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Anisotropic pairing in superconducting Sr_2RuO_4: Ru NMR and NQR studies

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Ru NMR and nuclear quadrupole resonance studies are reported on single-crystal Sr_2RuO_4 ($T_c=0.7$ K) with the same layered perovskite structure as La_2CuO_4. The Pauli spin susceptibility deduced from the Ru Knight shift is found to be largely enhanced by a factor of ~ 5.4 as compared with the value from the band calculation. In the superconducting state, the nuclear spin-lattice relaxation rate $1/T_1$ exhibits a sharp decrease with no coherence peak just below T_c and the $T_1T=$constant behavior well below T_c, suggesting that the anisotropic pairing state is realized as in heavy-fermion and high-T_c superconductors. [S0163-1829(97)50626-6]

Since the discovery of the high-T_c cuprate superconductors, much attention has been paid to the synthesizing of new superconducting materials. Recently, Maeno *et al.* discovered superconductivity with an onset temperature around 1 K in a ruthenious oxide, Sr_2RuO_4 having the same layered perovskite structure as $La_{2-x}(Sr, Ba)_xCuO_4$.[1] It has widely been accepted that the antiferromagnetic (AF) spin fluctuation in the CuO_2 plane plays a key role in the occurrence of the high-T_c superconductivity, and its Cooper pairing occurs in the d-wave channel.[2] By contrast, the superconducting nature in Sr_2RuO_4 is not fully addressed yet in experiments.

In spite of their structural similarity, there exist many differences between the two systems in the electronic and magnetic properties. Recent de Haas-van Alphen experiments have revealed the presence of three approximately cylindrical Fermi surfaces,[3] which is consistent with the band-structure calculation.[4] In addition, the conduction along the c axis is nonmetallic above $T\sim 130$ K, although the conduction in the ab plane is highly metallic.[1] These experimental results indicate that the two-dimensional (2D) character of the electronic structure is remarkable. The electric resistivity shows a 2D Fermi-liquid behavior below $T\sim 130$ K, exhibiting a T^2 dependence along all the crystal directions upon cooling.[1] If the cyclotron masses are compared to those of the band-structure calculation,[4] a substantial mass enhancement, $m^*/m_0\sim 4$ is deduced which points to a signature of strong electron correlations.[3] This mass renormalization of quasiparticles due to the electron correlation results in an enhancement of the T-linear coefficient of the specific heat, $\gamma=39$ mJ/K^2 mol as compared with 10 mJ/K^2 mol estimated from the band-structure calculation.[1,4] The Pauli spin susceptibility was suggested to be also enhanced by a factor of 6.9, if the Van Vleck contribution to the observed susceptibility is ignored. Recent photoemission experiments gave an additional support for correlation effects as well.[5]

Rice and Sigrist argued that the triplet pairing might be favored in Sr_2RuO_4 from following experimental results. A local moment with $S=1$ observed for Ru^{4+} ions dilutely substituted for Ir in the insulator Sr_2IrO_4 indicates a strong Hund's coupling among the holes in the (d_{xz}, d_{yz}) orbits, which may favor ferromagnetic fluctuations in Sr_2RuO_4.[7] Furthermore, the related 3D perovskite $SrRuO_3$ exhibits a ferromagnetic transition at $T_c=160$ K with a saturation moment of $\sim 1.1\mu_B$.[8] They have pointed out that these renormalized states are similar to those of ^{3}He at ambient pressure,[6] and proposed that the superconductivity in Sr_2RuO_4 may be more similar to the superfluid phase of ^{3}He such as the Balian-Werthamer (BW) and the Anderson-Brinkman-Morel (ABM) phase with the spin triplet pairing than to the singlet d-wave state in cuprate oxide superconductors.[6]

In this paper, we report Ru NMR and nuclear quadrupole resonance (NQR) experiments of superconducting Sr_2RuO_4 in order to shed light on the normal and superconducting properties. From the Knight-shift measurement, it is demonstrated that the spin susceptibility in Sr_2RuO_4 is largely enhanced as compared with the value of the band-structure calculation, even if the Van Vleck contribution is taken into account. In the superconducting state, the T dependence of the nuclear-spin lattice relaxation rate, $1/T_1$ is unconventional, decreasing sharply without the coherence peak just below T_c and following the $T_1T=$constant relation below $0.5T_c$. From this relaxation behavior below T_c, an anisotropic pairing is suggested in Sr_2RuO_4 rather than a conventional s-wave pairing.

The synthesizing process of Sr_2RuO_4 was described elsewhere.[1] The Ru NMR and NQR experiments are not so easy owing to their low natural abundance and gyromagnetic ratio, i.e., ^{99}Ru($I=5/2$):12.7% and $\gamma_n=1.96$(MHz/T), and ^{101}Ru($I=5/2$):17.1%, and $\gamma_n=2.19$(MHz/T).[9] To improve the signal-to-noise (SN) ratio, several pieces of single crystals with $T_c=0.7$ K were stacked with their c axis parallel to each other. Systematic measurements of the Knight shift above T_c and T_1 in both the normal and superconducting states allowed us to extract valuable information about the

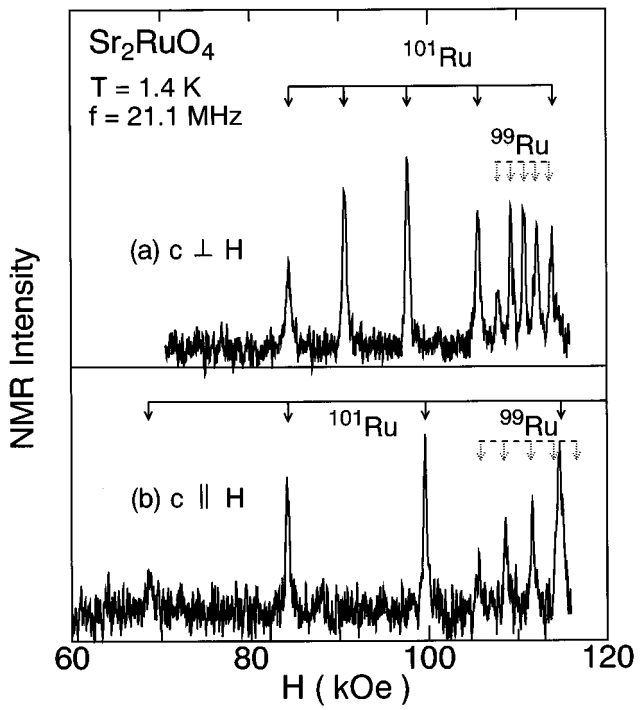

FIG. 1. Ru NMR spectra in Sr_2RuO_4 with the external field parallel (a) and perpendicular (b) to the c axis.

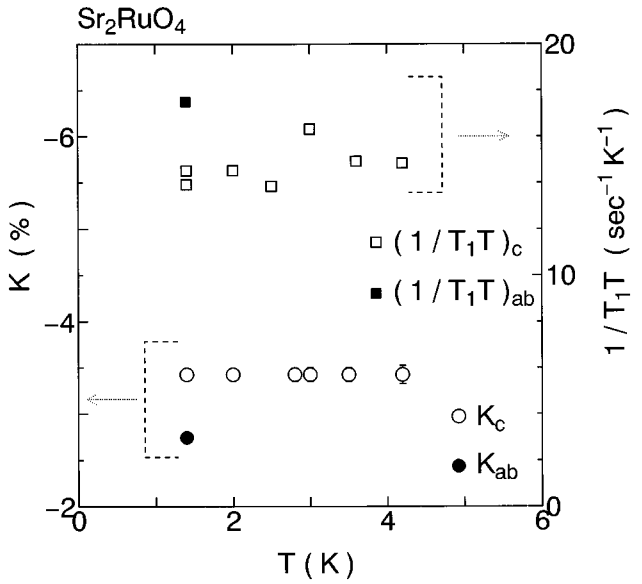

FIG. 2. T dependence of Knight shift (○) and $1/T_1T$ (□) along the c axis between 1.4 and 4.2 K, and Knight shift (●) and $1/T_1T$ (■) perpendicular to the c axis at 1.4 K.

normal and superconducting characteristics. The field-swept Ru NMR spectrum was obtained at a constant frequency of 21.1 MHz and in a temperature range of 1.4–4.2 K. $^{101}(1/T_1)$ of ^{101}Ru was measured in a temperature range of 1.4–4.2 K in the field of 11 T by NMR, whereas $1/T_1$ was measured in a lower temperature range of 0.1–1.4 K by NQR, using the dilution refrigerator. The Ru NMR measurement in the superconducting state is difficult because of the extremely low upper critical fields as $H_{c2\perp ab}\sim 0.79$ T and $H_{c2\|c}\sim 0.030$ T.[10] The successful observation of the Ru NQR enabled us to get valuable information about the pairing nature of Sr_2RuO_4 from the relaxation behavior in the superconducting state. T_1 was uniquely determined by the saturation recovery technique. For the NMR and NQR experiments, the relaxation function of the nuclear magnetization $m(t)$ was well fitted to the theoretical one given by

$$m(t)=\frac{M(\infty)-M(t)}{M(\infty)}=0.028\exp\left(-\frac{t}{T_1}\right)+0.178\exp\left(-\frac{6t}{T_1}\right)+0.794\exp\left(-\frac{15t}{T_1}\right)$$

and

$$m(t)=0.43\exp\left(-\frac{3t}{T_1}\right)+0.57\exp\left(-\frac{10t}{T_1}\right),$$

for the central $(+1/2\leftrightarrow -1/2)$ transition in quadrupole-split NMR and the $\pm 3/2\leftrightarrow\pm 5/2$ transition in NQR, respectively.[11,12] Here $M(t)$ is the nuclear magnetization at time t after saturation pulses.

Figures 1(a) and 1(b) display the Ru NMR spectra with the magnetic field parallel and perpendicular to the c axis, respectively. As seen in Fig. 1, the well-separated peaks arise from the electric quadrupole interaction for the two isotopes. From the two sets of Ru NMR spectra for $c\perp H$ and $c\|H$, the quadrupole frequency and the asymmetry parameter of ^{101}Ru were found to be $\nu_Q\sim 3.3$(MHz) and $\eta\sim 0$ with the principal axis along the c axis, respectively. Furthermore, the respective Knight shifts, $K_\|$ and $K_\perp$ were estimated to be -3.44(%) and -2.75(%), which exhibit no appreciable T dependence in the range of 1.4–4.2 K as indicated in Fig. 2. From the relations of $K_{iso}=(K_\|+2K_\perp)/3$ and $K_{aniso}=(K_\|-K_\perp)/3$, the isotropic and anisotropic shift, K_{iso} and K_{aniso}, are estimated as $K_{iso}=-2.98\%$ and $K_{aniso}=-0.23\%$, respectively. The negative sign of K_{iso} is due to the dominant spin contribution through the inner core-polarization effect by $4d$ electrons.

Since the observed Knight shift, K_{obs} is T invariant, a conventional $K(T)$ vs $\chi(T)$ analysis does not work in the present case. Alternatively, by using the hyperfine coupling constant, H_{cp}, due to the core polarization by $4d$ electron of Ru, which is estimated to be -299 kOe/μ_B from the zero-field NMR of Ru in the ordered state of $SrRuO_3$[13] and the orbital hyperfine field, $H_{orb}=2\mu_B\langle r^{-3}\rangle$ estimated to be $+380$ kOe/μ_B from the Hartree-Fock calculation of $\langle r^{-3}\rangle=4.2$(a.u.), on free Ru^{+4} with the reduction factor of $\xi=3/4$,[14] we extract $\chi_{s,NMR}=7.6\times 10^{-4}$emu/mol, $\chi_{orb}=1.54\times 10^{-4}$emu/mol, $K_s=-4.06\%$, and $K_{orb}=1.08\%$ from a set of relations as

$$K_{obs}=K_s+K_{orb}=(H_{cp}/N_A\mu_B)\chi_s+(H_{orb}/N_A\mu_B)\chi_{orb},$$

$$\chi_{obs}=\chi_s+\chi_{orb},$$

with $K_{obs}=-2.98\%$ and $\chi_{obs}=9.1\times 10^{-4}$ emu/mol.[1] N_A is the Avogadro's number. By comparing the spin susceptibility from the NMR study, $\chi_{s,NMR}$, with that from the band calculation,[4] the enhancement factor $\chi_{s,NMR}/\chi_0$ is found to be ~ 5.4. From the present Knight-shift study, Sr_2RuO_4 is concluded to be a Pauli paramagnet with an exchange-enhancement factor, $\alpha\sim 0.82$. If we compare $\chi_{s,NMR}$ with

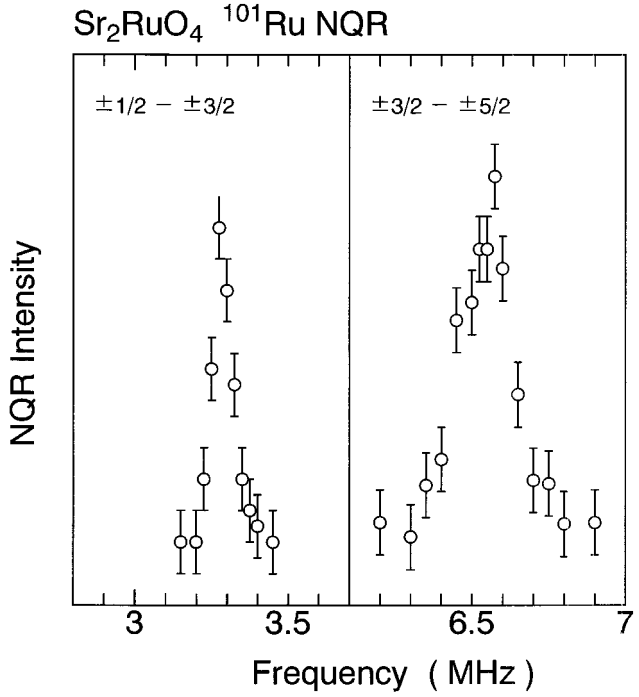

FIG. 3. ^{101}Ru NQR spectra in Sr_2RuO_4 corresponding to $\pm 1/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 5/2$, respectively.

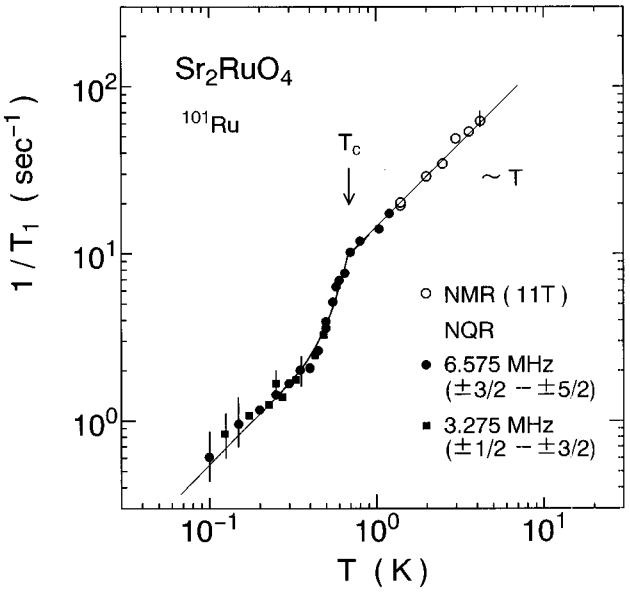

FIG. 4. T dependence of $1/T_1$ at Ru site in Sr_2RuO_4. Arrow indicates T_c. The solid curve below T_c is the calculation using the anisotropic pairing model with line node $[\Delta(\phi)=\Delta_0\cos(2\phi)]$ with $2\Delta_0/k_BT_c=7$ and $N_{res}/N_0=0.62$ in a two-dimensional cylindrical Fermi surface.

γ, the Wilson ratio R_W is estimated to be 1.36, indicating that the enhancements in χ and γ are the same in origin.

In Fig. 2, the T dependence of $(T_1T)^{-1}$ in the normal state is shown together with the result of the Knight shift. $1/T_1$ exhibits a small anisotropy with respective values along and perpendicular to the c axis, $(1/T_1T)_c \simeq 14.5(\mathrm{sec}^{-1}\ \mathrm{K}^{-1})$ in a T range between 1.4 and 4.2 K, and $(1/T_1T)_{ab} \simeq 17.5(\mathrm{sec}^{-1}\ \mathrm{K}^{-1})$ at 1.4 K. These rather conventional relaxation behaviors contrast with those observed in high-T_c cuprates such as $La_{2-x}Sr_xCuO_4$ which showed the characteristic Curie-Weiss behavior of $(T_1T)^{-1} \sim c/(T+\theta)$ with a large anisotropy of $(1/T_1)_{ab}/(1/T_1)_c \sim 3$ above T_c.[15]

Figure 3 shows the ^{101}Ru NQR spectra corresponding to the $(\pm 1/2 \leftrightarrow \pm 3/2)$ and $(\pm 3/2 \leftrightarrow \pm 5/2)$ transitions. Figure 4 displays the T dependence of $1/T_1$ at zero field (closed circles) and at 11 T (open circle). T_1 in the superconducting state was measured at two frequencies, 3.275 and 6.575 MHz corresponding to two NQR transitions. It should be noted that the T dependence of $1/T_1$ in Sr_2RuO_4 shows a steep decrease without the coherence peak just below T_c and a T_1T=constant relation well below T_c. T_1 was uniquely determined without any distribution even at low temperatures. This result means that the T_1T=constant relation is not due to the presence of some nonsuperconducting part. If this was the case, T_1 would be distributed with a short component close to the value of the T_1T=constant in the normal state and long components arising from the superconducting part. Importantly, the T_1T=constant relation in the superconducting state reveals the presence of the residual density of states (RDOS) at the Fermi level, providing an evidence for the gapless superconductivity. A fraction of RDOS, N_{res}/N_0 is estimated to be $\sim$ 0.62 from the ratio of $(T_1T)_s^{-1}$ to $(T_1T)_n^{-1}$ above T_c, $\sqrt{(1/T_1T)_s/(1/T_1T)_n}$. This fraction of the RDOS seems to be in agreement with the value of the residual electronic specific heat, $\gamma_0/\gamma_N(=N_{res}/N_0) \sim 0.67$ estimated tentatively from the entropy balance.[16]

Contributing insights to the pairing symmetry in Sr_2RuO_4 are extracted from comparing the Ru relaxation behaviors with those in the s-wave[17] or anisotropic p- and d-wave pairing states. The latter are extensively argued in heavy-fermion and high-T_c superconductors. In the s-wave picture, the gapless superconductivity with a finite density of states (DOS) at the Fermi level is induced by magnetic impurities with the concentration being close to a criticality suppressing T_c completely.[19] This possibility is, however, ruled out because no trace of magnetic impurity is observed at all from magnetic susceptibility, transport, thermal, and NMR measurements. The damping effect of quasiparticles originating from electron-phonon and/or electron-electron interactions can qualitatively explain the suppression of the coherence peak of $1/T_1$, but not the presence of low-energy excitation.

It was reported that this effect did not play a role below $\sim 0.8T_c$ where the opening of the isotropic energy gap was well evidenced by the exponential decrease of $1/T_1$ even though the coherence peak was absent.[18] Apparently, any interpretations based on the s-wave model are not consistent with the Ru relaxation behaviors.

Alternately, we point out that the T dependence of $^{101}(1/T_1)$ in Sr_2RuO_4 below T_c is rather similar to those in high-T_c superconductors, for example, to that of ^{63}Cu in $Bi_2Sr_2CaCu_2O_8$ (Bi2212) revealing the sharp decrease with no coherence peak and the T-linear behavior at low temperatures.[20] These unconventional results in high-T_c superconductors were well described in terms of the d-wave model in which the nonmagnetic *impurity scattering* in the unitarity limit induced the finite RDOS at the Fermi level.

As a matter of fact, by assuming either a *dirty* p- or d-wave model with a line node and RDOS at the Fermi level,

a fairly reasonable fit to $1/T_1$ in a whole T range is possible as drawn by the solid curve in Fig. 4. The obtained parameters are $2\Delta_0/k_BT_c=7$ and a fraction of RDOS, $N_{res}/N_0=0.62$ with respect to a gapless model with $\Delta(\phi)=\Delta_0\cos(2\phi)$ for two-dimensional cylindrical Fermi surfaces. Thus either a *dirty d*- or *p*-wave model produces a quite larger fraction of RDOS in Sr_2RuO_4 than $N_{res}/N_0 \sim 0.25$ in Bi2212. This suggests that the sample quality in Sr_2RuO_4 would be much worse than in Bi2212, in other words, an effective impurity content in the unitarity limit would be larger in the former than in the latter. The quality in Sr_2RuO_4 used here is, however, characterized as rather good from the sharply articulated NMR spectra in Fig. 1. By contrast, the broad NMR spectrum in Bi2212 pointed to some inhomogeneity of the sample.[20] Furthermore, the same Sr_2RuO_4 was shown to be in a clean limit from the very low value of residual resistivity and the large value of the transport mean free path measured from the Schubnikov-de Haas oscillation.[3] Accordingly, any *dirty p*- or *d*-wave model fails to interpret the T_1T=constant law well below T_c. This conclusion is also supported by the specific heat measurement which has revealed a large fraction of the residual value, $\gamma_0/\gamma_N \sim 0.57$ even in the sample with a relatively high T_c of ~ 1.2 K.[22] Note that this T_c value is very close to a possible maximum value of $T_{c0} \sim 1.5$ K in pure Sr_2RuO_4 for $N_{res}/N_0=0$, which is estimated with $T_c=0.7$ K for $N_{res}/N_0=0.62$ based on the *dirty p*- or *d*-wave model.[21] The remarkable finding is hence that the low-energy excitation yielding the RDOS should be inherent to the superconducting nature in Sr_2RuO_4.

Other scenario to explain the large fraction of RDOS is to assume nonunitary *p*-wave states with gapless quasiparticle excitations.[23,24] In this model, the RDOS at the Fermi level would be intrinsic with $N_{res}/N_0=0.5$. However, since the RDOS arises from gapless excitations of one state in equal spin pairing as in the superfluid A_1 phase of ^{3}He, the process of a nuclear spin flip is not allowed by the gap formation in the nonunitary state. Namely, a T_1T=constant relation would be expected only in the case when both states with up and down equal spin pairing mixed with each other by the spin-orbit interaction, as pointed out theoretically.[24,23] On the other hand, the band calculation showed that the orbital current induced by the spin-orbit interaction is negligible, suggesting that the spin state is well defined in Sr_2RuO_4,[25] which contradicts with the above scenario of the nonunitary pairing state. At the present stage, it is not decisive yet to identify the symmetry of the order parameter in Sr_2RuO_4. Further systematic Ru NQR/NMR and ^{17}O NMR investigations on single crystals with higher T_c will enable us to gain more detailed insights into the pairing state in Sr_2RuO_4, and are now in progress.

In conclusion, it has been established from the ^{101}Ru Knight-shift measurement in the normal state of Sr_2RuO_4 that the spin susceptibility is exchange enhanced by a factor ~ 5.4 as compared with the value from the band-structure calculation, and the Wilson ratio is ~ 1.36. This contrasts with the cuprate oxides in which the AF spin fluctuations play important roles. In the superconducting state, it has been found that the T dependence of $1/T_1$ is unconventional, showing a sharp decrease without the coherence peak just below T_c and the T_1T=constant relation well below T_c. Since these behaviors cannot be explained by the *s*-wave model, the anisotropic *p*- or *d*-wave pairing has been considered to be realized in Sr_2RuO_4.

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