Measurement of the ^{101}Ru-Knight Shift of Superconducting Sr_2RuO_4 in a Parallel Magnetic Field

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^{101}Ru-Knight shift (^{101}K) in the spin-triplet superconductor Sr_2RuO_4 was measured under magnetic fields parallel to the c axis (perpendicular to the RuO_2 plane), which is the promising superconducting (SC) $\boldsymbol{d}$-vector direction in a zero field. We succeeded in measuring K_c in the field range from 200 to 1200 Oe and at temperatures down to 80 mK, using nuclear-quadrupole-resonance spectra. We found that $^{101}K_c$ is invariant with respect to the field and temperature on passing through H_{c2} and T_c above 200 Oe. This indicates that the spin susceptibility along the c axis does not change in the SC state, at least, in the field greater than 200 Oe. The results imply that the SC $\boldsymbol{d}$ vector is in the RuO_2 plane when the magnetic field is applied to the c axis.

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Since the discovery of superconductivity in Sr_2RuO_4 [1], numerous experiments have been performed [2]. Until now, the following superconducting (SC) properties have been confirmed by experiments. (1) ^{17}O [3,4] and Ru [5] Knight shifts in the field parallel to the RuO_2 plane reveal that the SC pairs are in a spin-triplet state with the spin component in the RuO_2 plane, which is supported by spin-polarized neutron scattering [6]. This SC state can be expressed using a vector order parameter (the $\boldsymbol{d}$ vector, which is perpendicular to the spin component of the pairs) pointing to the c axis. (2) Small-angle neutron scattering [7] as well as muon spin resonance (μSR) [8] experiments suggest that time-reversal symmetry is broken in the SC state. (3) From various measurements [9–11], the SC energy gap contains nodes, zero or very deep gap minima. Recently, the strongly anisotropic gap structure expressed as $\boldsymbol{d} = \hat{z}\Delta_0(\sin k_x \pm i \sin k_y)$ has been confirmed from the precise angle-dependent specific-heat measurement [12]. The above experimental results strongly suggest that Sr_2RuO_4 is the spin-triplet superconductor discovered subsequent to the heavy-Fermion superconductor UPt_3 [13,14]. The above $\boldsymbol{d}$ vector consists of the spin component of the Cooper pairs parallel to the RuO_2 plane and the orbital moments aligned to the c axis. This SC state is the two-dimensional analogue of the A phase of superfluid ^{3}He [15].

In general, spin susceptibility χ_{spin} of spin-triplet superconductors shows anisotropic temperature dependence, reflecting the direction and magnitude of the applied magnetic field. For example, if the spin-orbit coupling is strong enough to lock the $\boldsymbol{d}$ vector to the crystal lattice, χ_{spin} perpendicular to the $\boldsymbol{d}$ vector is unchanged, whereas χ_{spin} parallel to the $\boldsymbol{d}$ vector becomes zero as $T \rightarrow 0$, following the Yosida function. On the other hand, χ_{spin} is unchanged in all field directions when the energy of the spin-orbit coupling is weaker than that of the applied magnetic field, because the spin of the SC pairs can be rotated by the external field. Such dependence of χ_{spin} on the direction and magnitude of the external field was actually observed in UPt_3, although the decrease of χ_{spin} and the energy of the spin-orbit coupling are much smaller than the theoretically expected values [16].

In Sr_2RuO_4, the Knight shift (K) has been measured only in the field parallel to the RuO_2 plane from 3 to 11 kOe [4]. For the complete understanding of the spin state of the spin-triplet SC pairs in Sr_2RuO_4, it has been highly desired to measure K for field parallel to the c axis (we denote the Knight shift along the c axis as K_c). However, the measurement of K_c in the SC state has been considered extremely difficult due to the small SC critical field (H_{c2} along the c axis is less than 750 Oe [17]), which makes the NMR frequency too low. To overcome such difficulties, we employed a nuclear quadrupole resonance (NQR) spectrum for observing ^{101}Ru signals in small magnetic fields, and measured K_c in the SC state. To the best of our knowledge, this is the first successful measurement of K down to 200 Oe using NQR spectra instead of NMR spectra.

We used three pieces of high-quality single crystals from the same batch, showing a high SC transition temperature of $T_c = 1.5$ K. The samples were identical to those used in previous measurements [5,11]. We measured K of ^{101}Ru, ^{101}K, rather than that of ^{17}O in small fields. This is because ^{101}K is large enough to detect a small change in the SC state since it is strongly affected by Ru 4d electronic spins through the large hyperfine coupling constant of $H_{hf} = -250$ kOe$/\mu_B$ [5]. In addition, a large electric quadrupole moment of ^{101}Ru is an advantage for observing NQR signals in zero and small magnetic fields.

In the following, we explain how to measure the ^{101}Ru Knight shift in a small magnetic field less than 1 kOe. The gyromagnetic ratios of ^{99}Ru and ^{101}Ru are very small as shown in Table I; it is quite difficult to observe the Ru

TABLE I. The data of Sr and Ru isotopes: the nuclear gyromagnetic ratio, γ_n; the nuclear quadrupolar moment, Q; NQR frequency, ν_Q; natural abundance, N.A.; and the nuclear spin, I.

	$\gamma_n/2\pi$ (MHz/T)	Q (10^{-24} cm^2)	ν_Q (MHz)	N.A. (%)	I
^{87}Sr	1.845	0.3	0.822	7.0	9/2
^{99}Ru	1.954	0.076	0.96	12.7	5/2
^{101}Ru	2.193	0.44	3.282	17.1	5/2

NMR signal from a conventional NMR transition between $1/2 \leftrightarrow -1/2$, since the NMR frequency for $H \sim$ 1 kOe is as low as 0.2 MHz [see Fig. 1(b)]. An NMR measurement at such a low frequency is impossible without using a special technique, e.g., SQUID-NMR. To overcome this difficulty, we use NQR transitions at $\nu_Q \sim$ 3.3 MHz to observe the Ru signal in small magnetic fields.

Let us describe the measurement principle using the NQR transitions in detail. The upper panel of Fig. 1(a) shows the zero-field NQR signal mainly arising from the ^{101}Ru-NQR transition between $I_z = \pm 1/2 \leftrightarrow \pm 3/2$. It should be noted that the quadrupole interaction cannot lift the degeneracy of the spin degree of freedom. When a small magnetic field is applied parallel to the principal axis of the quadrupole interaction (c axis in this case), the Zeeman interaction $-\gamma_n \hbar I_z H_z$, which can be treated as a perturbation to the quadrupole interaction, lifts the degeneracy in the NQR levels as shown in Fig. 1(b). As a result, a single Ru NQR peak in zero magnetic field splits into two peaks as shown in the bottom frame of Fig. 1(a),

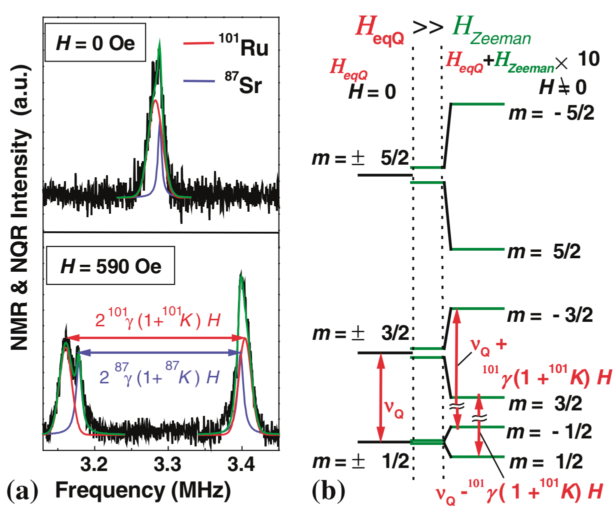

FIG. 1 (color online). (a) ^{101}Ru-NQR spectrum arising from the $I_z = \pm 1/2 \leftrightarrow \pm 3/2$ transition and ^{87}Sr-NQR spectrum arising from the $I_z = \pm 7/2 \leftrightarrow \pm 9/2$ transition under zero field (upper) and magnetic field along the c axis (bottom) at 80 mK. (b) NQR-transition levels under zero field, and a small magnetic field which is treated as a perturbative interaction. For the level scheme on the right, the relevant level splitting is magnified by a factor of 10.

which arise from $I_z = 1/2 \leftrightarrow 3/2$ and $I_z = -1/2 \leftrightarrow -3/2$ transitions, respectively. Since the frequency interval between the two peaks arises from the magnetic field at the nuclear sites, which is decomposed into the external field and the hyperfine field from Ru-4d spin, the interval can be expressed as

$$2\pi\Delta\nu = 2\gamma_n(H_{\rm ext} + H_{4d}) = 2\gamma_n(1 + {}^{101}K_s)H_{\rm ext} \quad (1)$$

using $^{101}K_s$ originating from Ru-4d spins. Therefore precise measurements of both the two-peak interval and the external field enables the Ru-Knight shift to be evaluated. This is the method we employed to measure $^{101}K_s$ in small magnetic field, and it is quite different from the ordinary method using an NMR transition between $1/2 \leftrightarrow -1/2$.

When small magnetic fields are applied parallel to the c axis, we find that a sharp NQR signal with long T_1 ($\sim$100 s) overlaps with broad ^{101}Ru signals. This overlap is clearly seen in lower- and higher-frequency signals as shown in Fig. 1(a). From the field dependence of the sharp peaks, it was revealed that these originate from ^{87}Sr-NQR signals of $I_z = 7/2 \leftrightarrow 9/2$ and $-7/2 \leftrightarrow -9/2$ transitions, respectively. The gyromagnetic ratio, ν_Q, and electric quadrupole moment Q in ^{87}Sr are also listed in Table I [18,19]. Note that the ^{87}Sr-NQR frequency arising from $I_z = \pm 7/2 \leftrightarrow \pm 9/2$ is $4\nu_Q$ ($\sim$3.288 MHz), which happens to be very close to ν_Q of ^{101}Ru. The Knight shift of ^{87}Sr was reported as $\sim$0.18% from the high-field NMR [19], which is negligibly small compared with $-{}^{101}K_s \sim$ 6.3%. Because of the sharp peaks and small Knight shift, the ^{87}Sr-NQR signal can be used as a precise reference of the external field at the sample position.

We first observed zero-field ^{101}Ru and ^{87}Sr-NQR signals in the temperature range from 80 mK to 1.8 K, and ensured that both NQR frequencies ν_Q indeed show no change in the measured temperature range. Therefore, the shift of the spectra under a constant magnetic field can be attributed to the change of the Knight shift.

The onset of the SC transition in magnetic fields was determined by ac susceptibility ($\chi_{\rm ac}$) measurements using the *in situ* NMR coil. As shown in Fig. 2(a), we observed a clear Meissner signal in magnetic fields up to 590 Oe, but not at 920 Oe. We plot $T_c(H)$ determined by the present measurement in Fig. 2(b), which is in good agreement with $T_c(H)$ determined from the specific heat [20]. In the following, we present in detail the field dependence of $^{101}K_c$ at $\sim$90 mK and the temperature dependence of $^{101}K_c$ at 440 Oe measured along the lines in Fig. 2(b).

Figure 3(a) shows $^{101}K_c$ measured at $T \sim$ 90 mK in the field range from H = 200 to 1200 Oe. The Knight shift is -6.3% at $H_{c2} \sim$ 750 Oe, and shows very weak field dependence even below 750 Oe. We did not observe any substantial change of $^{101}K_c$ when superconductivity sets in. The absolute value of the shift in the normal state is larger by 2.5% than that reported by the previous high-field measurement [5]. This difference is ascribable to the

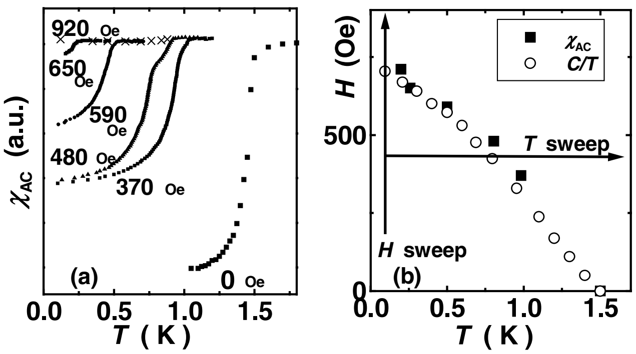

FIG. 2. (a) Temperature dependence of χ_{ac} at 3.3 MHz in various fields along with the c axis. (b) Temperature dependence of H_{c2} obtained by the present measurements along with previous results by the specific-heat measurement [20]. The arrows show the Knight-shift scans in the present measurements.

misorientation of the c axis from the external-field direction. The misorientation in the present measurement is estimated as 5.5° from the difference [21]. The spin part of the Knight shift, $K_{spin} = (H_{hf}/\mu_B)\chi_{spin}$, was derived as -4.5% from the K-χ plot by the high-field NMR study [5]. Compared with $\gamma(H)$ [12], ${}^{101}K_c$ would change to -1.8% following the solid curve in Fig. 3(a), if χ_{spin} decreases in the SC state. The field dependence of this curve is deduced from the field dependence of $\gamma(H)$ at $T = 90$ mK, which arises from the field-induced quasiparticle effect [12].

One may suspect that the rf field for NMR measurements cannot penetrate sufficiently into the sample due to the SC Meissner-shielding effect, which causes the broadening of the NMR spectra. Although broadening of the signal was observed in a field below 200 Oe, appreciable broadening was not detected in a field above 200 Oe. We estimate the spectral-broadening effect due to the SC Meissner effect by assuming $H(r) \propto \sum_n \exp(-r_n/\lambda)$ for field distribution from vortices ($r_n = 0$) and the square-vortex-lattice structure shown by the small-angle neutron-scattering [7] and μSR [22] experiments. Our

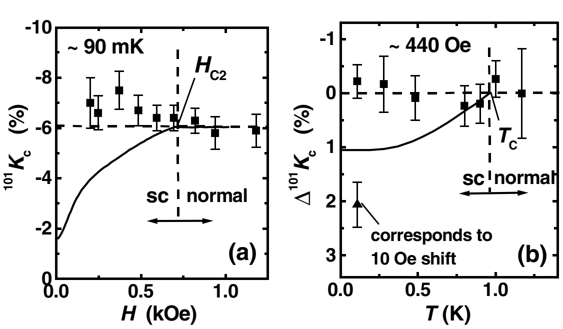

FIG. 3. (a) Field dependence of ${}^{101}K_c$ at 90 mK. (b) Temperature dependence of ${}^{101}K_c$ at 440 Oe. The solid curve in (a) is the conceivable field dependence of ${}^{101}K_c$ deduced from that of C/T at 90 mK, and the curve in (b) is the Yosida function, both of which are expected when the SC $\boldsymbol{d}$ vector is locked in the c axis.

estimation of the SC broadening of a full width at half maximum (FWHM) of spectrum is approximately 9 Oe ($\sim$2 kHz) even at 200 Oe, which is much smaller than FWHM of the NQR line in the normal state ($\sim$18 kHz) arising from the distribution of the electric field gradient. The absence of the appreciable broadening in the SC state is attributable to respectable $\lambda \sim 1900$ Å in the RuO_2 plane [22]. NMR intensity at 90 mK does not change down to 250 Oe as the magnetic field decreases on passing through H_{c2}, but decreases remarkably below 200 Oe. This also shows that the rf field is penetrating into essentially the whole sample in the field above 250 Oe. Therefore the field dependence of ${}^{101}K_c$ in Fig. 3(a) indicates that the c-axis χ_{spin} at 90 mK does not change beyond experimental error. Since the slight change below H_{c2} is the opposite direction from the decrease of ${}^{101}K_c$, it is probably due to the SC diamagnetic effect.

Next we discuss the temperature dependence of the Knight shift measured at 440 Oe shown in Fig. 3(b). To investigate the relative shift of the ^{101}Ru spectra, the frequency of the lower-frequency peak shown in Fig. 1(a) was recorded, since separation between ^{101}Ru and ^{87}Sr signals is larger than that in the higher-frequency signal. No appreciable change was observed beyond the experimental error. To check the experimental accuracy, we measured the spectral shift when the applied field, 440 Oe, is changed to 450 Oe. The field change of 10 Oe corresponds to the Knight-shift change of $10/440 = 2.3\%$, which is indeed observed as shown in Fig. 3(b).

Let us examine the consequences of a small value of $\kappa = \lambda/\xi = 2.6$, which implies that the region with a depressed gap amplitude is largely induced by the applied field. However, the NMR signal from the field-induced quasiparticles is estimated at most $\sim$30% in total because the vortex distance at 440 Oe is $\sim$2000 Å to be compared with $\xi = 660$ Å. Therefore we can safely say that a large part of the NMR signal is from the SC state. Moreover, the NMR line shape would change if the Knight shift of the SC signal changes in the SC state since the observed NMR signal arises from both regions. Obviously, this is not the case.

The solid curve shown in Fig. 3(b) is the theoretical curve when χ_{spin} in the c direction decreases following the Yosida function after the field-induced quasiparticle density of states (DOS) is taken into account on the basis of the specific-heat data under fields. At $H = 440$ Oe, the ratio of the field-induced DOS to the normal-state DOS, $N(H)/N_0$ is $\sim$0.75 [20]. Even though $N(H)/N_0$ is incorporated, it is obvious that the conceivable behavior when χ_{spin} decreases in the SC state is inconsistent with the experimental results.

Now we discuss the possible SC state which is suggested by the present results. As seen in the field and temperature dependence of the Knight shift along the c axis, the χ_{spin} is unchanged in the SC state, suggestive of the spin component being along the field direction above

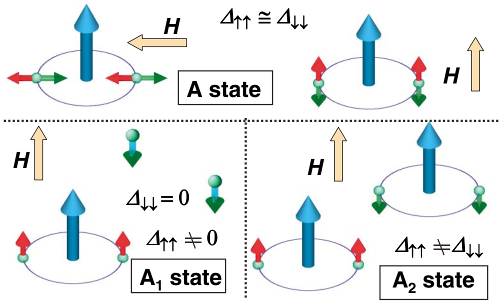

FIG. 4 (color online). Sketches of Cooper pair ***S*** and ***L*** vectors for two variant A states, as well as A_1 and A_2 states, in the magnetic field. The small arrows denote the spins ***S*** and the large arrows denote the orbital moment ***L*** (see text).

200 Oe. In the A phase of superfluid ^{3}He under magnetic fields, A_1 and A_2 phases are known where the magnetic fields rotate the spin direction and change the population of up-spin ($\uparrow\uparrow$) and down-spin ($\downarrow\downarrow$) pairs while leaving the orbital structure unchanged [23]. Sketches of the A_1 and A_2 states are depicted in Fig. 4. In the weak-coupling regime, the up- and down-spin pairs are independent, so that each pair species has its own transition temperature or SC gap. In the A_1 state, an SC gap of the up-spin pairs ($\Delta_{\uparrow\uparrow}$) is finite while a gap of the down pairs ($\Delta_{\downarrow\downarrow}$) remains zero. The A_2 state has two SC gaps $\Delta_{\uparrow\uparrow}$ and $\Delta_{\downarrow\downarrow}$ with different magnitudes. However, since the double-transition behavior consistent with these two gaps is not observed in the field parallel to the c axis, we consider that the gap difference between $\Delta_{\uparrow\uparrow}$ and $\Delta_{\downarrow\downarrow}$ is negligibly small. Such a state with $\Delta_{\uparrow\uparrow} \simeq \Delta_{\downarrow\downarrow}$ is empirically described as a state in which the ***d*** vector, defined perpendicular to ***S***, always resides in the plane perpendicular to the external fields and points to any direction in the RuO_2 plane due to the degeneracy. This state is denoted in the right-upper sketch in Fig. 4. From a theoretical point of view, it is most promising that under zero magnetic field the ***d*** vector points to the c axis which is the orbital-moment direction of the pairs, since it is energetically favorable for the dipolar interaction of triplet pairs [23] as well as for the spin-orbit interaction in the normal state [24]. One possible scenario which consistently explains all the available experimental results so far is that the ***d*** vector pointing to the c axis in zero field can flip perpendicular to the c axis by a small magnetic field along the c axis. This can happen if the Zeeman interaction by applied field overcomes the pinning interaction which locks the spins within the RuO_2 plane. Therefore the pinning is considered to be so weak that small field less than 200 Oe can easily change the spin direction.

In order to confirm the above scenario as well as the ***d***-vector direction in zero field [25], we need to measure $^{101}K_{ab}$, in small magnetic fields within the RuO_2 plane, since previous Knight-shift measurements were performed in fields greater than 3 kOe [3–5]. The precise measurement of the T dependence of $^{101}K_{ab}$ in the small field, however, requires highly accurate orientation of the sample since the broadening effect by the misorientation in $H \parallel ab$ is 3 times larger than that in $H \parallel c$ [21]. In order to achieve such accurate field alignment for the NQR measurement, we are now developing a new system with *in situ* sample rotation at 90 mK.

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