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Charge and spin states of Ru and Cu in magnetic superconductor $RuSr_2GdCu_2O_8$ studied by NMR

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Electronic and magnetic properties of $RuSr_2GdCu_2O_8$ have been investigated by electric resistivity, magnetization, and Cu-, Ru-NMR measurements. Magnetic order ($T_M=133$ K) and superconductivity [T_s(onset)~ 52 K] have been confirmed. We observed two kinds of Ru-NMR signals (the hyperfine fields of ^{101}Ru are 590 kOe and 290 kOe), suggesting a charge segregation of Ru^{5+} ($S=3/2$) and Ru^{4+} ($S=1$) in the RuO_2 layers. The hyperfine field at the Cu site is diminishingly small, indicating magnetic interactions between CuO_2 and RuO_2 layers are weak. Assuming that holes are inherently doped in the CuO_2 layers from the (Ru^{4+}, Ru^{5+})O_2 layers, the high-T_c superconductivity can occur under weak magnetic interactions between Ru and Cu spins in $RuSr_2GdCu_2O_8$.

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For studies on so-called magnetic superconductors, recent reports on the coexistence of superconductivity and ferromagnetic order in $RuSr_2RCu_2O_8$ (R: rare earth)(Ru1212) are intriguing,[1–6] as the ruthenate class of materials has been the focus of considerable work. $SrRuO_3$, for example, is a $4d$ band metallic ferromagnet ($T_c\sim 165$ K),[7] while Sr_2RuO_4 is known as an exotic triplet superconductor ($T_s=1.5$ K).[8] The structure of $RuSr_2RCu_2O_8$ is an analog of $YBa_2Cu_3O_7$ with complete replacement of the Cu-O chains by Ru-O layers. The RuO_6 octahedra are connected through apical oxygens to two layers of CuO_5 square pyramids. The magnetic order of Ru ions in $RuSr_2RCu_2O_8$ is believed to be associated with the hybridization of Ru-$4d$ and oxygen $2p$ orbital in the RuO_2 planes, while superconductivity could occur in the CuO_2 planes, if holes are doped inherently into Cu-O $3d$-$2p$ orbitals. In this sense, the valence states of Cu and Ru ions are crucial for understanding the origin of ferromagnetism and superconductivity. It is also quite interesting if $RuSr_2RCu_2O_8$ is a particular ferromagnetic superconductor with a high magnetic ordering temperature, as this would suggest a superconducting order parameter of the Fulde-Ferrell-Larkin-Ovchinnikov type[9] or a possible triplet superconductivity.[4] An interplay between both the order parameters through electromagnetic interactions would produce an exotic state such as a self-induced vortex state,[10] as investigated previously for a magnetic superconductor, $Ce_{1-x}Gd_xRu_2$.[11]

Concerning the magnetic nature, the ferromagnetism is still puzzling. Though large magnetic moments would be expected for the ionic state of Ru^{5+} ($S=3/2$) or Ru^{4+} ($S=1$), an upper limit of the saturated magnetic moments under applied field are obtained to be $\sim 1.05\mu_B$ by the magnetization measurements.[2–4] Moreover, a weak ferromagnetism is observed by the spontaneous magnetization at zero field cooling, and the ferromagnetic component is estimated to be $0.28\mu_B$.[2,3] The Ru moments in the ferromagnetic state are suggested to be perpendicular to the c axis by a μSR experiment.[3] However, the recent neutron diffraction measurement on $RuSr_2GdCu_2O_8$ (Ref. 12) demonstrates that the magnetic order of the Ru moments ($\sim 1.18\mu_B$) is antiferromagnetic along the c axis in contrast to the conclusion of the ferromagnetic ordering. The ferromagnetic contribution is presumed to be a canting component in the antiferromagnetic arrangements. A recent band calculation[13] supports the lowest energy for an antiferromagnetic arrangement. Thus, the magnetic nature of $RuSr_2RCu_2O_8$ is still controversial.

Magnetic order and superconductivity are believed to be mutually exclusive in general. Therefore, a naive question arises: how does the superconducting order parameter develop under the ferromagnetically ordered state with very high T_M? In order to gain insight into the true origin of the coexistence of the magnetism and superconductivity, further extended experiments, especially from a microscopic point of view, are required. Here, we have carried out nuclear magnetic resonance (NMR) measurements on this particular Ru1212 family in order to shed light on the magnetic and electronic properties. We have successfully observed $^{63/65}$Cu and $^{99/101}$Ru-NMR in the magnetically ordered state of $RuSr_2GdCu_2O_8$,[14] and here discuss the magnetic and charged state of Cu and Ru ions in $RuSr_2GdCu_2O_8$.

$RuSr_2GdCu_2O_8$ was prepared from the stoichiometric mixtures of RuO_2, $SrCO_3$, Gd_2O_3, and CuO. The mixtures were pelletized and heated at 960 °C for 10 h in air and 1010 °C for 10 h in N_2 atmosphere, following a procedure reported previously.[3] Then, the as-sintered samples were annealed for a long time in O_2 atmosphere around 1055 °C with several intermediate grindings. X-ray powder diffraction patterns at room temperature show that the sample is single phase material. The magnetization was measured using a superconducting quantum interference device (SQUID) magnetometer. The electrical resistivity was measured by a four-probe method. NMR measurement was carried out with a phase coherent spin echo spectrometer. We observed NMR signals at zero external field (ZFNMR) and under applied magnetic field (NMR).

The magnetic transition is clearly observed at 133 K from a temperature dependence of the magnetization, as shown in Fig. 1. We could not see any anomalies in the temperature dependence of magnetization due to possible magnetic impurity phases such as Sr_2GdRuO_6 ($T_N=30$ K),[15] and

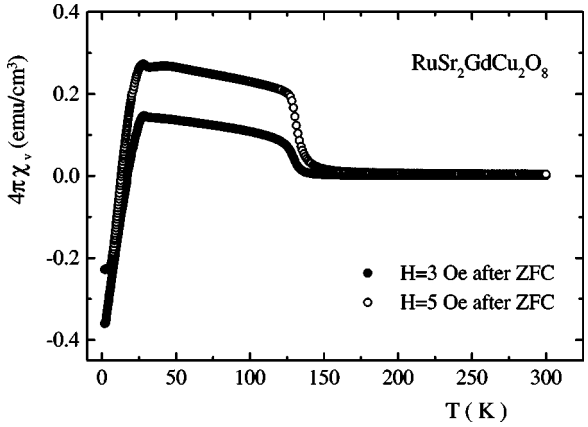

FIG. 1. Temperature dependence of magnetic susceptibility of $RuSr_2GdCu_2O_8$ measured at $H=3\sim5$ Oe after zero field cooling.

$SrRuO_3$ ($T_c=165$ K),[7] indicating the good quality of the present sample. A ferromagnetic component of the magnetization ($\sim0.1\mu_B$) at $H=3$ Oe appears below T_M, suggesting a weak-ferromagnetic nature. The magnetization below T_M increases with increasing external field and a saturated ferromagnetic component of $\sim1.1\mu_B$ for Ru ions is obtained at $H=7$ T. This ordered moment is smaller than those expected from $S=1$ (the low spin state) or $S=2$ (the high spin state) of Ru^{4+} ($4d^4$) and from $S=3/2$ of Ru^{5+} ($4d^3$).

Diamagnetism due to the Meissner effect (about 50% volume fraction) is observed for $RuSr_2GdCu_2O_8$ at low temperature, suggesting the bulk nature of superconductivity. Also, an electrical resistivity of the present sample showed evidently the superconducting transition at T_S (onset) ~52 K [$T_S(R=0)\sim34$ K (at zero resistivity)], as shown in Fig. 2. The transition width became broader, and $T_S(R=0)$ decreased largely and then slowly with increasing magnetic field. The inset of Fig. 2 shows the phase diagram for $RuSr_2GdCu_2O_8$. The result indicates a quite large upper critical field ($H_{C2}\gg10$ T) of $RuSr_2GdCu_2O_8$.

Figure 3 shows the NMR spectra of $RuSr_2GdCu_2O_8$ at 1.8 K. For several resonance frequencies (30–70 MHz), the observed NMR spectrum shifts nearly with the gyromagnetic

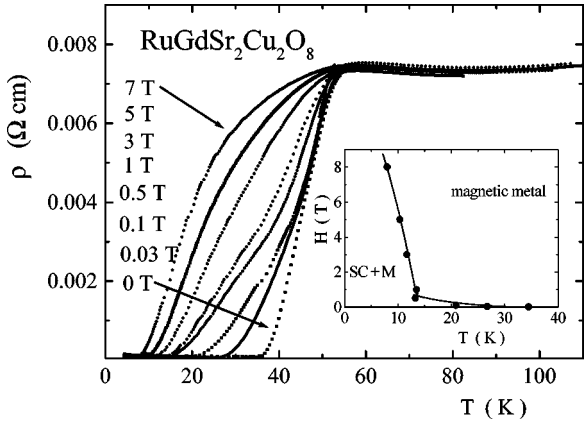

FIG. 2. Temperature dependence of the electrical resistivity of $RuSr_2GdCu_2O_8$. The inset is the phase diagram obtained from the electrical resistivity [for $T_c(R=0)$].

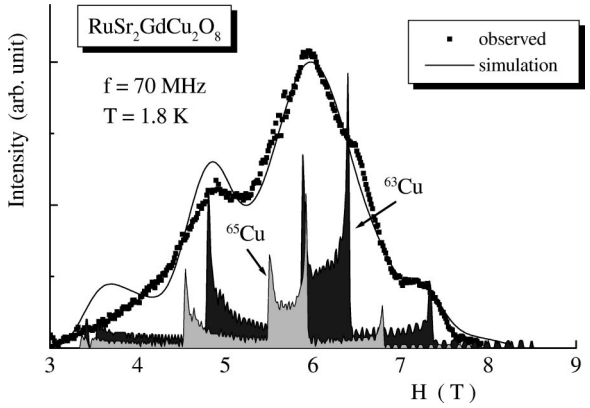

FIG. 3. $^{63/65}$Cu-NMR spectrum of $RuSr_2GdCu_2O_8$ as a function of external field at 1.8 K (in the magnetically ordered state.). Trial simulation spectra with a line broadening of 200 G for both ^{63}Cu and ^{65}Cu nuclei and the best fitted spectrum with a broadening of 5000 G (solid line) are given.

ratio of $^{63/65}$Cu nuclei. We conclude that the observed NMR spectrum is attributed to the Cu nuclei in the CuO_2 planes. The broadened NMR spectrum for the powder sample results partly from nuclear quadrupole interactions (so-called powder pattern) and from magnetic origin in the magnetically ordered state. In general, the nuclear spin Hamiltonian is expressed by[16]

$$H=H_M+H_Q, \tag{1}$$

where a magnetic Zeeman term, $H_M=-\gamma_N\hbar H_0 I$, and a quadrupolar term, $H_Q=(1/6)\hbar\nu_Q[3I_z^2-I(I+1)+(1/2)\eta(I_+^2+I_-^2)]$. Here, ν_Q is $(3/2)e^2qQ/I(2I-1)$ and η is an asymmetric parameter describing the electric field gradient (EFG) defined by $(V_{xx}-V_{yy})/V_{zz}$ ($|V_{zz}|\geqslant|V_{yy}|\geqslant|V_{xx}|$). H_0 is a magnetic field at a polar angle, θ with respect to the principle axis of the EFG, $V_{zz}(=eq)$. The maximum principle axis at the Ru and the Cu sites is determined to be the c axis from the calculation of the EFG by a point charge model. With the second order perturbation calculation for Eq. (1) in the case of $H_M\gg H_Q$, the calculated positions for the center ($\pm1/2\leftrightarrow\mp1/2$) and satellite lines ($\pm3/2\leftrightarrow\pm1/2$) for two Cu ($I=3/2$) isotopes are shown in Fig. 3. The observed spectrum is fitted with the quadrupole frequency ν_Q of ~30 MHz for ^{63}Cu whose value is close to the ones for ^{63}Cu nuclei in the CuO_2 plane of most HTSC's.[17] Here, from the simulation results, the broadening of the spectrum is at most 5000 G and there exists no sizable (less than 2 kOe of the NMR shift) internal fields at the Cu sites.

We observed NMR signals under zero applied field (ZFNMR) in a wide frequency range of $30\sim150$ MHz for $RuSr_2GdCu_2O_8$. The ZFNMR spectra consist of three distinct components, namely, signals at 30 MHz, the broad spectra around 40 and 80 MHz, and signals with a set of well-separated peaks between 110 and 150 MHz, as shown in Fig. 4. First, we would like to point out that the signals at 30 MHz are assigned to be the Cu-NQR in accordance with the NMR result.

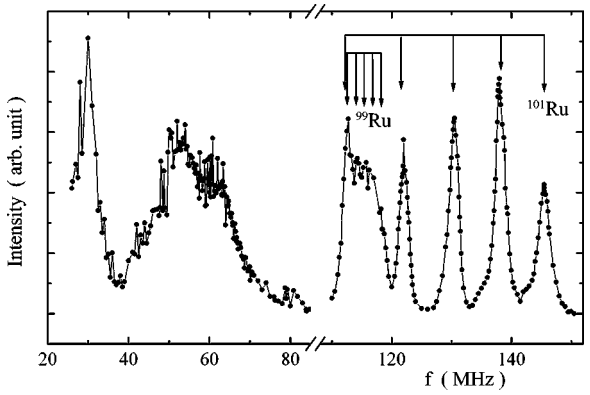

FIG. 4. ZFNMR spectra as a function of frequency for $RuSr_2GdCu_2O_8$. All the data were measured at 1.4 K. Intensities are corrected by the f^2 relation. The arrows in the range of 110–150 MHz show the resonance positions for ^{99}Ru and ^{101}Ru obtained from the second-order perturbation calculations with large H_{int} and small e^2qQ interactions (see text).

Next, we assign the signals between 110 and 150 MHz to the $^{99/101}$Ru ($I=5/2$) signals. With the second order perturbation calculation for Eq. (1) in the case of $H_M \gg H_Q$, the resonance positions for Ru nuclei are well fitted with the following parameters: internal field, $H_{int} \sim -590$ kOe, $\nu_Q = 17$ MHz for ^{101}Ru and 2.6 MHz for ^{99}Ru, $\theta = 85°$ and $\eta \sim 0$. The calculated resonance positions for ^{99}Ru and ^{101}Ru are shown by arrows in Fig. 4. As the V_{zz} of EFG at the Ru sits along the c axis from a point charge model with structural data,[5] we conclude that the Ru moments are almost perpendicular to the c axis. This conclusion is inconsistent with that from the recent neutron scattering study.[12]

The negative value of H_{int} of Ru, which was confirmed by an external-field dependence of the peak positions, is indicative of a dominant contribution from a core polarization. The internal field is given by $H_{int} = A_{hf}\langle S \rangle$, where A_{hf} is a hyperfine coupling constant and $\langle S \rangle$ is a spin of Ru. From a reasonable value of $A_{hf} \sim -300$ kOe/μ_B for the core polarization of $4d$ electrons,[18] the value of $\langle S \rangle$ is estimated to be $1.97\mu_B$, which is larger than the value of $1\mu_B$ expected for the low spin state ($S=1/2$) of the $Ru^{5+}(t_{2g}^3)$, but is smaller than that for the high spin state ($S=3/2$) of Ru^{5+}, and the low spin state ($S=1$) of Ru^{4+}.

In order to identify the valence state of the Ru ions, we observed ZFNMR of Sr_2GdRuO_6 which is considered as a reference compound with Ru^{5+}.[15] In a family of antiferromagnetic insulator M_2RRuO_6 (M=Ca, Ba, Sr, and R=Y, La), ferromagnetic sheets are coupled antiferromagnetically along [100] with the spins lying in the basal planes. The ordered moments are calculated to be $1.9\mu_B$ for Sr_2YRuO_6 per Ru^{5+} ions. (The spin state is $S=3/2$.)[15] Ru-ZFNMR signals in Sr_2GdRuO_6 are observed at 118.7 (132.9) MHz for ^{99}Ru (^{101}Ru), as shown in Fig. 5. The hyperfine field for Ru^{5+} is obtained to be -606 kOe. Therefore, we may conclude the signals around 110–150 MHz for $RuSr_2GdCu_2O_8$ are assigned as the ZFNMR of Ru^{5+} with the high spin state of $S=3/2$. The low spin state of $S=1/2$ for Ru^{5+} is ruled out.

The pulse conditions for the ZFNMR signals for $^{99/101}$Ru are quite different from those for $^{63/65}$Cu-NMR signals under magnetic field. The enhancement factor for the ZFNMR signals is roughly estimated to be 200. This indicates very small magnetic anisotropy for the magnetically ordered Ru moments. We would like to emphasize the fact that no preferred orientation of loose powder particles was achieved, even when high field (9.4 T) was applied. This may be due to the rotation of the Ru moments with the applied field direction because of extremely small magnetic anisotropy energy. This is one of the peculiar aspects of the magnetism of $RuSr_2GdCu_2O_8$. Note that the recent neutron diffraction study[12] supports the present conclusion of an extremely small magnetic anisotropy.

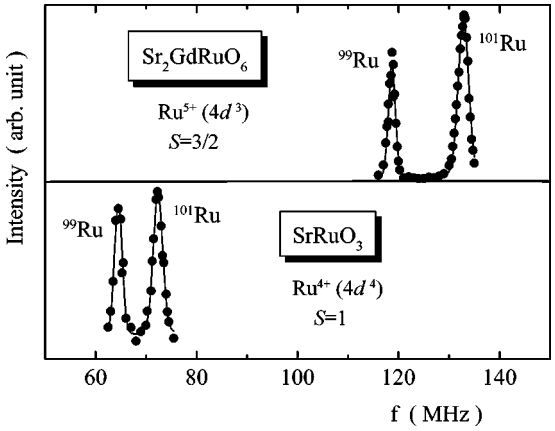

FIG. 5. Ru-ZFNMR spectra of Sr_2GdRuO_6 (insulating antiferromagnet with Ru^{5+}) and $SrRuO_3$ (metallic ferromagnet with Ru^{4+}).

We consider the signals around 40–80 MHz. The spectrum is broad but seems to have two separated peaks. The peak positions correspond to the difference of the gyromagnetic ratio of ^{99}Ru and ^{101}Ru ($^{101}\gamma_N/^{99}\gamma = 1.12$). Considering the relatively large enhancement of NMR signals, we may conclude that the signals around 40–80 MHz are associated with Ru nuclei in the presence of a large internal field. The overall profile is fitted with a large magnetic field perturbed by a small quadrupole interaction, just similar to the case of the signals around 100–150 MHz. We determine the hyperfine field of $H_{hf} \sim -290$ kOe and $\nu_Q \sim 2$ MHz for ^{101}Ru. The hyperfine field is nearly a half of that of the other Ru sites, implying that the spin state of this Ru site is $S=1$, which is expected for the electron configuration of the low spin state of t_{2g}^4 for Ru^{4+}. Because of the largely lifted t_{2g} and e_g levels of Ru ions, the high spin state of $S=2$ for Ru^{4+} is not realized. In fact, this conclusion should be supported firmly, as we observed ZFNMR signals at the same frequency range around 60–70 MHz for the reference compound $SrRuO_3$ (Ref. 18) (metallic ferromagnet $T_N = 165$ K) with low spin state of Ru^{4+}, as shown in Fig. 5.

From the present NMR results, we conclude that there exists two kinds of Ru-ZFNMR signals, namely one is Ru^{5+} with $S=3/2$ ($H_{hf} = -590$ kOe) and the other is Ru^{4+} with $S=1$ ($H_{hf} = -290$ kOe). Thus, the segregation of the charge state of Ru^{5+} and Ru^{4+} is realized in $RuSr_2GdCu_2O_8$. The ratio of signal intensity, thus the num-

ber of nuclei in each state may be comparable, though a quantitative evaluation for the relative intensity between the two Ru sites is rather difficult giving the present experimental uncertainty. Assuming an equal number of Ru^{4+} and Ru^{5+} ions, the mixed valence state of $(Ru^{4+}, Ru^{5+})O_2$ layers gives a formal valence of Cu of 2.25, which is just corresponding to an optimum hole number for most of the high-T_c cuprates. Charge transfer between CuO_2 and RuO_2 layers is highly expected for the superconducting $RuSr_2GdCu_2O_8$.

In the limit of only Ru^{5+}, there are no doped holes in the system, and thus both the CuO_2 and the RuO_2 planes are expected to be insulating and antiferromagnetically ordered, as observed in the Cu^{2+} d_{x2-y2} band and in the t_{2g}^3 configuration of Ru^{5+} as found in Sr_2GdRuO_6.[15] In the other limit of only Ru^{4+}, the valence of Cu is expected to be 2.5, which would be overdoped for superconductivity. According to x-ray and neutron diffraction experiments,[8] the RuO_6 octahedra are confirmed to be tilted around the c axis by 14°. The distortion of the atomic positions would produce a superstructure in the basal planes, and then charge transfer between CuO_2 and RuO_2 planes is expected. Therefore, the segregation of the charge state of Ru^{4+} and Ru^{5+} is highly expected in $RuSr_2GdCu_2O_8$. The ionic configuration of Ru^{4+} and Ru^{5+} is favorable for superconductivity from a point of hole doping into CuO_2 layers.

As described already, the internal field (the transferred hyperfine field from the Ru moments) at the Cu site is very small even in the ordered state. The transferred hyperfine field from the ordered Ru moments is canceled out. This suggests an antiferromagnetic spin-alignment[12] and weak interactions between the RuO_2 and CuO_2 layers. This magnetic situation is favorable for superconductivity, because of the lack of pair breaking effects by strong exchange interactions. One may imagine that the magnetically ordered state with weak ferromagnetism in $RuSr_2GdCu_2O_8$ results from a ferrimagnetic structure of the Ru moments of $S=3/2$ and $S=1$. However, any type of two components for the Ru moments is not reported from neutron scattering experiments.[12,19] The itinerant nature of the Ru site would be expected in a band structure calculation.[13] At present, a firm conclusion on the real magnetic structure in this particular Ru compound is not settled.

Finally, we mention preliminary results of the nuclear spin lattice relaxation time, T_1. We observed characteristic temperature dependences ($1/T_1 \propto T^3$ for Cu-NMR and Ru^{5+}-NMR) below the superconducting transition temperature under external fields where dominant contributions from magnetic Gd moments are strongly suppressed. The results of the dynamical properties indicate that spin fluctuations in both the Cu and weak-ferromagnetic Ru sites are affected by superconductivity in $RuSr_2GdCu_2O_8$. Needless to say, without magnetic rare earth ions ($RuSr_2YCu_2O_8$ is a suitable candidate), we can obtain intrinsic information on magnetic spin fluctuations in the CuO_2 layers and the RuO_2 layers. That is a task to be done in the near future.[20]

In summary, the present NMR results reveal two kinds of Ru moments in $RuSr_2GdCu_2O_8$, suggesting the charge segregation and a possible charge ordering of Ru^{5+} ($S=3/2$) and Ru^{4+} ($S=1$). The transferred hyperfine field at the Cu site is almost completely canceled out in the magnetically ordered state. Thus, the Ru spins in the RuO_2 layers must be antiferromagnetic in nature. However, the NMR (the existence of large enhancements of signals) and the magnetization (small spontaneous Ru moments) results suggest the weak-ferromagnetic nature of the ordered state. These imply that a ferrimagnetic spin structure is plausible in $RuSr_2GdCu_2O_8$. The real magnetic structure should be clarified by further studies such as a neutron scattering experiment. With possible charge segregation to Ru^{4+} and Ru^{5+}, the introduction of carriers into the CuO_2 layers from the $(Ru^{4+}, Ru^{5+})O_2$ layers occurs and is responsible for the high-T_c superconductivity in the magnetically ordered $RuSr_2RCu_2O_8$ family.

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