Texture in the Superconducting Order Parameter of $CeCoIn_5$ Revealed by Nuclear Magnetic Resonance

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We present a ^{115}In NMR study of the quasi-two-dimensional heavy-fermion superconductor $CeCoIn_5$ believed to host a Fulde-Ferrel-Larkin-Ovchinnikov (FFLO) state. In the vicinity of the upper critical field and with a magnetic field applied parallel to the *ab* plane, the NMR spectrum exhibits a dramatic change below $T^*(H)$ which well coincides with the position of reported anomalies in specific heat and ultrasound velocity. We argue that our results provide the first microscopic evidence for the occurrence of a spatially modulated superconducting order parameter expected in a FFLO state. The NMR spectrum also implies an anomalous electronic structure of vortex cores.

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A myriad of fascinating properties has been proposed for unconventional superconductors in the presence of a strong magnetic field. Among the possible exotic superconducting (SC) phases, a spatially nonuniform SC state originating from the paramagnetism of conduction electrons has become a subject of intense theoretical investigation after the pioneering work by Fulde and Ferrel as well as by Larkin and Ovchinnikov (FFLO) in the mid-1960s [1]. In the FFLO state, pair breaking due to the Pauli effect is reduced by the formation of a new pairing state ($\boldsymbol{k}\uparrow, -\boldsymbol{k}+\boldsymbol{q}\downarrow$) with $|\boldsymbol{q}| \sim 2\mu_B H/\hbar v_F$ (v_F is the Fermi velocity) between exchange-split parts of the Fermi surface, instead of ($\boldsymbol{k}\uparrow, -\boldsymbol{k}\downarrow$) pairing in ordinary superconductors. In other words, spin up and spin down electrons can stay bound only if the Cooper pairs have a drift velocity in the direction of magnetic field. As a result, a new SC state with spatially oscillating order parameter and spin polarization with a wavelength of the order of $2\pi/|\mathbf{q}|$ should appear in the vicinity of upper critical field H_{c2} [2,3].

The issue of the actual observation of the FFLO phase has only been addressed especially in the last several years. Although several type-II superconductors (including heavy-fermion and organic compounds) have been proposed as likely candidates for the observation of the FFLO state, subsequent research has called the interpretation of the data into question [4]. No solid evidence, which is universally accepted as proof of the FFLO state, has turned up. In this context, the case of $CeCoIn_5$ has aroused great interest, because several measurements have led to a renewed discussion of a possible high field FFLO state [5–8]. $CeCoIn_5$ is a new type of heavy-fermion superconductor with quasi-2D electronic structure [9] and is identified as an unconventional superconductor with, most likely, *d*-wave gap symmetry [10–14]. Very recent heat capacity measurements revealed that a second order phase transition takes place at $T^*(H)$ within the SC state in the vicinity of the upper critical field with $\boldsymbol{H}$ parallel to the *ab* plane $H_{c2}^{\parallel}$ at low temperatures [5,6]. The transition line branches from the $H_{c2}^{\parallel}$ line and decreases with decreasing T, indicating the presence of a novel SC phase. (Hereafter we refer to the phase below $T^*(H)$ as the *high field SC phase.*) In the inset of Fig. 1 the *H*-*T* phase diagram for $CeCoIn_5$ is illustrated in the vicinity of $H_{c2}^{\parallel}$ and at low temperatures.

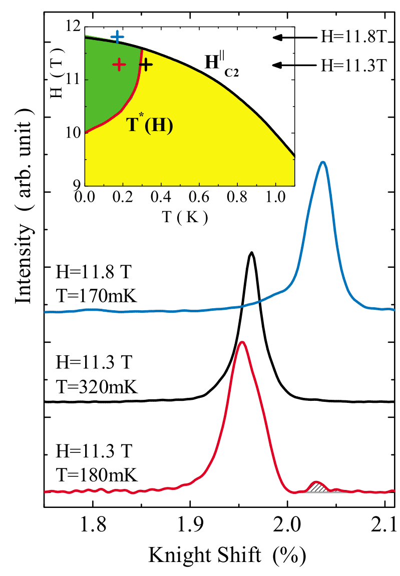

FIG. 1 (color). Inset: Experimental *H*-*T* phase diagram for $CeCoIn_5$ below 1 K in the $\boldsymbol{H} \parallel a$ axis. The region shown by green depicts the high field SC phase discussed in the text. Horizontal arrows indicate the magnetic fields at which the NMR spectrum was measured. Main panel: ^{115}In-NMR spectra outside, slightly above $H_{c2}^{\parallel}$ (blue line), slightly above T^* (black line), and well inside (red line) the high field SC phase. The resonance feature at higher frequency is marked by hatching. The (H, T) points at which each NMR spectrum was measured are shown by crosses in the inset.

Subsequent ultrasound [7] and thermal conductivity [8] investigations were presented in support of the FFLO nature. Thus, as new results accumulate, there is a growing experimental evidence that the FFLO state may indeed be realized in the high field SC phase of $CeCoIn_5$.

$CeCoIn_5$ appears to meet in an ideal way the strict requirements placed on the existence of the FFLO state. First, an extremely high $H_{c2}^{\parallel}$ ($\sim$12 T at $T = 0$) is favorable for the occurrence of the FFLO state because then the Pauli effect may overcome the orbital effect. Pauli-limited superconductivity is, in fact, supported by the fact that the phase transition from SC to normal metal at the upper critical fields is of the first order below $\sim$1.3 K [11,15]. Second, it is in the extremely clean regime. Third, d-wave pairing symmetry greatly extends the stability of the FFLO state with respect to a conventional superconductor [16].

While these experimental and theoretical results make the FFLO scenario a very appealing one for $CeCoIn_5$, there is no direct experimental evidence so far which verifies the spatially nonuniform SC state expected in the FFLO state. A central matter related to this issue is the quasiparticle structure in the high field SC phase. Therefore, a powerful probe of the quasiparticle excitations in the high field SC phase is strongly required to shed light on this subject. NMR is particularly suitable for the above purpose because NMR can monitor the low energy quasiparticle excitations sensitively. Here we present the NMR spectrum in the vicinity of $H_{c2}^{\parallel}$ to extract microscopic information on the quasiparticle structure for the first time. The spectrum we observed in the high field SC phase is quite unique, and we argue that our results provide the first microscopic evidence for the occurrence of a spatially inhomogeneous SC state expected in a FFLO state.

Single crystals of $CeCoIn_5$ were grown by a flux method as described in Ref. [9]. No detectable secondary phases were found in powder x-ray diffraction and scanning electron microscopy. Specific heat revealed a sharp transition at $T_c = 2.3$ K with a transition width less than 0.1 K, indicative of high quality of the sample. The ^{115}In ($I = 9/2$) NMR measurements were performed on single crystal by using a phase-coherent pulsed NMR spectrometer. Experiments were always carried out in the magnetic field $\boldsymbol{H}$ parallel to the [100] direction under the field-cooled condition. The rf excitation (H_1) power which was 10^{-2} times smaller than that used in ordinary measurements was used in order to prevent the rise in temperature of the single crystal sample. The spectra were obtained from a convolution of Fourier transform signals of spin echo which were measured at each 20 kHz interval. The tetragonal crystal structure of $CeCoIn_5$ consists of alternating layers of $CeIn_3$ and $CoIn_2$ and so has two inequivalent In sites per unit cell [9]. We report NMR results at the In(1) site with axial symmetry in the $CeIn_3$ layer, which locates in the center of the square lattice of Ce atoms. The Knight shift ^{115}K was obtained from the central ^{115}In line ($\pm 1/2 \leftrightarrow \mp 1/2$ transition) using a gyromagnetic ratio of $^{115}\gamma_N =$ 9.3295 MHz/T and by taking into account the electric quadrupole interaction.

Figure 1 depicts the NMR spectra outside and well inside the high field SC phase. At T slightly above $T^*(H = 11.3\ \mathrm{T}) \simeq 300$ mK, the NMR spectrum is almost symmetric as shown by the black solid line. Generally, the spatial distribution of the magnetic field arising from the flux line lattice structure gives rise to an asymmetric NMR spectrum [17], indicating that the influence of the field distribution is negligible in the present high field region. A most remarkable feature in the NMR spectrum well inside the high field SC phase shown by the red solid line is an appearance of a new resonance peak with small but finite intensity at higher frequency, as seen clearly at $^{115}\mathrm{K} \simeq 2.03\%$. The intensity of the higher resonance line is about 3%–5% of the total intensity and is nearly T independent below 180 mK. This higher resonance line is an important clue to elucidate the nature of the high field SC phase. We stress that the occurrence of the magnetic ordering is a highly unlikely source for the higher resonance in view of the large difference in the intensity of the two lines. Should antiferromagnetic order set in, the alternating hyperfine fields would produce two inequivalent ^{115}In(1) sites, which give rise to the two resonance lines with equal intensities.

In Fig. 1, the NMR spectrum at H slightly above $H_{c2}^{\parallel}$ is also shown by the blue line. A noteworthy feature in the spectrum inside the high field SC phase (red solid line) is that the position of the higher resonance line within the high field SC phase coincides well with that of the resonance line above $H_{c2}^{\parallel}$ (blue), while the position of the lower resonance line locates close to that of the SC state above $T^*(H)$ (black line). Therefore, it is natural to deduce that the higher resonance line originates from a normal quasiparticle regime, which is newly formed below $T^*(H)$, while the lower resonance line corresponds to the SC regime, which appears to have a similar quasiparticle structure above $T^*(H)$. These results lead us to conclude that an appearance of the new resonance line at a higher frequency is a manifestation of a novel normal quasiparticle structure in the high field SC phase.

Figure 2 displays the temperature evolution of the spectra at $H = 11.3$ T. The higher resonance line grows rapidly with T just below $T^*(H)$. A double peak structure shows up at $T = 240$ mK, followed by a shoulder structure at $T =$ 260–300 mK, indicating that the intensity of the higher resonance line dominates. Two lines merge into a single line above $T^*(H) \sim 300$ mK. The T dependences of the ^{115}K evaluated from the peak position is plotted in Fig. 3 [18]. The ^{115}K at $H = 11.3$ T exhibits quite unusual T dependence. As the temperature is lowered below $T^*(H)$, the ^{115}K of the higher resonance line increases rapidly and coincides with the ^{115}K above $H_{c2}^{\parallel}$ below 180 mK. On the other hand, below $T^*(H)$, the ^{115}K of the lower resonance line changes slightly.

So far, we have established that the high field SC phase is characterized by the formation of normal regions. This

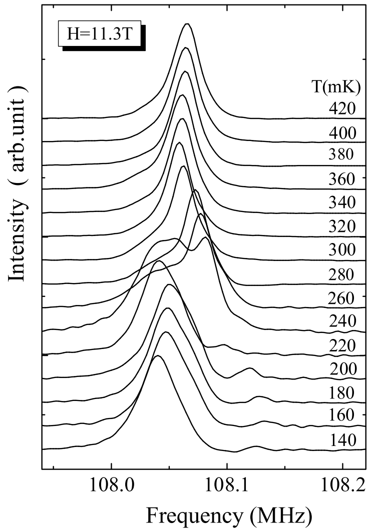

FIG. 2. The ^{115}In-NMR spectra (central line of the $\pm1/2 \leftrightarrow \mp1/2$ transition) as a function of frequency for various temperatures at $H = 11.3$ T.

brings us to the next question on whether the NMR spectrum below $T^*(H)$ is an indication of a FFLO phase. It has been predicted that in a FFLO phase the SC order parameter exhibits one-dimensional spatial modulations along the magnetic field, forming planar nodes that are periodically aligned perpendicular to the flux lines (see the inset of Fig. 5 below). Therefore, the formation of the normal regions is consistent with a phase expected in a FFLO state. We show that the NMR spectra just below $T^*(H)$ in Fig. 2 can be accounted for by considering such planar structures.

The field induced layered structure expected in a FFLO phase resembles the SC states of stacks of superconductor-normal-superconductor (*S*-*N*-*S*) Josephson tunnel junctions. In the NMR experiments, rf magnetic field H_1 is applied perpendicular to the dc magnetic field ($H_0 \parallel a$, $H_1 \parallel b$). The shielding supercurrent currents flow passing across the planar nodes. Because of the second order transition at $T^*(H)$, the modulation length of the order parameter parallel to H_0 or the thickness of the SC layers, $\Lambda(= 2\pi/|\mathbf{q}|)$, diverges as $\Lambda \propto (T^* - T)^{-\alpha}$ with $\alpha > 0$, upon approaching $T^*(H)$. Therefore Λ exceeds the in-plane penetration length λ in the vicinity of T^*. In such a situation, the rf field penetrates into the normal sheets much deeper than into the SC sheets, which results in a strong enhancement of the NMR intensity from the normal sheets. At low temperature where Λ becomes comparable to $\xi(\ll \lambda)$, penetration of the rf field into the normal sheets is the same as that into the SC sheets.

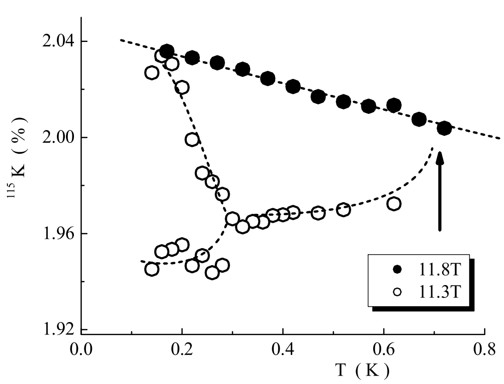

FIG. 3. Temperature dependence of Knight shift ^{115}K at $H = 11.8$ T (●) and 11.3 T (○). The arrow shows the SC transition temperature at the corresponding field. The broken lines are guide for eyes.

We estimate the above effect semiquantitatively, assuming a simple sinusoidal modulation of the gap function along the applied field (x axis), $\Delta(x) = \Delta_0 \sin qx$ [19]. From the London equation, the spatial modulation of $H_1(x)$ in the FFLO state is given as

$$H_1(x) \propto \frac{\sinh\frac{\Lambda/2-x}{\lambda} + \sinh\frac{x}{\lambda}}{\sinh\frac{\Lambda}{2\lambda}} \tag{1}$$

for the boundary condition of $H_1(x)/H_1^{\mathrm{normal}} = 1$ at $x = 0$ and $x = \Lambda/2$, The present measurement was done at the condition with very small H_1 and short pulse width τ_w (10 μs) which was kept to be constant throughout the measurement. This means a very small tipping angle of nuclear spin by a NMR pulse, namely, $\theta = \gamma_N H_1 \tau_w \ll \pi/2$. As the amplitude of spin echo intensity is proportional to $\sin(\gamma_N H_1 \tau_w) * \sin^2(\gamma_N H_1 \tau_w/2)$ [20], the NMR intensity shows the H_1^3 dependence for the case of $\gamma_N H_1 \tau_w \ll \pi/2$.

As the NMR spectrum depends on the Knight shift, which is spatially dependent in the FFLO state, we need to compute the number of nuclei at the position of the particular local field in the spatially distributed case. The NMR spectrum is given by a convolution of spatial dependences of those effects, and is given by

$$I(k) \propto \int_0^{\Lambda/2} \delta\left(K\left(\frac{\Delta(x)}{T}\right) - k\right)[H_1(x)]^3 dx, \tag{2}$$

where $K(\Delta/T)$ is the Yoshida function for the Knight shift in the SC state [21]. The inevitable inhomogeneity of H_1 leads to a distribution of spin echo intensity across the sample. Nevertheless, since there is a cutoff in H_1 from Eq. (1), the assumed form probably is a crude phenomenological model for the actual intensity. From a mathematical procedure similar to a powder pattern calculation, we obtain the functional form of the NMR intensity and then calculate a spectrum numerically to fit the experimental data. Adjustable parameters are only two, $\frac{\Lambda}{\lambda}$ and $\frac{T}{\Delta_0}$.

Figure 4 depicts the calculated spectrum just below $T^*(H)$, where we have used $\frac{T}{\Delta_0} = 0.049$ and $\frac{\Lambda}{\lambda} = 11.5$ at $T = 240$ mK, and $T/\Delta_0 = 0.053$ and $\frac{\Lambda}{\lambda} = 19$ at $T = 260$ mK. The spectrum is also convoluted with a Lorentzian shape for an inhomogeneous broadening. This simulation, in which planar nodal structure is assumed, reproduces well the observed spectra. In Fig. 5, we show

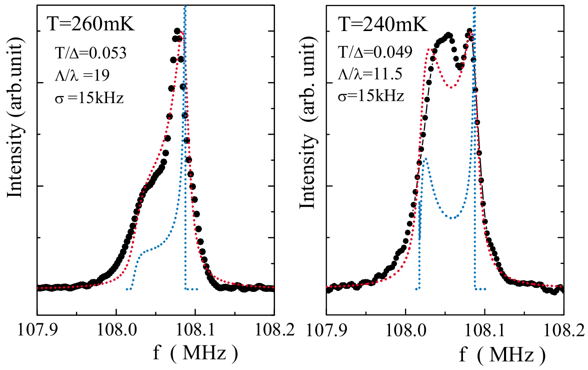

FIG. 4 (color). The ^{115}In-NMR spectra (●) at $T = 260$ and 240 mK. The red dotted line and the blue dotted line represent the simulation spectra with and without a convolution of an inhomogeneous broadening with a Lorentzian function ($\sigma = 15$ kHz), respectively. For details, see the text.

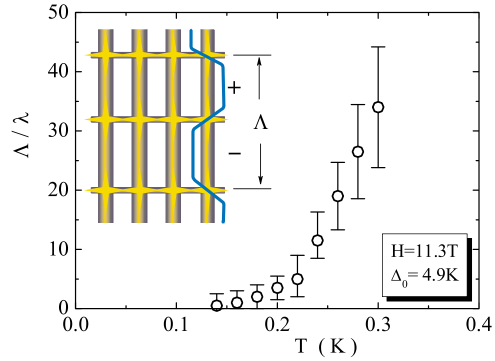

FIG. 5 (color). Temperature dependence of $\frac{\Lambda}{\lambda}$ for $H = 11.3$ T and $\Delta_0 = 4.9$ K. The inset illustrates the quasiparticle structure in the FFLO state. The planar nodes are periodically aligned perpendicular to the vortices. The SC order parameter exhibits one-dimensional spatial modulation along the vortices (blue line).

the temperature dependence of $\frac{\Lambda}{\lambda}$ obtained from the fitting. As the magnetic field penetration depth, λ, is expected to nearly temperature independent ($\sim$2000 Å) at the temperature range concerned [$T^*(H) \ll T_{sc} \sim 0.7$ K] the wavelength of the spatial oscillation of the SC order parameter Λ decreases largely with lowering temperature. The expected divergence of Λ at $T^*(H)$ for the second order transition is smeared out in the simulation. We stress that, in spite of the very crude model, the evolution of the NMR spectrum with temperature is compatible with what is expected in a FFLO phase.

The presence of well-separated NMR lines implies that the quasiparticle excitation around the planar nodes is spatially localized. We speculate that the spatial dependence of the order parameter along the magnetic field may be Bloch wall-like or rectangular, rather than sinusoidal far below $T^*(H)$ [19]. We note that a peculiar electronic structure of vortex cores in $CeCoIn_5$ is inferred from the present results. A peculiar double peak structure in the NMR spectra directly indicates that the Knight shift within the vortex core deviates from that in the normal quasiparticle sheets. This implies that the vortex core is to be distinguished from the normal state above $H_{c2}^{\parallel}$, a feature in sharp contrast to conventional superconductors, where the Knight shift within the core coincides with the Knight shift in the normal state. These results call for further investigations on the real space structure of the SC order parameter and the vortex core structure.

To conclude, the ^{115}In NMR spectrum in $CeCoIn_5$ exhibits a dramatic change in the vicinity of $H_{c2}^{\parallel}$. Below $T^*(H)$ a new resonance line appears at a higher frequency, which can be attributed to the normal quasiparticle sheets formed in the SC regime. On the basis of the NMR spectrum, we are able to establish clear evidence of the spatially inhomogeneous SC state at high field and low temperatures, as expected in a FFLO state. The NMR spectrum also indicates that the vortex core structure of $CeCoIn_5$ appears to be markedly different from that of ordinary superconductors.

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