the NMR spectra can be nicely fitted to the calculated magnetic field distribution arising from the vortex supercurrents with SC coherence length ($\xi \approx 34$ Å) and penetration depth ($\lambda \approx 1580$ Å) as fitting parameters. To explain the observed increase of the spin susceptibility with H_0, we conclude that the dominant low energy excitations are the Zeeman and Doppler-shifted quasiparticles extending outside the vortex cores, implying that CeCoIn$_5$ is of d-wave gap symmetry. For the high-field (above 10.2 T) low-T phase we find that it cannot correspond to a simple VL rearrangement. It is consistent with an FFLO state with 2D incommensurate modulation of the quasiparticle density in which the spin susceptibility strongly increases as H_0. If the magnetism appears there in the spatially localized fashion, we show that magnetic cores extend on a length scale larger than 2ξ.

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