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Ru NMR probe of spin susceptibility in the superconducting state of Sr_2RuO_4

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We report ^{99}Ru Knight-shift (^{99}K) measurement on the high-quality Sr_2RuO_4 with a superconducting transition temperature $T_c \sim 1.5$ K. Its spin component, $^{99}K^s$ due to the core polarization effect caused by Ru-4*d* spins, is nearly one order of magnitude larger than that of the ^{17}O Knight shift ($^{17}K^s$). The $4d$-spin susceptibility that has been more precisely measured from $^{99}K^s$ than $^{17}K^s$ shows no change across T_c at all. The present result reinforces that Sr_2RuO_4 is the spin-triplet *p*-wave superconductor in which electrons are bound together in parallel-spin pairs parallel to the RuO_2 plane.

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The layered perovskite Sr_2RuO_4 has become a subject of intense research activity since the discovery of superconductivity.[1] In a Ru^{4+} ionic state in the tetragonal symmetry, there exist two holes in the degenerate $4d$-t_{2g} orbitals. Even in a metallic state, the orbital degeneracy and the on-site Hund's coupling are expected to lead to ferromagnetism. As a matter of fact, its three-dimensional (3D) analogue, $SrRuO_3$ shows the ferromagnetism with a Curie temperature $T_C = 160$ K. Noting these features in ruthenate oxides, Rice and Sigrist[2] proposed the possibility of spin-triplet *p*-wave superconductivity in Sr_2RuO_4. Motivated by their suggestion, various experiments were promoted to identify the symmetry of the superconducting (SC) order parameter. The Ru nuclear-quadrupole-resonance (NQR) measurement on a low-T_c sample with $T_c = 0.7$ K provided evidence against a simple *s*-wave picture in Sr_2RuO_4.[3] Subsequently, the temperature (T) dependence of ^{17}O Knight shift (^{17}K) was measured on the high-quality single crystals that reveal the SC transition at a higher $T_c \sim 1.5$ K. From the measurement at various magnetic fields parallel to the RuO_2 plane, $^{17}K(T)$ shows no change across T_c. This result gave decisive evidence for the spin-triplet superconductivity in Sr_2RuO_4.[4,5] Furthermore, the measurement of nuclear spin-lattice relaxation rate, $1/T_1$ by means of Ru NQR on the high-quality sample revealed that the SC gap is highly anisotropic, consistent with a line-nodelike gap.[6] Such anisotropic gap was also suggested from the specific-heat[7] and the penetration-depth[8] experiments. The unconventional spin-triplet SC state with the line-nodelike gap in Sr_2RuO_4 has also been theoretically discussed.[9,10]

We should remark that the μSR study revealed an appearance of the internal field in the SC state,[11] suggesting that the time-reversal symmetry is broken, i.e., the SC pairs have a finite angular moment of $L=1$. This result was also confirmed by another group.[12] Furthermore, the specific-heat and ac-susceptibility measurements suggested that multiple SC phases exist below the upper critical field H_{c2}.[13] Existence of multiple phases in the pairs-condensed state is well known in superfluid ^{3}He, in which the order parameter possesses the internal degree of freedom.[14] The existence of multiple SC phases was also reported in the heavy-fermion superconductor UPt_3,[15] which was identified to be an odd-parity superconductors from the Pt Knight-shift measurement.[16] These unusual SC properties are believed to be characteristic of the spin-triplet *p*- or *f*-wave superconductivity.

In these unconventional superconductors, it is promising that the binding of electrons in the paired state (Cooper pairs) are magnetically mediated via spin-fluctuation exchange. As for the character of spin fluctuations in the normal state, the Ru- and ^{17}O-NMR, and the neutron-diffraction (ND) experiments have provided a valuable set of data.[17–19] Mukuda *et al.* reported from the ^{17}O-NMR study that the spin fluctuations in Sr_2RuO_4 are anisotropic.[17] Namely, the in-plane component in dynamical susceptibility is exchange-enhanced without a marked wave-number $\mathbf{q}$ dependence, whereas the out-of-plane one is significantly enhanced by antiferromagnetic (AF) spin fluctuations below $T^* \sim 130$ K. Imai *et al.* claimed, on the other hand, that ferromagnetic (FM) spin fluctuations are dominant in the RuO_2 plane from the result that the similar T dependence of $1/T_1$ is observed at the Ru and O sites.[18]

Meanwhile, the ND experiment reported by Sidis *et al.* revealed the existence of *incommensurate* AF fluctuations at a $\mathbf{q}_0 = (\pm 0.6\pi/a, \pm 0.6\pi/a, 0)$.[19] This wave vector is in accord with a nesting vector connecting between α and β branches in the Fermi surfaces. Note that these branches have a quasi-one-dimensional (quasi-1D) character. Stoner factor $\alpha_{\mathbf{q}_0} \simeq 0.97$ at $\mathbf{q}_0$ was estimated, indicative of the closeness to the AF instability. Enhancement in $1/T_1T$ below 200 K is considered to be caused by the incommensurate AF fluctuations that develops below 200 K as well. It should be noted that the similar behavior in $1/T_1T$ at the Ru and O sites[18] does not evidence any strong FM fluctuations at $\mathbf{q}=0$. This is because such a behavior is reproduced *provided that AF fluctuations is of the incommensurate type* with the wave vector $\mathbf{q}_0$. In this context, a scenario in which FM fluctuations mediate a spin-triplet superconductivity with analogy of the superfluid ^{3}He seems to be inadequate. A question arises how the spin-triplet *p*-wave state can be stabilized under the incommensurate AF fluctuations. Competition between spin-triplet vs -singlet superconductivity in Sr_2RuO_4

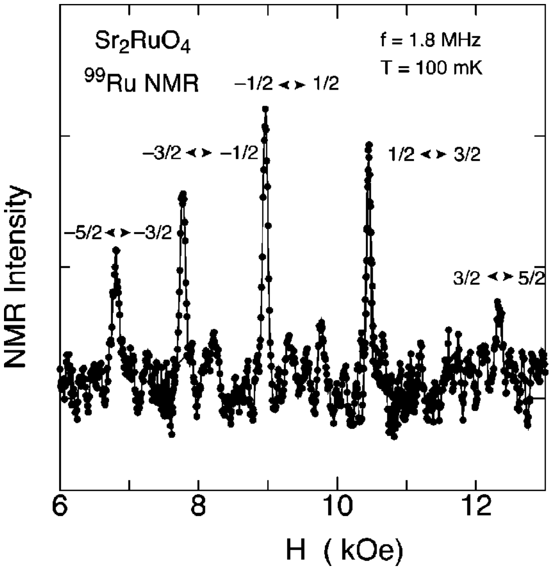

FIG. 1. ^{99}Ru-NMR spectrum taken by sweeping the external field $H \| c$.

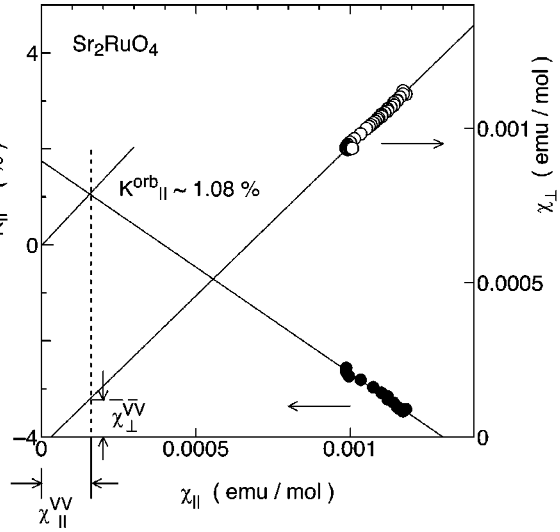

FIG. 2. Plot of $^{99}K_{\|}$ (Ref. 18) against $\chi_{\|}$ (left scale). The relation between $\chi_{\perp}$ and $\chi_{\|}$ are also plotted (right scale).

is now under active theoretical debate.[20] Therefore it is quite important to present further experimental proof to reinforce that Sr_2RuO_4 is the triplet superconductor.

In this paper, we present further convincing results that prove unambiguously the spin-triplet superconductivity in Sr_2RuO_4 through the ^{99}Ru Knight-shift (^{99}K) measurement. Since its spin part $^{99}K^s$ is nearly one order of magnitude larger than that in the ^{17}O Knight shift (^{17}K) reported previously, the *d*-spin susceptibility has been more precisely deduced from $^{99}K^s$ than $^{17}K^s$. $^{99}K^s$ does not change across $T_c(H)$ at all. The result reinforces that Sr_2RuO_4 is the spin-triplet *p*-wave superconductor in which electrons are bound together in parallel-spin pairs parallel to the RuO_2 plane.

Single crystal shows the SC transition at $T_c \sim 1.48$ K with a transition width $\Delta T_c \sim 50$ mK. The crystal that was used in the previous measurement of T_1 of Ru revealed that the residual density of states is less than 10% at low temperatures.[6] This ensures the high quality of the sample in a microscopic scale. The Ru-NMR measurement was carried out at a frequency $f = 1.8$ MHz with a magnetic field (H) perpendicular to the c axis ($H_{\perp}$) in $T = 0.06$–1.5 K. The quadrupole-split Ru-NMR spectrum was taken by sweeping H over a wide range, and the precise T dependence of each peak frequency in the spectrum was obtained by means of the Fourier transformed technique of spin-echo signal. Since the upper critical field H_{c2} shows a large value for $H_{\perp}$, $H_{c2}^{\perp} \sim 15$ kOe at low temperatures, whereas $H_{c2}^{\|}$ parallel to the c axis is less than 1 kOe (Ref. 21) which is too small for the NMR measurement, the ^{99}Ru Knight-shift measurement in the SC state was performed only for $H_{\perp}$.

The quadrupole-split ^{99}Ru-NMR spectrum consists of five peaks as indicated in Fig. 1 for $f = 1.8$ MHz and $T = 100$ mK. A nuclear-quadrupole frequency $\nu_Q(\mathrm{NMR}) = 0.54$ MHz is estimated, consistent with $\nu_Q(\mathrm{NQR}) = 0.56$ MHz deduced from the previous NQR measurements.[3] The $^{99}K_{\perp}$ for $H_{\perp}$ is estimated as -2.7% at $T = 1.5$ K. This value is nearly one order of magnitude larger than ^{17}K.[17] The $^{99}K_{\|}(T)$ of ^{99}Ru for $H_{\|}$ at low T was identical to $^{101}K_{\|}(T)$ of ^{101}Ru which was measured up to 300 K.[18] In order to decompose the spin and orbital components in $^{99}K_{\|}$, a plot of $^{99}K_{\|}(T)$ vs the bulk susceptibility $\chi_{\|}(T)$ is shown in Fig. 2. Using the following relations,

$$\chi_{\|}(T) = \chi_{\|}^{spin}(T) + \chi_{\|}^{VV},$$

$$\begin{aligned} ^{99}K_{\|}(T) &= {}^{99}K_{\|}^{s}(T) + {}^{99}K_{\|}^{orb} \\ &= (H_{hf,\|}/N_A\mu_B)\chi_{\|}^{spin}(T) + (H_{VV}/N_A\mu_B)\chi_{\|}^{VV}, \end{aligned}$$

as well as, the orbital hyperfine-coupling constant of $H_{VV} = 2\mu_B\langle r^{-3}\rangle = 385$ kOe/μ_B,[3] we deduce the hyperfine-coupling constant $H_{hf,\|} = -250$ kOe/μ_B, the spin component $^{99}K_{\|}^{s} = -4.0\%$ and the orbital component $^{99}K_{\|}^{orb} = 1.08\%$, and the Van-Vleck susceptibility $\chi_{\|}^{VV} = 1.61 \times 10^{-4}$ emu/mol, respectively. A large negative value of $H_{hf,\|}$ and hence a dominant isotropic component in ^{99}K is due to the inner core-polarization effect caused by $4d$ spins.[3] Furthermore, a relation between $\chi_{\|}$ and $\chi_{\perp}$ shown in Fig. 2 allows us to deduce the Van-Vleck susceptibility $\chi_{\perp}^{VV} \sim 1.21 \times 10^{-4}$ emu/mol and $K_{\perp}^{orb} \sim +0.82\%$. A linear relation between $^{99}K_{\|}(T)$ and $^{17}K(T)$ which is valid below 250 K suggests that one spin-component model is appropriate as in high-T_c cuprates.

As shown in Fig. 3 an onset of superconductivity under H was confirmed by an ac-susceptibility measurement using an ''in-situ'' NMR coil . The inset in Fig. 3 indicates the H dependence of SC diamagnetism at $T = 100$ mK. The upper critical field of $H_{c2} \sim 15$ kOe at 100 mK is in good agreement with H_{c2} determined by the resistivity as seen in Fig. 4 along with other data at various fields.[21] The $^{99}K_{\perp}(T)$ was measured at $H_{\perp} = 10.5$, 9, and 6.8 kOe as shown by dotted arrows in Fig. 4. The onset of the SC transition at $H_{\perp} = 9$ kOe was also ensured from the decrease in $1/T_1T$ that probes the opening of the bulk SC gap.

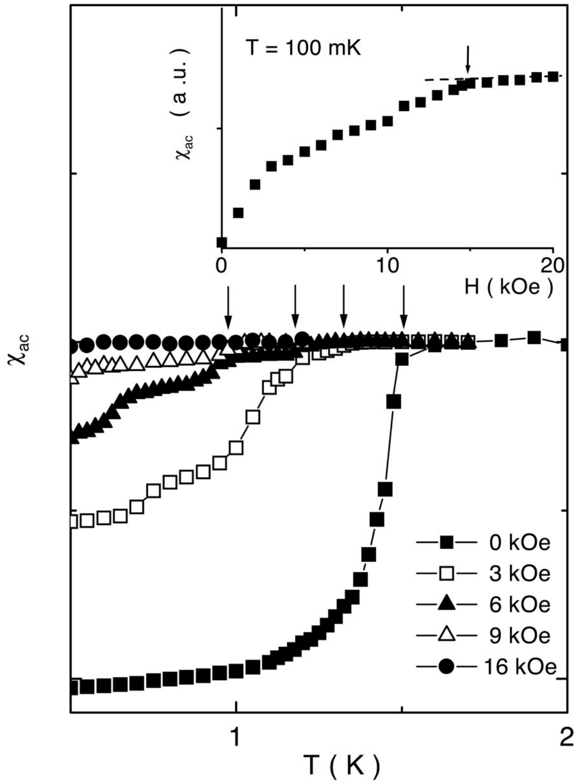

FIG. 3. Variation of ${}^{ac}\chi$ taken by the NMR coil under various fields. An inset is H dependent of ${}^{ac}\chi$ at 100 mK.

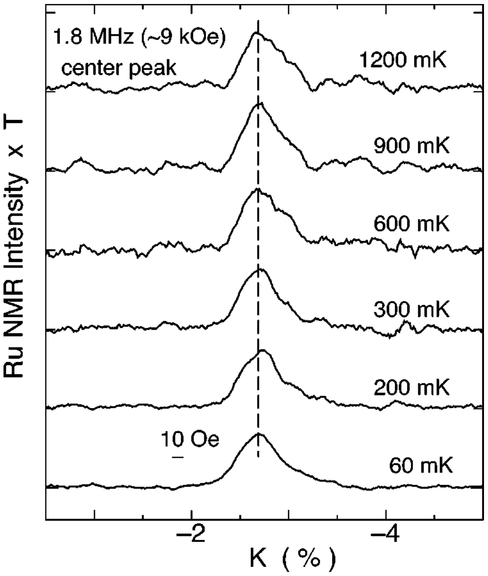

FIG. 5. ^{99}Ru-NMR spectra of the $1/2 \leftrightarrow -1/2$ central transition at various temperatures. T_c (9 kOe) is ~ 1.0 K. Signal intensity was multiplied by T. In the bottom spectrum, the scale of 10 Oe is shown.

Figure 5 indicates the T dependence of the central peak in the quadrupole-split NMR spectrum at $H_\perp = 9$ kOe. Here each NMR intensity is multiplied by the temperature. Note that the NMR intensity (I) increases according to the Curie law ($1/T$) of nuclear-spin susceptibility with decreasing T. As shown in Fig. 5, $I \times T$ is almost T independent. This ensures that the application of radio-frequency pulses for the NMR measurement does not heat up the sample and that the Knight shift measurement was carried out in a thermal equilibrium condition with a heat bath. It is clear that the spectral peak does not change at all across $T_c \sim 1.0$ K at $H_\perp = 9$ kOe. This is also the case for the spectra at $H_\perp = 6.8$ and 10.5 kOe. We note that none of the spectra are significantly affected by any appreciable shift and/or some broadening due to the SC diamagnetic shielding effect and the field distribution in the vortex state below T_c. Square root of the second moment of the NMR spectrum for $H_\perp$, $\sqrt{(\Delta H_\perp)^2}$ in the SC state is calculated as $\sqrt{(\Delta H_\perp)^2} = \phi_0/(4\sqrt{\pi^3}\lambda_\parallel\lambda_\perp)\{1-(H/$

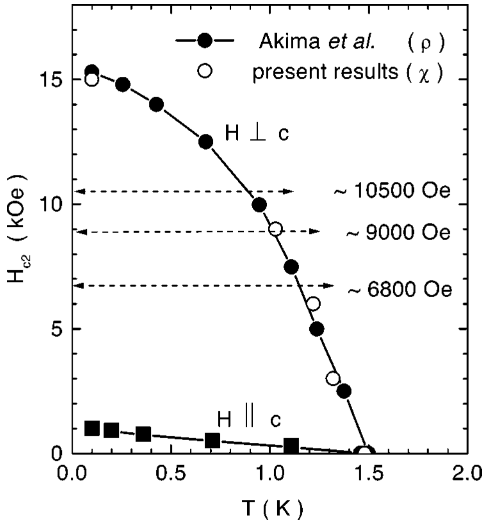

FIG. 4. Temperature dependence of the anisotropic upper critical fields, $H_{c2\perp c}$ (closed circles) and $H_{c2}^{\parallel}$ (closed squares) determined by resistivity measurements (Ref. 21). The present results determined by ${}^{ac}\chi$ are also plotted (open circles).

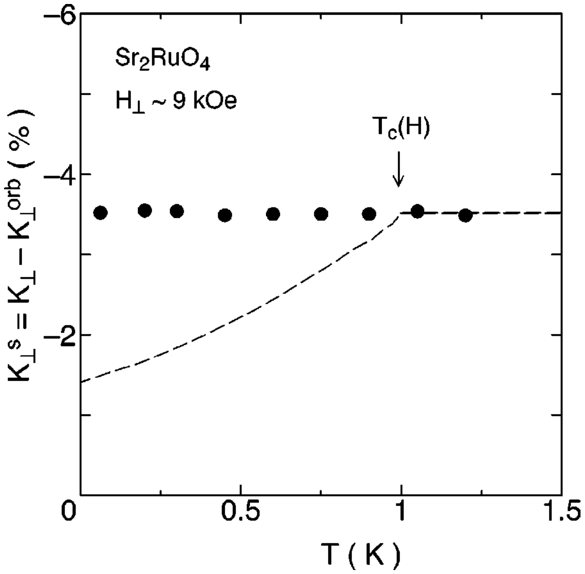

FIG. 6. Temperature dependence of ${}^{99}K_\perp^s$. The dotted curve is the calculation based on the spin-singlet d-wave ($d_{x^2-y^2}$) model with a line node (see text).

$H_{c2}^{\perp})\}^{1/2}$.[22] Here ϕ_0 is the flux quantum. This value at $H_\perp \sim 9.0$ kOe is estimated as ~ 0.82 Oe by using the penetration depth $\lambda_\parallel \sim 3.7\times10^4$ Å and $\lambda_\perp \sim 1.8\times10^3$ Å for $H_\parallel$ and $H_\perp$, respectively.[21]

The diamagnetic shift $H_{dia}^{\perp}$ is also estimated to be ~ 2.0 Oe from the relation of $H_{dia}^{\perp} \sim H_{c1\perp} \ln(H_{c2\perp}/H_{\rm ext})/\ln \kappa$.[23] Here we used $H_{c1\perp} \sim 10$ Oe and the GL parameter, $\kappa = \sqrt{\kappa_\perp \kappa_\parallel} \sim 6.1$.[21] In general, the former and latter contributions make the Ru-NMR spectrum broaden and shift below T_c, respectively. However, these values in $\mathrm{Sr_2RuO_4}$ are much smaller than the spectral width and the Knight shift, entering a range of experimental error. Such contributions are safely neglected in the present measurement.

Figure 6 shows the T dependence of ${}^{99}K_\perp^s (\equiv K_\perp - K_\perp^{orb})$. The ${}^{99}K_\perp^s$ does not change on passing through $T_c \sim 1.0$ K at $H_\perp = 9$ kOe. If a spin-singlet d wave were realized, the T dependence of ${}^{99}K_\perp^s$ would be predicted as drawn by dotted curve in Fig. 6. Here the $d_{x^2-y^2}$ model with a line-node gap is applied with a parameter of energy gap $\Delta_0 = 2k_BT_c$ that was deduced in the literature.[6] In the calculation, noting that the magnetic field induces the extended quasiparticle state due to the line-node gap, the density of states $N(H)$ at the Fermi level is incorporated. At $H_\perp = 9$ kOe, $N(9\ \mathrm{kOe})/N_{normal} \sim 0.39$ is estimated at low temperatures from the H dependence of the specific heat.[7] Even though $N(H)$ is incorporated, it is obvious that the spin-singlet d-wave model is not consistent with the experiment. The invariant behavior of ${}^{99}K_\perp^s$ gives the evidence that electron pairs are in the parallel-spin state parallel to the $\mathrm{RuO_2}$ plane. The decreasing behavior of $K_\parallel^s$ following the Yosida function is expected for $H \parallel c$ in this spin state, however, the measurement of $K_\parallel^s$ is technically difficult since $H_{c2}^{\perp}$ is only 750 Oe.

In conclusion, the spin component in the ^{99}Ru Knight shift ${}^{99}K^s$ is one order of magnitude larger than that in the ^{17}O Knight shift. The spin susceptibility in $\mathrm{Sr_2RuO_4}$ was thus much more precisely determined from the Ru NMR measurement. It was ensured that the spin susceptibility does not change across T_c. The present result gives unambiguous evidence for the spin-triplet p-wave superconductivity in $\mathrm{Sr_2RuO_4}$. If the spin-fluctuation properties revealed by the ND and NMR experiments are taken into account, it is considered that a mechanism which is different from that in the superfluid ^{3}He may lead to the occurrence of the spin-triplet superconductivity in charged many-body systems in general.

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[1] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz, and F. Lichtenberg, Nature (London) **372**, 532 (1994).

[2] T. M. Rice and M. Sigrist, J. Phys.: Condens. Matter **7**, L643 (1995).

[3] K. Ishida, Y. Kitaoka, K. Asayama, S. Ikeda, S. Nishizaki, Y. Maeno, K. Yoshida, and T. Fujita, Phys. Rev. B **56**, R505 (1997).

[4] K. Ishida, H. Mukuda, Y. Kitaoka, K. Asayama, Z. Q. Mao, Y. Mori, and Y. Maeno, Nature (London) **396**, 658 (1998).

[5] H. Mukuda, K. Ishida, Y. Kitaoka, K. Asayama, Z. Q. Mao, Y. Mori, and Y. Maeno, J. Low Temp. Phys. **117**, 1587 (1999).

[6] K. Ishida, H. Mukuda, Y. Kitaoka, Z. Q. Mao, Y. Mori, and Y. Maeno, Phys. Rev. Lett. **84**, 5387 (2000).

[7] S. NishiZaki, Y. Maeno, and Z. Q. Mao, J. Phys. Soc. Jpn. **69**, 572 (2000).

[8] I. Bonalde *et al.*, Phys. Rev. Lett. **85**, 4775 (2000).

[9] K. Miyake and O. Narikiyo, Phys. Rev. Lett. **83**, 1423 (1999).

[10] Y. Hasegawa, K. Machida, and M. Ozaki, J. Phys. Soc. Jpn. **69**, 336 (2000).

[11] G. M. Luke, Y. Fudamoto, K. M. Kojima, M. I. Larkin, J. Merrin, B. Nachumi, Y. J. Uemura, Y. Maeno, Z. Q. Mao, Y. Mori, H. Nakamura, and M. Sigrist, Nature (London) **394**, 558 (1998).

[12] W. Higemoto (private communication).

[13] Z. Q. Mao, Y. Maeno, S. Nishizaki, T. Akima, and T. Ishiguro, Phys. Rev. Lett. **84**, 991 (2000).

[14] D. M. Lee, Rev. Mod. Phys. **69**, 645 (1997).

[15] K. Hasselbach, L. Taillefer, and J. Flouquet, Phys. Rev. Lett. **63**, 93 (1989).

[16] H. Tou, Y. Kitaoka, K. Asayama, N. Kimura, Y. Onuki, E. Yamamoto, and K. Maezawa, Phys. Rev. Lett. **77**, 1374 (1996); H. Tou *et al.*, *ibid.* **80**, 3129 (1998).

[17] H. Mukuda, K. Ishida, Y. Kitaoka, K. Asayama, Z. Q. Mao, Y. Mori, and Y. Maeno, J. Phys. Soc. Jpn. **67**, 3945 (1998).

[18] T. Imai, A. W. Hunt, K. R. Thurber, and F. C. Chou, Phys. Rev. Lett. **81**, 3006 (1998).

[19] Y. Sidis, M. Braden, P. Bourges, B. Hennion, S. NishiZaki, Y. Maeno, and Y. Mori, Phys. Rev. Lett. **83**, 3320 (1999).

[20] I. I. Mazin and D. J. Singh, Phys. Rev. Lett. **82**, 4324 (1999).

[21] T. Akima, S. NishiZaki, and Y. Maeno, J. Phys. Soc. Jpn. **68**, 694 (1999).

[22] P. Pincus, A. C. Gossard, V. Jaccarino, and J. H. Wernick, Phys. Lett. **13**, 21 (1964).

[23] M. Tinkham, *Introduction To Superconductivity* (McGraw-Hill, Inc., New York, 1975).