NMR Evidence for Coexistence of Superconductivity and Ferromagnetic Component in Magnetic Superconductor $RuSr_2YCu_2O_8$: $^{99,101}Ru$ and ^{63}Cu NMR

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From Ru- and Cu-NMR studies, we present evidence for coexistence of superconductivity and ferromagnetism in a cuprate superconductor $RuSr_2YCu_2O_8$ (RuY1212). The observation of a large enhancement of a radio-frequency field for the Ru-NMR signal at zero field reveals the existence of a ferromagnetic (FM) component in the ordered RuO_2 plane below a Curie temperature of $T_M = 150$ K. Just below the onset temperature of superconductivity $T_c^{\rm onset} = 45$ K, a remarkable decrease of the nuclear spin-lattice relaxation rate $1/T_1$ was observed within the ordered RuO_2 plane as well as the CuO_2 plane, revealing that the superconducting gap coexists with the FM component in the RuO_2 plane on a microscopic scale. In addition, from the observation of a sharp peak in $^{101}(1/T_1)$ at $T_c^{\rm zero} \sim 23$ K where the resistivity becomes zero, we suggest that the motion of *self-induced vortices* originating from fluctuations of the FM component induces the resistivity between $T_c^{\rm onset}$ and $T_c^{\rm zero}$ in RuY1212.

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Since the discovery of hybrid ruthenium-copper oxides, $RuSr_2RCu_2O_8$ with R = Gd and Eu (denoted as RuR1212) [1], numerous experimental and theoretical investigations have been made to examine the coexistence of superconductivity and ferromagnetism in the RuR1212 compounds [2–7]. The crystal structure of RuR1212 is similar to $YBa_2Cu_3O_{7-y}$ except for the replacement of one dimensional (1D) CuO chains by 2D RuO_2 layers. In these compounds, a ferromagnetic (FM)-like order is observed at a higher Curie temperature of $T_M = 130$–150 K, whereas superconductivity appears at a significantly lower superconducting (SC) transition temperature of $T_c = 15$–45 K [2]. They have thus been called FM superconductors. In general, however, ferromagnetism and superconductivity have been considered to be mutually exclusive of each other. Therefore questions arise as to how the SC order parameter develops under the predominance of the magnetically ordered state, and how the magnetic order parameter is modified by the emergence of the SC state. The possibility of a Fulde-Ferrell-Larkin-Ovchinnikov–type state [8] or of a "self-induced vortex" (SIV) state [4] has been argued, and quite recently, the possibility of a "cyptro-superconducting structure" has been proposed to reply to the above issues [9].

In the study of the RuR1212 compounds, however, it is still debated whether the SC phase coexists with the predominant magnetic phase at a microscopic scale, since a bulk Meissner effect was not clearly observed in the RuGd1212 samples at an early stage. Afterward, evidence suggesting a bulk SC phase was presented from heat-capacity measurements in RuGd1212 by Tallon *et al.* [3]. Recently, it was also suggested that a bulk Meissner state seems to develop in the RuGd1212 compound at temperatures lower than $T^{\rm ms} \sim 30$ K [4]. However, no convincing *microscopic* data are reported so far to identify the coexistence of the superconductivity and the magnetism in these materials.

Likewise, the magnetic properties in RuR1212 are not clearly understood yet. Magnetization and zero-field muon spin-rotation studies initially suggested a FM-like order with the spontaneous magnetization directed along the ab plane [5]. However, recent neutron-diffraction (ND) studies on RuGd1212 have indicated an antiferromagnetic (AF) order of Ru moments, which are canted from the c axis at low fields [6]. A recent magnetization study on RuEu1212 was also interpreted in terms of the AF order with a small FM component ($\sim 0.05\mu_B$/Ru at 5 K) [7]. In order to settle these issues, however, further experimental data, especially from a microscopic point of view, are highly desired.

In this paper, we report the first NMR measurements in the newly synthesized ruthenium(Ru)-copper(Cu) oxide $RuSr_2YCu_2O_8$ (denoted as RuY1212) [10]. The advantage of a RuY1212 sample for the NMR measurement is that the R ion is replaced by nonmagnetic Y^{3+}. This advantage enabled us to investigate the detailed spin dynamics in both the RuO_2 and CuO_2 planes without the influence from other magnetic elements, e.g., Gd^{3+} in the case of RuGd1212. From the observation of zero-field ^{99,101}Ru-NMR signals we conclude that magnetic ordering with a ferromagnetic component occurs in the RuO_2 plane below $T_M \sim 150$ K, and from the $^{99,101}(1/T_1)$ measurement we conclude that a SC gap coexists with the ferromagnetic component below $T_c^{\rm onset} = 45$ K at a microscopic level.

Polycrystalline samples of RuY1212 have been synthesized by the solid-state reaction as described elsewhere [10]. The sample was confirmed to consist of almost a single phase from x-ray diffraction. A magnetic transition was clearly observed at $T_M \sim 150$ K from magnetic susceptibility measurements at $H = 1$ kOe. On the other

hand, resistivity measurements revealed a significant broad SC transition as shown in Fig. 2. The onset of the SC transition and zero resistivity were observed at $T_c^{\text{onset}} = 45$ K and $T_c^{\text{zero}} \sim 23$ K, respectively. These values are consistent with the typical values of T_c^{onset} and T_c^{zero} reported in RuR1212 compounds so far. A powder ND measurement was recently performed on the same sample as the one we used in this work [10]. The ND showed the (0,0,1) nuclear and the $(1/2, 1/2, 1/2)$ AF reflections at $H = 0$, consistent with the results on RuGd1212 [6]. Spin-echo NMR measurements were performed using a conventional phase-coherent-type NMR spectrometer. The nuclear spin-lattice relaxation time T_1 was measured by means of the saturation-recovery method. T_1 was determined by fitting the recovery of nuclear magnetization to the theoretical relaxation function for $I = 5/2$ (Ru) and $3/2$ (Cu), respectively.

Figure 1 shows a zero-field ^{99,101}Ru-NMR spectrum obtained at $T = 4.2$ K well below T_M. The Ru-NMR signal was observed by applying radio-frequency (rf) pulses with very small amplitude due to the large enhancement of the rf field. This enhancement is characteristic of the NMR measurements in FM substances (so-called H_1 *enhancement* effect), which originates from the coherent motion of FM moments caused by the application of the rf field. The enhancement of H_1 is estimated as $\sim$100 from the comparison with NMR conditions for paramagnetic compounds [11]. Therefore, this observation of H_1 *enhancement* for the Ru-NMR signal can be taken as evidence for the existence of a FM component in the RuO_2 plane.

As seen in Fig. 1, the ^{99,101}Ru-NMR spectrum consists of several well-separated peaks in the high frequency range $f = 100-150$ MHz and a broad line extending over the frequency range $f = 30-80$ MHz. This result indicates

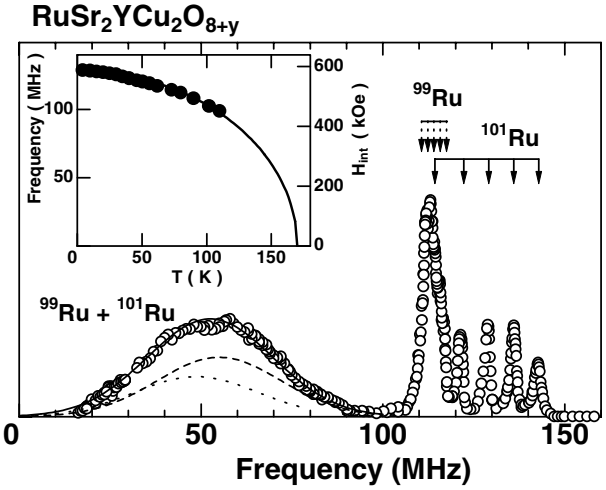

FIG. 1. Zero-field ^{99,101}Ru-NMR spectra in $RuSr_2YCu_2O_8$. Arrows are the peak position calculated by $H_{\text{hf}} \sim 600$ kOe in the plane and $^{99}\nu_Q = 2.5$ and $^{101}\nu_Q = 14.6$ MHz, respectively. The inset gives the temperature dependence of H_{hf}. The solid curve is a calculation based on the mean-field theory.

that there exist microscopically two inequivalent Ru sites in the RuO_2 plane. The former and latter are denoted as Ru(I) and (II) sites, respectively. The quadrupole-split spectrum for the Ru(I) site originates from both ^{99}Ru and ^{101}Ru isotopes. Taking an internal hyperfine field H_{hf} and a quadrupole frequency ν_Q into account, the Ru(I)-site spectrum is well assigned as shown by the arrows in Fig. 1. Fitting the spectra leads to an estimation of $^{99}\nu_Q = 2.4$ MHz and $^{101}\nu_Q = 15.1$ MHz with an asymmetry parameter $\eta = 0$ and an angle between the direction of H_{hf} and the principal axis of the electric field gradient (EFG), $\theta \sim 90°$. The value of ν_Q in RuY1212 is smaller than that in RuGd1212 [12,13]. Note that the quadrupole-split spectrum for the Ru site (I) indicates that the Ru site (I) is located at a uniaxially symmetric position in distorted RuO_6 octahedra. This is in good agreement with the recent powder ND result showing that RuO_6 octahedra have a flattened shape in RuGd1212 with a O-Ru-O bond shortened along the c axis [14].

The inset in Fig. 1 shows the temperature dependence of H_{hf}(I) at the Ru(I) site that is induced by the spontaneous magnetization below T_M. The H_{hf}(I) is estimated from the frequency of the central peak $(-1/2 \leftrightarrow +1/2)$ in the NMR spectrum for the ^{101}Ru(I) site [ν_p(I) $\sim$ 130 MHz at 4.2 K]. Above 125 K, the signal is not visible due to the divergence of $1/T_1$ caused by magnetic fluctuations near T_M. Application of an external field makes the spectrum shift to the lower frequency side, evidencing the negative sign of H_{hf}(I). As seen in the figure, H_{hf}(I) increases smoothly with decreasing T and saturates at low T. A saturated value of H_{hf}(I) $\sim$ 600 kOe is evaluated from an extrapolation to $T \to 0$. Using the relation of $H_{\text{hf}} = A_{\text{hf}} M_{\text{FM,AF}}$ in the magnetically ordered state, a spontaneous magnetic moment is estimated to be M_{AF}(I) $\sim 2\mu_B$ for the Ru(I) site. Here we adopt the hyperfine coupling constant, $A_{\text{hf}} \sim -300$ kOe/μ_B obtained in the FM state of $SrRuO_3$ [11]. Following the same relation, M_{AF}(II) $\sim 0.9\mu_B$ is estimated for the Ru(II) site from ν_p(II) $\sim$ 58 MHz.

We note that M_{AF}(II) is comparable to $M_{\text{FM}} = 1.1\mu_B$ in the FM metal $SrRuO_3$ [15] and $M_{\text{AF}} \sim 1.25\mu_B$ in the AF insulator Ca_2RuO_4. In both compounds, Ru is in the Ru^{4+} state with a low-spin state ($S = 1$) [16]. On the other hand, a size of M_{AF}(I) $\sim 2\mu_B$, which is nearly double of M_{AF}(II) $\sim 0.9\mu_B$, indicates that the Ru site (I) is in the Ru^{5+} state with $S = 3/2$ due to three electrons in t_{2g} orbitals. The present Ru-NMR spectra thus suggest a mixed valence state of Ru^{4+} and Ru^{5+} in the RuO_2 plane. It is considered that this mixed valence state is due to hole doping through charge transfer from RuO_2 planes into CuO_2 planes. From the Cu nuclear-relaxation behavior presented later, the hole concentration p in the CuO_2 plane is suggested to be comparable to that in $YBa_2Cu_3O_7$ (Y1237), i.e., $p \sim 0.2$. In this case, if one RuO_2 plane is assumed to supply holes to two CuO_2 planes, the ratio of Ru^{4+}/Ru^{5+} should simply be 40%/60%. The intensity ratio in the

Ru(I)- and Ru(II)-NMR spectrum supports this scenario. Recently, the same conclusion has been suggested from the Ru-NMR studies on RuGd1212 [12,13].

The $Ru^{5+}(S = 3/2)$ state in RuY1212 has three electrons in the t_{2g} orbitals, which is regarded as a half-filled state [17]. On the other hand, the Ru^{4+} $(S = 1)$ state with four electrons is expected to be similar to that in Ca_2RuO_4, since the O-Ru-O bond length along the c axis is shortened in both compounds. In this case, the three t_{2g} orbitals will split into d_{xy} with a lower energy and two degenerate d_{yz} and d_{zx} with a higher energy. In the case when four electrons are in the t_{2g} orbits, we may expect a half-filled configuration with two electrons in d_{xy} and two electrons in two d_{yz} and d_{zx} orbits [18]. This suggests that $4d$-electron spins at both the Ru^{5+} site (I) and the Ru^{4+} site (II) prefer to be antiferromagnetically coupled via the superexchange interaction in the RuO_2 plane. The observation of charge differentiation at the RuO_2 plane may support a partially localized picture of $4d$ electrons, since their delocalization would average out some charge differentiation at the RuO_2 plane. It is considered that the reduced spontaneous moments at both the Ru^{5+} $(2\mu_B)$ and Ru^{4+} $(0.9\mu_B)$ (that are smaller than the respective theoretical values $3\mu_B$ and $2\mu_B$) are mainly associated with a 2D character and/or strong $4d$-$2p$ mixing effect in the compound.

From the Ru-NMR spectral shape, it is difficult to deduce the spin structure in RuY1212, since the $H_{\rm hf}$(I) and $H_{\rm hf}$(II) are determined by the on-site ordered moments at the Ru(I) and (II) sites. However, the result that the angle between the direction of $H_{\rm hf}$ and the principal axis of EFG (along the c axis) is $\sim 90°$ in the Ru site (I) indicates that the ordered moment is in the RuO_2 plane. This is contrary to the recent ND experiment that suggests the ordered moments are along the c axis [6]. In addition, the Ru-NMR result that probes the FM component at $H = 0$ is not in agreement with the ND result that probes the AF structure. In order to reconcile this inconsistency, further experiments, especially precise ND study, are highly desired.

Figure 2 shows the temperature dependence of $^{101}(1/T_1T)$ at the Ru(I) site measured at the central peak $(-1/2 \leftrightarrow +1/2)$ at $H = 0$. In the figure, we also plot the T dependence of $1/T_1T$ of ^{63}Cu measured at $H \sim 100$ kOe parallel to the ab plane. The ^{63}Cu-NMR spectrum at 280 K shows a typical powder-pattern shape affected by the quadrupole interaction. Its linewidth broadens from $\sim$0.25 kOe at 280 K to $\sim$3 kOe at 20 K with decreasing T below T_M. This broadening originates from the dipolar field of the ordered Ru moments in the RuO_2 plane. $^{63}(1/T_1T)$ increases with decreasing T, as commonly observed in other high-T_c cuprates. No anomaly is observed around $T_M \sim 150$ K, suggesting that the Cu nuclear relaxation is dominated by AF fluctuations among Cu-$3d$ spins, not by Ru-$4d$ spin fluctuations. We found that the T dependence and the magnitude of $1/T_1T \sim C/(T + \theta)$ in the normal state are quite similar to those

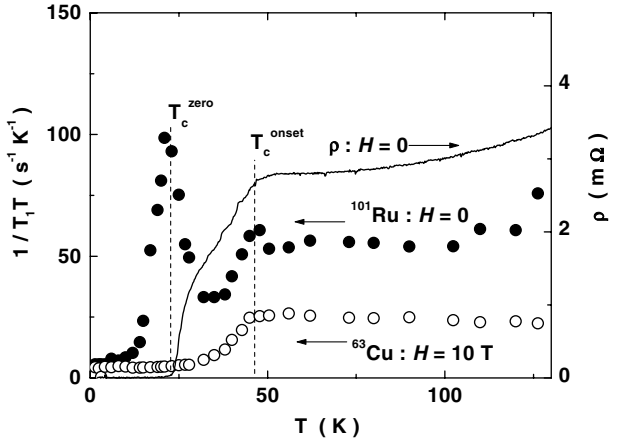

FIG. 2. Temperature dependence of the resistivity and $^{101}(1/T_1T)$ at zero field and $^{63}(1/T_1T)$ at $H \sim 100$ kOe.

in Y1237 [19]. This implies that the doping level in RuY1212 is comparable to that in Y1237. The further detailed Cu-NMR results will be discussed in a separate paper. On the other hand, $^{101}(1/T_1T)$ of Ru(I) is independent of temperature with a value of $^{101}(T_1T)^{-1} = 57\ \mathrm{s^{-1}\,K^{-1}}$ between 50 and 100 K, well below $T_M = 150$ K. This relaxation channel is apparently dominated by the density of states in the RuO_2 plane.

In the SC state, $^{63}(1/T_1T)$ of Cu shows a steep decrease without any coherence peak below $T_c^{\rm onset} = 45$ K. This behavior is commonly observed in other high-T_c superconductors, and thus provides decisive evidence for the opening of a d-wave SC gap in the CuO_2 plane. A remarkable result is that a steep decrease in $^{101}(1/T_1T)$ is also observed at the ordered Ru sites below $T_c^{\rm onset} = 45$ K, followed by an *anomalous peak* around 23 K. This reveals that the SC gap develops also at the ordered RuO_2 plane with the FM component below $T_c^{\rm onset}$. From the present NMR results, we conclude that the SC gap coexists with the FM component in the RuO_2 plane on a microscopic scale.

Another important finding is that a sharp peak in $^{101}(1/T_1T)$ emerges around $T_c^{\rm zero} \sim 23$ K where the resistivity becomes zero. This indicates that some slowing down of the fluctuations of Ru moments exists in the RuO_2 plane in the SC state. As mentioned above, the SC gap develops below $T_c^{\rm onset} = 45$ K, although the T dependence of the resistivity $\rho(T)$ shows a rather broad SC transition over 20 K from $T_c^{\rm onset} = 45$ K to $T_c^{\rm zero} = 23$ K as seen in Fig. 2. From the peak of $^{101}(1/T_1T)$ around $T_c^{\rm zero} = 23$ K, we suggest that the finite resistivity between $T_c^{\rm onset} = 45$ K and $T_c^{\rm zero} = 23$ K may be caused by the motion of SIV's, and that the SIV state is realized in RuY1212 from the following discussions.

In most high-T_c cuprates, a similar broad SC transition is observed in $\rho(T)$ under the magnetic field, which is ascribed to the motion of magnetic-field induced vortices in the CuO_2 plane. In RuY1212, however, the measurements

of $\rho(T)$ and $^{101}(1/T_1T)$ were performed at $H = 0$, where field induced vortices are absent. Alternatively, it is possible in FM superconductors that the spontaneous FM moments give rise to the SIV so that the ferromagnetism coexists with the superconductivity. Such a possibility has been theoretically proposed by Tachiki *et al.* [20]. They argued that the self-energy of a vortex becomes negative under an appropriate condition in the FM superconductor, and thus the vortices would be induced without applying an external magnetic field. A necessary condition for the SIV state was given by $H_{c1}^0 < 4\pi M_{\mathrm{FM}} < H_{c2}^0$, indicating that the average spontaneous FM magnetization ($4\pi M_{\mathrm{FM}}$) plays a role of the external magnetic field. In RuY1212, H_{c1}^0 and H_{c2}^0 may be comparable to the values for Y1237. Since $4\pi M_{\mathrm{FM}}$ is approximately 700 Oe at 5 K in RuY1212 larger than $H_{c1} \sim 100$ Oe in Y1237, the condition for the SIV state seems to be satisfied. The SIV state originates from the spontaneous magnetization induced by the FM component of the ordered Ru moments. Therefore, the slow fluctuations of Ru moments that are probed by the T_1 measurement will cause a slow motion of SIV in the CuO_2 planes. We suggest that this slow motion of SIV gives rise to a finite resistivity between T_c^{onset} and T_c^{zero} in RuY1212, in analogy with the motion of field induced vortices. In this context, the broad SC transition may be regarded as the liquid SIV state in the FM superconductor RuY1212 and the zero resistivity would be realized in the solid state of SIV.

Recently, Bernhard *et al.* reported magnetization measurements at low fields in RuGd1212 in which a sizable diamagnetic signal was observed below $T_c^{\mathrm{ms}} \sim 30$ K $\ll T_c^{\mathrm{onset}}$ [4]. They found that M_{FM} is not T independent even far below T_M, and hence the total amount of SIV should increase with decreasing T in the SC state [7]. We consider that the appearance of the diamagnetism below $T_c^{\mathrm{ms}} \sim 30$ K does not necessarily imply that the Meissner state excludes vortices perfectly below T_c^{ms}. Rather, the appearance of diamagnetism below $T_c^{\mathrm{ms}} \sim 30$ K may be relevant to some change in spatial distribution of SIV at a liquid to solid transition of the SIV state that occurs at $T_c^{\mathrm{ms}} \sim 30$ K in RuGd1212. We propose that the observation of the diamagnetism should be accounted for in the framework of the SIV state.

In conclusion, the coexistence of superconductivity and ferromagnetism in RuY1212 has been examined by microscopic probes of ^{99,101}Ru and ^{63}Cu NMR. From the observation of a large enhancement of the rf field for the zero-field Ru-NMR signal, it was confirmed that magnetic ordering with a FM component exists in the RuO_2 planes. The study of the Ru-NMR spectrum also reveals that a Ru^{5+}-like site (I) and a Ru^{4+}-like site (II) are present in the RuO_2 plane, probably as a result of holes that are doped through charge transfer from the RuO_2 plane into the CuO_2 plane. On the other hand, the opening of the SC gap is observed in $1/T_1T$ at the Ru sites as well as the Cu sites. These NMR results reveal that the SC gap coexists with the FM component in the RuO_2 plane on a microscopic scale. Furthermore, we found that a slowing down of fluctuations of the Ru moments emerge around $T_c^{\mathrm{zero}} \sim 23$ K where the resistivity becomes zero. We suggest that the broad SC transition between T_c^{zero} and T_c^{onset} in RuY1212 is due to the slow motion of the SIV, which is induced by the slow fluctuations of the FM component.

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[1] L. Bauernfeind, W. Widder, and H. F. Braun, Physica (Amsterdam) **254C**, 151 (1995).
[2] J. L. Tallon *et al.,* IEEE Trans. Appl. Supercond. **9**, 1696 (1999).
[3] J. L. Tallon *et al.,* Phys. Rev. B **61**, R6471 (2000).
[4] C. Bernhard *et al.,* Phys. Rev. B **61**, R14 960 (2000).
[5] C. Bernhard *et al.,* Phys. Rev. B **59**, 14 099 (1999).
[6] J. W. Lynn *et al.,* Phys. Rev. B **61**, R14 964 (2000).
[7] G. V. Williams and S. Kramer, Phys. Rev. B **62**, 4132 (2000).
[8] W. E. Pickett, R. Weht, and A. B. Shick, Phys. Rev. Lett. **83**, 3713 (1999).
[9] C. W. Cho *et al.,* Physica (Amsterdam) **335C**, 231 (2000).
[10] H. Takagiwa *et al.,* J. Phys. Soc. Jpn. **70**, 333 (2001).
[11] H. Mukuda *et al.,* Phys. Rev. B **60**, 12 279 (1999).
[12] Y. Furukawa *et al.,* Physica (Amsterdam) **341C–348C**, 453 (2000).
[13] K. Kumagai *et al.,* Phys. Rev. B **63**, 180509 (2001).
[14] O. Chmaissem *et al.,* Phys. Rev. B **61**, 6401 (2000).
[15] T. Kiyama *et al.,* Phys. Rev. B **54**, R756 (1996).
[16] M. Braden *et al.,* Phys. Rev. B **58**, 847 (1998).
[17] P. D. Battle and C. W. Jones, J. Solid State Chem. **78**, 108 (1989).
[18] S. Nakatsuji and Y. Maeno, Phys. Rev. Lett. **84**, 2666 (2000).
[19] Y. Kitaoka *et al.,* J. Phys. Soc. Jpn. **57**, 30 (1988).
[20] M. Tachiki *et al.,* Solid State Commun. **34**, 19 (1980).