Absence of $^{17}\text{O}$ Knight-Shift Changes across the First-Order Phase Transition Line in Sr$_2$RuO$_4$

Masahiro Manago, Kenji Ishida, Zhiqiang Mao and Yoshiteru Maeno

Department of Physics, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

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We performed $^{17}\text{O}$ nuclear magnetic resonance measurements on superconducting (SC) Sr$_2$RuO$_4$ under in-plane magnetic fields. We found that no new signal appears in the SC state and that the $^{17}\text{O}$ Knight shifts obtained from the double-site measurements remain constant across the first-order phase-transition line, as well as across the second-order phase-transition line as already reported. The present results indicate that the SC spin susceptibility does not decrease in the high-field region, although a magnetization jump in the SC state was reported at low temperatures. Because the spin susceptibility is unchanged in the SC state in Sr$_2$RuO$_4$, we suggest that the first-order phase transition across the upper critical field should be interpreted as a depairing mechanism other than the conventional Pauli-paramagnetic effect.

The layered perovskite Sr$_2$RuO$_4$ has attracted special attention, because it has been suggested that Sr$_2$RuO$_4$ may be a chiral $p$-wave spin-triplet superconductor. The chiral state is shown from the broken time-reversal symmetry probed by $\mu\text{SR}$ and Kerr-effect measurements. The existence of spin-triplet equal-spin pairing is based on experimental results that show the spin susceptibility is unchanged on passing through the superconducting (SC) transition temperature $T_c$, as revealed by nuclear magnetic resonance (NMR) Knight-shift measurements at the Ru and O sites and polarized neutron scattering measurements. The chiral $p$-wave spin-triplet state would be an SC state analogous to the superfluid $^3\text{He}$ A$\alpha$-phase with two dimensionality.

However, several recent experimental results are difficult to interpret with the above SC state. The first-order (FO) SC-normal (S-N) transition accompanied by a clear magnetization jump is observed in a low-temperature region near the upper critical field $H_{c2}$ for fields parallel to the $ab$ plane. This abrupt S-N transition suggests that Sr$_2$RuO$_4$ is a spin-singlet superconductor, because this cannot be interpreted by the conventional orbital depairing effect but seems to be explained consistently by the conventional Pauli-paramagnetic effect. Indeed, the experimental $\mu_0H_{c2}$ for $T \rightarrow 0$ nearly matches the Pauli-limiting field $\mu_0H_{\text{Pauli}}$ estimated using the well-known formula $\mu_0H_{\text{Pauli}} = \frac{2\mu_0E_{\text{cond}}/(\chi_n - \chi_{\text{sc}}))^{1/2}}{\chi_{\text{sc}} \sim 1.4}$ T with $\chi_{\text{sc}} = 0$, where $E_{\text{cond}}$ is the SC condensation energy and $\chi_n$ and $\chi_{\text{sc}}$ are the spin susceptibilities in the normal and SC states, respectively. Here, $\chi_{\text{sc}} = 0$ means that the spin susceptibility totally vanishes in the SC state, which contradicts the above spin-susceptibility results showing $\chi_n \sim \chi_{\text{sc}}$.

Recently, we performed $^{99}\text{Ru}$ Knight-shift ($^{99}\text{K}$) measurements again to re-examine the previous results, and found a new phenomenon that the spin susceptibility slightly increases in the SC state at lower magnetic fields. We reported that this experimental result further suggests the spin-triplet equal-spin pairing state. Because the hyperfine coupling constant $A_{\text{hf}}$ at the $^{99}\text{Ru}$ site is largest among the nuclei that are feasible for NMR in Sr$_2$RuO$_4$ ($^{99}A_{\text{hf}} \sim -25$ T/$\mu_\text{B}$) the shift of the $^{99}\text{Ru}$-NMR spectrum is also largest. Thus, the $^{99}\text{K}$ measurement is suitable for detecting tiny changes of the spin susceptibility $\Delta\chi_n$ through the change of the Knight shift $\Delta^{99}\text{K}$ using the relation of $\Delta^{99}\text{K} \propto A_{\text{hf}}\Delta\chi_n$. However, if the $^{99}\text{Ru}$ NMR signal arising from the SC fraction appears far from that of the normal state owing to the large $\Delta\chi_n$ and is much weaker than the latter signal, it might be possible that we have not detected the SC signal owing to the poor signal-to-noise ratio. Indeed, such a separation between the normal- and SC-state signals was observed in the FO region in CeCoIn$_5$, and the SC-state NMR signal in the FO region is weaker than the normal-state signal depending on the temperatures and fields.

To exclude this possibility, we performed $^{17}\text{O}$-NMR measurements to take advantage of the NMR intensity of $^{17}\text{O}$ being roughly a hundred-times larger than that of $^{99}\text{Ru}$. Because $A_{\text{hf}}$ of the planar O site is one order of magnitude smaller than that of Ru, as discussed later, the separation between the signals of the normal and SC states in the case of spin-singlet pairing is not large, and both the signals can be recorded by a Fourier-transformed spectrum at one frequency. In addition, the previous $^{17}\text{O}$-NMR Knight-shift measurements were mainly performed at lower magnetic fields below 1.1 T to avoid the suppression of the superconductivity by the field. In this study, we focused on the $^{17}\text{O}$ Knight shift mainly in the field range of the FO transition, and also measured the Knight shift across the S-N transition driven by field rotation at low temperatures. We found that no new signal appears in the SC state, and that the $^{17}\text{O}$ Knight shift exhibits no anomaly even across the FO transition line, as well as in the lower-field region. These can exclude the possibility that the $^{99}\text{Ru}$ Knight shift decreases in the SC state, and suggest that the electrons form triplet-pairing just below $H_{c2}$ even at low temperatures, where the superconductivity is strongly suppressed by magnetic fields.

We performed the $^{17}\text{O}$ NMR measurements on an $^{17}\text{O}$-enriched single crystalline Sr$_2$RuO$_4$ with $T_c \sim 1.5$ K. Sr$_2$RuO$_4$ has two inequivalent O sites, O(1) in the RuO$_2$ plane and the apical O(2) in the SrO plane, as shown in
The (O(1) signal splits into two lines, O(1)∥ and O(1)⊥, in the magnetic field along the a axis, where the || (⊥) symbol denotes the O site with the magnetic field parallel (perpendicular) to the Ru-O-Ru bonds. Thus, three distinct NMR central lines are observed as shown later. The hyperfine coupling constant of the planar O(1) nucleus with the electronic spins is larger than that of the apical O(2) nucleus (\( A_{hf}^{s} \)). We examined the Knight-shift difference between the O(1) and O(2) sites, because the Meissner diamagnetization in the SC state and the small drift of the applied magnetic field, which can be macroscopic variations, are eliminated by this subtraction, and a precise Knight-shift measurement can be performed. The difference of the Knight shift is expressed as

\[
\Delta K_{\parallel,\perp} = K_{1\parallel,\perp} - K_{2} = (A_{hf}^{\perp} - A_{hf}^{\\text{apical}})\chi_{s} + \text{const.} \quad (1)
\]

Here, \( K_{i} \) are the Knight shifts at the O(i) sites \((i = 1, 2)\), and \( \chi_{s} \) is the spin susceptibility. Multiple spin components were introduced for the spin part of the Knight shift in this system. This will be discussed later in this paper. The constant term corresponds to the orbital shift, which is usually temperature-independent and small in the \(^{17}\text{O}\) nucleus. The O(2) line can be approximately regarded as a reference signal of the internal magnetic field owing to the smaller hyperfine coupling constant than that of the O(1) site. Such a double-site Knight-shift measurement was also performed in the previous \(^{99}\text{Ru}\) NMR. The temperature-sweep NMR measurements were performed in various magnetic fields as shown in Fig. 1(b). The Meissner-shielding signal was also measured to confirm that the NMR measurements were indeed performed in the SC state and to detect some anomalies related to the FO transition nature.

The temperature dependence of the Knight-shift differences defined by Eq. (1) is summarized in Fig. 1(c). The Knight shifts remain constant at both the first- and second-order phase transition regions. The lower-field results reproduce the previous results, and the detailed higher-field results of O constitute the new information obtained in this study.

The spectra at 1.30 T are shown in Fig. 2. The spin part of the Knight shifts at the O(1) sites are shown with the horizontal arrows. If a spin-singlet pairing is realized in \( \text{Sr}_2\text{RuO}_4\), roughly 20% of \( \chi_{s} \) decreases at 1.3 T, as estimated from the specific-heat measurement under the magnetic field. This can be detected for the present resolution, because the frequency changes are recognizable quantities as shown by the vertical arrows. No line shift or new lines were detected in the SC state. This is the main result of this paper, and indicates that \( \chi_{s} \) is unchanged even in the field-region of the FO transition.

In the recent \(^{99}\text{Ru}\)-NMR measurement at lower fields, a tiny increase of the spin susceptibility was reported as mentioned above. However, no clear increase of the spin susceptibility was detected in the present \(^{17}\text{O}\) measurement. The additional \( \sim 2\% \) spin polarization, which was detected by the \(^{99}\text{Ru}\)-NMR measurement, corresponds to the \( \Delta f \sim 0.2 \text{kHz} \) line shift in the O(1)∥ line.
Because the estimated shift is comparable to the present frequency resolution of $\sim 0.3$ kHz, the absence of a clear increase would be reasonable.

We performed the NMR measurement carefully to avoid any heating of the sample by the NMR rf pulse fields. The sample was immersed in $^3$He-$^4$He mixture to avoid any rf heating. Nevertheless, rf heating becomes recognizable with decreasing temperature, and thus the rf pulse-power-dependence of the NMR spectra were measured to inspect the rf heating effect. No clear power dependence of the NMR spectra was detected at 0.13 K at 1.30 T in the SC state when the rf pulse power was reduced to 1/8 of the ordinary level with a fixed pulse width of 7 µs (not shown here). Although the pulse power cannot be made arbitrarily small owing to the weak NMR intensity with weaker rf pulse fields, destruction of the superconductivity is unlikely to occur in the power range used in this study. Thus, we conclude that the unchanged Knight shift is not caused by the rf heating, but an intrinsic property of Sr$_2$RuO$_4$.

The field-angle dependence of the Knight shift was measured at 0.15 K. The field immediately exceeds $H_{c2}$ by tilting the applied field from the $ab$ plane, and thus the Knight shifts in the SC and normal states can be compared at a fixed temperature with the same NMR pulse conditions. There was no clear change of the Knight shift or broadening observed in the SC state at 1.00 and 1.30 T as shown in Fig. 3, where $\theta$ is the angle between the applied field and the $ab$ plane. This result suggests that the spin susceptibility is unchanged even across the S-N transition induced by the small tilt of the applied field.

The field-angle dependence of the shielding effect shown in Fig. 3 obtained by an ac field parallel to the $ab$ plane, has a double-peak structure, and becomes weak where the field is in the $ab$ plane. This dependence is understood as the suppression of the Meissner shielding, which is characteristic of the quasi-two-dimensional supercurrent of the SC Sr$_2$RuO$_4$, as discussed in Refs. 8 and 19. Because the line width is independent of the strength of the shielding, the diamagnetic field is considered to be extremely small and cannot be detected by the nuclear spins with relatively small gyromagnetic ratios. However, at 1.00 T, the NMR intensity at the O(1) site in the SC state decreases to about 1/2 that of the normal state; this is because the shielding of the rf field is larger in the SC state than in the normal state. This indicates that the present NMR spectra are indeed obtained in the SC state.

Although the signs of the superconductivity were detected in the field-region of the FO transition, features of the FO transition were not observed in the present sample with the $^{17}$O NMR and the Meissner-shielding measurements. Because the present sample has much larger mass ($\sim 70$ mg) than those used in the previous study detecting the FO transition, it may be difficult to detect it in the present sample even by another methods such.
as the specific-heat or magnetization. However, we can safely say that the present sample is a high-quality sample with \( T_c \sim 1.5 \) K and as good as the samples showing the FO transition.

One may consider that the unchanged Knight shift is a consequence of the cancellation of the Knight-shift changes in different orbitals because \( \text{Sr}_2\text{RuO}_4 \) is a multi-band system. We analyze the Knight shift in the SC state following the discussion by Imai et al.\(^{22} \) In their model, the \(^{17}\text{O} \) Knight shifts are expressed by the spin parts of the different Ru \( 4d \) and O \( 2s \) electrons, because the spin polarization in the Ru \( 4dx_y \) and \( 4dz_x \) orbitals is transferred to the O \( 2p_y \) and \( 2p_z \) orbitals, respectively, owing to the covalency of \( \pi \) bonds. The orbital Knight shifts of the O sites are assumed to be negligibly small, and a nearly temperature-independent isotropic component is ascribed to the O \( 2s \) electrons. The O \( 2p \) spin parts have anisotropic dipole symmetry: the dipolar field takes a maximum value along the lobe of the \( 2p \) orbital and \(-1/2\) of the maximum value along the two orthogonal directions. The spin part of in-plane components of the O(1) Knight shifts are then expressed as\(^{22} \)

\[
K_{1,\parallel} = \frac{1}{N_{\text{A}\text{H}B}} (-C\chi_{xy} - D\chi_{zz} + \sigma\chi_{2s}),
\]

\[
K_{1,\perp} = \frac{1}{N_{\text{A}\text{H}B}} (2C\chi_{xy} - D\chi_{zz} + \sigma\chi_{2s}),
\]

where \( N_{\text{A}} \) is Avogadro’s number, \( \chi_{xy} \), \( \chi_{zz} \), and \( \chi_{2s} \) are the partial spin susceptibilities of \( 4d_{xy} \), \( 4d_{zz} \), and \( 2s \) electrons, respectively, and \( C \) and \( D \) are the dipolar hyperfine coupling constants of the \( 2p \) electrons, and \( \sigma \) is the isotropic \( 2s \) hyperfine coupling constant. It is possible to set the coupling constants so that the spin part of the Knight shift is canceled for either the O(1)\( _\parallel \) or O(1)\( _\perp \) site, but not for both O(1) sites. Specifically, the constant \(^{17}\text{O} \) Knight shifts for both O(1)\( _\parallel \) and O(1)\( _\perp \) imply that at least \( \chi_{xy} \), which arises from the quasi-two-dimensional (Q2D) \( \gamma \) band, does not decrease in the SC state because \( \chi_{xy} \propto K_{1,\parallel} - K_{1,\parallel} \). This multiband treatment makes it clearer that the \(^{17}\text{O} \) Knight shift provides important information on the band-dependent electronic spin susceptibility.

Although we cannot rule out the possibility that \( \chi_{zz} \) and \( \chi_{2s} \) decrease in the SC state while keeping the Knight shifts unchanged, it is unlikely to occur for all measurement fields. We note that the Ru Knight-shift value is large and negative,\(^{20,22} \) because negative isotropic core polarization of the 4\( d \) orbitals is dominant and positive 5\( s \) spin contribution is small. Thus, in the Ru Knight shift the cancellation does not occur among the different orbitals. Therefore, it is also suggested from the constant (or even increasing) Ru Knight shift that all the components of the \( d \)-electron spin susceptibilities does not decrease in the SC state under the magnetic field.

Because the present results indicate that the spin susceptibility is unchanged in the SC state, it is necessary to consider a depairing mechanism other than the Pauli-paramagnetic effect in the magnetic field. In this case, we first need to assume that the spin part does not strongly contribute to the free energy under the magnetic field. One possibility is that the Cooper pair is formed between electrons in different layers by interlayer coupling, and the superconductivity is destroyed owing to suppression of the interlayer coupling by the external field parallel to the \( ab \) plane, because the coherence length along the \( c \) axis is somewhat longer than the interlayer spacing but of a similar magnitude.\(^{23} \) Although it is unlikely that the interlayer interaction is dominant in \( \text{Sr}_2\text{RuO}_4 \) because the conductivity is two dimensional, the three dimensionality might be crucially important for understanding the depairing mechanism on the superconductivity in \( \text{Sr}_2\text{RuO}_4 \).

Another important aspect to consider is the strong spin-orbit coupling in \( \text{Sr}_2\text{RuO}_4 \), as pointed out by Haverkort et al.\(^{23} \) The \( k \)-dependent orientation of the expectation value of the spin strongly mixes the spin-singlet and spin-triplet pairings as seen in the superconductors with inversion symmetry breaking.\(^{23} \) However, the Knight shift corresponding to the spin-singlet component should decrease in the SC state. Thus, even in this case, the unchanged Knight shift suggests that the spin-triplet component is dominant in \( \text{Sr}_2\text{RuO}_4 \).

Quite recently, Ramires and Sigrist have pointed out the importance of the inter-orbital effect in multi-orbital superconductors under magnetic fields.\(^{20} \) When the magnetic field is applied along the \( ab \) plane, the energy gain arising from the orbital polarization in the normal state could overcome the SC condensation energy. This mechanism could lead to the suppression of the SC phase, and would be able to explain why the \( H - T \) phase diagram of \( \text{Sr}_2\text{RuO}_4 \) is similar to the one where the Pauli-paramagnetic effect is present. We also speculate that the presence of multiple bands with different magnetic properties might be crucial: it is well known that incommensurate antiferromagnetic (AFM) fluctuations are present\(^{24} \) which arise from the Fermi-surface nesting between quasi-one-dimensional (Q1D) \( \alpha \) and \( \beta \) bands, and the fluctuations are close to magnetic instability. In contrast, strong AFM fluctuations do not exist in the Q2D \( \gamma \) band. If the triplet superconductivity arises from the \( \gamma \) band, the superconductivity of \( \text{Sr}_2\text{RuO}_4 \) would be immediately destroyed by the AFM fluctuations induced in the \( \gamma \) band when the coupling between Q1D and Q2D bands becomes stronger under the in-plane magnetic field. Further studies are required to clarify this possibility.

In summary, we found that no new signal appears in the SC state by precise \(^{17}\text{O-NMR} \) Knight-shift measurements in the SC \( \text{Sr}_2\text{RuO}_4 \), and that the spin susceptibility is unchanged across the FO transition line as well as across second-order one. Because the present and previous studies suggest that the Pauli-paramagnetic effect is absent in this system, an alternative depairing mechanism in the magnetic field is necessary.

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