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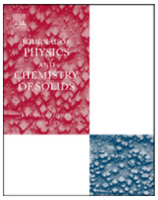

# NMR and NQR studies on superconducting $Sr_2RuO_4$

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ABSTRACT

We review our nuclear-magnetic resonance (NMR) and nuclear-quadrupole-resonance (NQR) studies in superconducting $Sr_2RuO_4$, which have been performed in order to investigate the gap structure and the pairing symmetry in the superconducting state and magnetic fluctuations in the normal state. The spin-lattice relaxation rate $(1/T_1)$ of a high-quality sample with $T_c{\sim}1.5$ K shows a sharp decrease without a coherence peak just below $T_c$, followed by a $T^3$ behavior down to 0.15 K. This result indicates that the superconducting gap in pure $Sr_2RuO_4$ is a highly anisotropic character with a line-node gap. The Knight shift, which is related to the spin susceptibility, is unchanged in the superconducting state irrespective of the direction of the applied fields and various magnitude of the field. This result strongly suggests that the superconducting pairs are in the spin-triplet state, and the spin direction of the triplet pairs is considered to be changed by small fields of several hundred Oe.

## 1. Introduction

Since the discovery of the superconductivity in $Sr_2RuO_4$, a lot of experiments have been performed to investigate the normal-state and superconducting properties in this compound [1]. $Sr_2RuO_4$ has the same crystal structure as a mother compound of high-$T_c$ cuprates, $La_2CuO_4$, and shows the superconducting transition at 1.5 K. Various experimental results as well as our NMR and NQR results indicate that $Sr_2RuO_4$ is an exotic superconductor [2]. Strong dependence of $T_c$ on disorder in $Sr_2RuO_4$ was pointed out by Mackenzie et al. from the measurements of chemical composition and of the transport properties [3]. This result supports models of non-*s*-wave pairing in this layered perovskite oxide. μSR experiments revealed that the superconducting state breaks time-reversal symmetry [4]. The broken time-reversal symmetry was recently reported from the high-resolution polar Kerr effect measurements [5]. From specific-heat [6] and penetration-depth measurements [7], the superconducting energy gap contains nodes, zero or very deep gap minima. The strongly anisotropic gap structure expressed as $\boldsymbol{d} = \hat{z}\Delta_0(\sin k_x \pm \mathrm{i}\sin k_y)$ has been confirmed from the precise angle-dependent specific-heat measurement [8]. In this article, we review experimental results of our nuclear-magnetic-resonance (NMR) and nuclear-quadrupole-resonance (NQR) measurements, which have been performed to investigate the paring symmetry and gap structure of the superconductivity and the spin dynamics in the normal state [9–16].

## 2. Experimental result

### 2.1. $1/T_1$ in the superconducting state

Nuclear spin-lattice relaxation rate $1/T_1$ of $^{101}$Ru $^{101}(1/T_1)$ was measured in two different quality of samples. One is the early-stage sample with $T_c{\sim}0.7$ K, and the other is the high-quality single crystals with $T_c = 1.48$ K. $^{101}(1/T_1)$ was measured at a peak of the $^{101}$Ru-NQR signal corresponding to $\pm\frac{3}{2} \leftrightarrow \pm\frac{5}{2}$ transition of 6.555 MHz, and was determined by a single component in the whole temperature range between 4.2 and 0.090 K from fitting experimental recovery behaviors of nuclear magnetization after saturation pulses to the theoretical function [9,12].

$T$ dependence of $1/T_1$ in the high-$T_c$ sample is plotted in Fig. 1, together with that in the previous low-$T_c$ sample with $T_c{\sim}0.7$ K [9,12]. In both samples, $1/T_1$ exhibits a sharp decrease with no coherence peak just below $T_c$, but a large difference is seen clearly in the low-$T$ behaviors of $1/T_1$ : $T_1T$ = constant behavior is seen in the low-$T_c$ sample, while $1/T_1$ in the high-$T_c$ sample continues to decrease down to 0.15 K.

Residual density of states (RDOS) is estimated from the saturating behavior of $1/T_1$ in a low-temperature region. RDOS in the early-stage is estimated to be more than 50%, but RDOS in the high-$T_c$ sample is less than 8.8%. This result suggests strongly that the origin of the RDOS seen in the low-$T_c$ samples is an extrinsic effect such as a scattering by impurities and/or crystal imperfections, which cause a significant decrease of $T_c$ in unconventional superconductors. The strong dependence of $T_c$ on disorder in $Sr_2RuO_4$ was already pointed out by Mackenzie et al. [3], and the similar effects were discussed intensively in the

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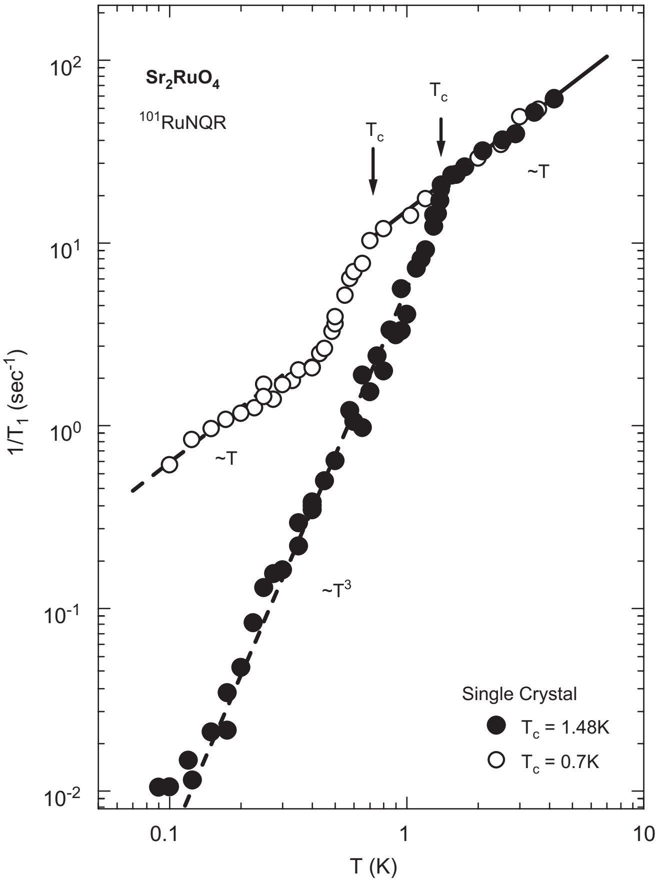

**Fig. 1.** $T$ dependence of $1/T_1$ in the early-stage sample with $T_c \sim 0.7\,\mathrm{K}$, and the high-quality single crystals with $T_c = 1.48\,\mathrm{K}$ [9,12].

cuprate superconductors with impurity-dopings [17,18]. If we plot the RDOS estimated by $1/T_1$ measurements against $T_c$, it was found that the experimental points are well on a theoretical relation between $T_c$ and RDOS calculated when the pair breaking is treated as the unitarity limit in the two-dimensional (2-D) anisotropic pairing state with a line-node gap [18]. From this relation, $T_c$ in the pure sample can be estimated as $T_{c0} \sim 1.5\,\mathrm{K}$, which is in good agreement with maximum $T_c$ reported so far.

The $1/T_1T$ in the superconducting state divided by that in the normal state, $R_s/R_n (\equiv (1/T_1T)_s/(1/T_1T)_n)$ in the high-quality sample is plotted against the renormalized temperature, $T/T_c$ in Fig. 2 [12]. In general, $R_s/R_n$ can be expressed by the DOS in the superconducting state $N_s$ as follows [19]:

$$\frac{R_s}{R_n} = \frac{2}{k_B T} \int_0^{\infty} (N_s^2 + M^2) f(E)(1 - f(E))\,\mathrm{d}E$$

where $M$ and $f(E)$ are the so-called "anomalous" DOS arising from the coherence effect and the Fermi-distribution function. The sharp decrease in $R_s/R_n$ can be explained reasonably by the anisotropic pairing state such as $p$- or $d$-wave states due to the diminishment of the coherence factor and weak divergence of $N_s$ at $E = \Delta$. It should be noted that $N_s \propto E$ as $E \to 0$ suggested by a line-node gap yields $T^3$ behavior in $1/T_1$ at low temperatures. The overall temperature dependence of $1/T_1$ can be explained by the line-node gap model such as $\boldsymbol{d} = \hat{z}\Delta_0 k_x$ state (model A) or the anisotropy-gap model with the $\boldsymbol{d} = \hat{z}\Delta_0(\sin k_x \pm \mathrm{i}\sin k_y)$ state (model B) if the existence of RDOS ~10%, which is induced by the tiny impurity scattering treated as the unitarity limit, is incorporated (model B′).

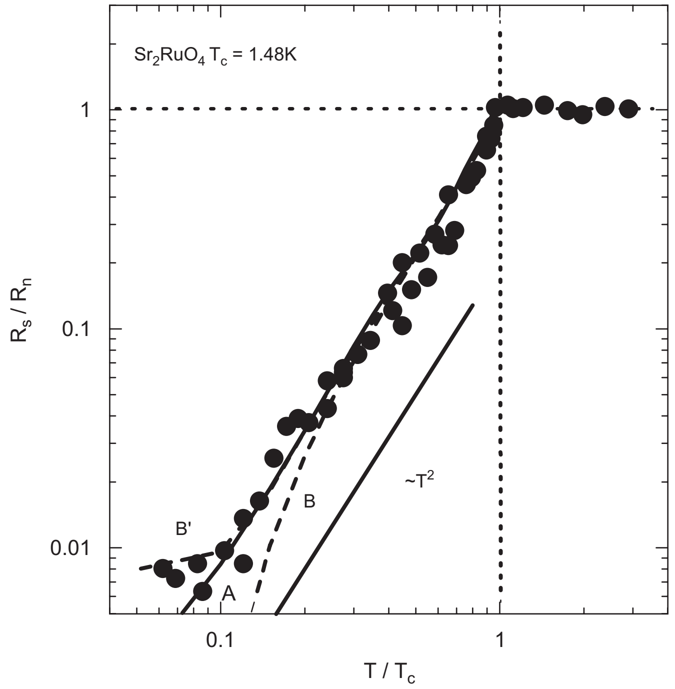

**Fig. 2.** Plot of $R_s/R_n$ against $T/T_c$ in the high-$T_c$ sample. Solid and dotted lines are the calculated $R_s/R_n$ using the line-node gap model with $\Delta_0 = 2k_BT_c$ (model A) and the anisotropic gap with the $\boldsymbol{d}(\boldsymbol{k}) = \hat{z}(\sin k_x + \mathrm{i}\sin k_y)$ state (model B) in the superconducting state [12].

### 2.2. Knight-shift measurement in the superconducting state

The Knight shift measures the effective field at the nucleus produced by the electrons, and thus is related to the microscopic spin susceptibility at the NMR nuclear site. The spin susceptibility in the superconducting state cannot be extracted from the bulk susceptibility due to the Meissner shielding, therefore the Knight-shift measurement is the most reliable method to measure the spin susceptibility in the superconducting state.

For the spin-singlet $s$-wave state, the spin susceptibility $\chi_s$ of Cooper pair was calculated by Yosida as [20]

$$\chi_s \propto -4\mu_B^2 \int_0^{\infty} N_s(E)[\partial f(E)/\partial E]\,\mathrm{d}E$$

At low $T$, $\chi_s$ decreases exponentially as $\exp(-\Delta/k_BT)$. In the spin-singlet $d$-wave state, since $N_s(E)$ is proportional to the energy $E$ for $|E| \ll \Delta$ in the $d_{x^2-y^2}$ symmetry as in high-$T_c$ cuprates, $\chi_s$ is proportional to $T$ at low $T$ [17,21]. In both cases $\chi_s$ diminishes to zero as $T \to 0$. In a spin-triplet state, if one can neglect the anisotropy in the system as in liquid $^3$He, $\chi_s$ stays constant in any direction as in the equal spin pairing state called as Anderson–Brinkmann–Morel (ABM) state for superfluid at high $T$ under pressure. On the contrary, provided that the spins are pinned along easy axis or plane owing to the crystal anisotropy below $T_c$, $\chi_s$ is reduced when the magnetic field ($H_{\mathrm{ext}}$) is applied perpendicular to the easy axis or plane. In any case, the Knight-shift measurement is most crucial for the determination of Cooper pair spin vector or the symmetry of the order parameter.

The Knight shift at the Ru and O sites was measured in the superconducting state of the high-quality $Sr_2RuO_4$ with $T_c \sim 1.48\,\mathrm{K}$. Here, $^{16}$O in the sample was replaced by $^{17}$O with a nuclear spin $I = \frac{5}{2}$ by annealing in the $^{17}$O atmosphere. Fig. 3 shows the temperature dependence of the $^{17}$O Knight shift at the $RuO_2$ plane (O(1) site), which was measured in the field parallel to the plane. When the external field is along the $a$-axis (Ru–O–Ru bonding direction), O(1) sites are no longer equivalent: as shown in the