


torted cubic perovskite structure \[16\]. Ca substitution into

PACS numbers: 75.40.Gb, 75.50.Cc, 76.60.–k

The Ruddlesden-Popper series of layered ruthenium oxides \((\text{Sr}, \text{Ca})_{n+1}\text{Ru}_n\text{O}_{3n+1}\) are so-called bad metals \[1\], whose electrical resistivity exceeds the Ioffe-Regel limit for conventional metals at elevated temperatures. The electronic, magnetic, and superconducting properties of the ruthenates have been attracting strong interest in the past few years \[2–15\] following the discovery of anisotropic superconductivity in the \(n = 1\) end member of the series \(\text{Sr}_2\text{RuO}_4\) \[3\]. A unique feature of the ruthenates is that one can control the electronic properties by substitution of smaller \(\text{Ca}^{2+}\) ions into the \(\text{Sr}^{2+}\) sites. Moreover, one can change the dimension of the electronic states from 2D to 3D by varying \(n\) from 1 to \(\infty\). The \(n = \infty\) end member of the series, \(\text{SrRuO}_3\), is a three dimensional itinerant ferromagnet \((\text{Curie temperature } T_C = 160\ \text{K}) with distorted cubic perovskite structure \[16\]. Ca substitution into \(\text{SrRuO}_3\) does not change significantly the effective magnetic moment \(p_{\text{eff}}\) estimated from the Curie-Weiss fit of uniform susceptibility \(\chi(T)\) between \(\text{SrRuO}_3\) \((p_{\text{eff}} = 2.8\mu_B)\) and \(\text{CaRuO}_3\) \((p_{\text{eff}} = 3.4\mu_B)\) around RT, and approaching \(3.0\mu_B\) at high temperatures. On the other hand, Ca substitution suppresses both \(T_C\) and the zero-temperature saturated moment \(p_s\) of \(\text{Sr}_1-x\text{Ca}_x\text{RuO}_3\) gradually to zero at \(x \sim 0.7\), and changes the sign of the Weiss temperature \(\theta\) from positive to negative (see Fig. 1). During the 1960’s, these observations led to an intuitive viewpoint that there is a localized moment with nearly full spin \(S = 1\) at each Ru site, as implicitly assumed in the Curie-Weiss fit, and that the sign of the exchange integral \(J\) crosses over from negative (ferromagnetic) to positive (antiferromagnetic) because of the buckling of the Ru-O-Ru bond angle caused by Ca substitution \[16,17\].

However, progress in the field of itinerant magnetism in the past three decades has made the validity of such a simple picture increasingly questionable, i.e., the Curie-Weiss behavior of \(\chi(T)\) is not proof of the local moment nature of Ru spins, and the temperature dependence of the amplitude of local spin density in itinerant magnets also results in Curie-Weiss behavior of \(\chi(T)\) with both positive and negative \(\theta\) \[18–20\]. In the past few years, new experimental techniques have been applied to achieve better understanding of the physical properties of \(\text{Sr}_1-x\text{Ca}_x\text{RuO}_3\). For example, measurements of magnetovolume effects have established that the Ru spins indeed maintain a certain level of itineracy \[7\]. Yet there is no consensus on the nature of Ru moments, because \textit{there has been no experimental report on spin dynamics in }\text{Sr}_1-x\text{Ca}_x\text{RuO}_3\text{ despite the long history of its study. On the other hand, attempts to construct a unified theoretical picture for itinerant ferromagnetism have been pushed forward in the past few years in the vicinity of the zero-temperature quantum critical point separating the ordered and paramagnetic ground states \[19–21\]. The presence of a zero-temperature phase transition from ferromagnetic to paramagnetic ground state at \(x \sim 0.7\) makes \(\text{Sr}_1-x\text{Ca}_x\text{RuO}_3\) a potential candidate to test these new theoretical frameworks.

In the field of itinerant magnetism, NMR measurements of nuclear spin-lattice relaxation rate \(1/T_1\) have been playing a pivotal role in probing spin dynamics \[19,22\].

\textbf{FIG. 1.} (a) Temperature dependence of the inverse spin susceptibility \(\chi^{-1}(T)\) for \(x = 0\) (○), \(x = 0.6\) (●), and \(x = 1\) (■). Solid lines represent theoretically calculated \(\chi^{-1}(T)\) based on Moriya’s SCR theory for weakly ferromagnetic metals utilizing experimental spin fluctuation parameters. (b) Phase diagram of \(\text{Sr}_1-x\text{Ca}_x\text{RuO}_3\). Solid and open circles represent the Curie temperature \(T_C\) and the Weiss temperature \(\theta\), respectively.
Furthermore, a recent renormalization group analysis based on the Hertz theory predicts a universal behavior of $1/T_1 \sim T^{-3/4}$ in the vicinity of the zero-temperature quantum critical point of ferromagnetically correlated itinerant systems [21,23], potentially making measurements of $1/T_1$ an ideal tool to investigate $\text{Sr}_{1-x}\text{Ca}_x\text{RuO}_3$. In this Letter, we report successful $^{17}$O NMR measurements of $1/T_1$ in $^{17}$O isotope enriched $\text{Sr}_{1-x}\text{Ca}_x\text{RuO}_3$ and present two surprising findings. First, we show that a ferromagnetic dynamical scaling law holds for all samples including $\text{CaRuO}_3$, even though the Weiss temperature for $\text{CaRuO}_3$ is negative, $\theta = -150$ K. This finding casts serious doubt on the intuitive picture that $\text{CaRuO}_3$ is an antiferromagnetically correlated metal, but is consistent with a viewpoint that $\text{CaRuO}_3$ is an exchange enhanced paramagnet [8,9]. Second, we demonstrate that ferromagnetic spin fluctuations exhibit a universal behavior independent of $T$ and $x$ at elevated temperatures, which points towards the presence of a quantum critical point.

We synthesized polycrystalline samples by standard solid-state chemical reactions at Kyoto. The details of the sample synthesis procedures, the measurements of $\chi(T)$, magnetovolume effects, and specific heat are discussed elsewhere [7,8]. We enriched $\text{SrRuO}_3$ ($T_C = 160$ K), $\text{Sr}_{0.9}\text{Ca}_{0.1}\text{RuO}_3$ ($T_C = 24$ K), and $\text{CaRuO}_3$ ($T_C = 0$ K) with $^{17}$O isotope by annealing in $^{18}$O gas at 900 °C, and conducted $^{17}$O NMR in the external magnetic field of 9 T at MIT. We found typical $^{17}$O NMR powder line shapes with the quadrupole splitting $^{17}I_Q \sim 0.95$ MHz convoluted by anisotropic Knight shifts. The line width $\Delta f$ for the $I_c = 1/2$ to $-1/2$ central transition ($\Delta f \sim 150$ KHz at 500 K in $\text{SrRuO}_3$) is broadened by large spin susceptibility with decreasing temperature [$\Delta f \sim \chi(T)$]. This effect gradually obscures the distinct edges of powder line shapes approaching $T_C$. We measured the powder averaged $^{17}$O NMR Knight shift $^{17}K$ and $^{17}$O nuclear spin-lattice relaxation rate $1/T_1$ at the maximum of the central peak. The fit of nuclear spin recovery for $1/T_1$ measurements was good enough, and the variation of $1/T_1$ across the central peak is small (less than 5%), making quantitative interpretation of $1/T_1$ possible. Even though we cannot rule out up to $\sim 30\%$ of systematic errors in the overall magnitude of $1/T_1$, the qualitative aspect of $T$ and $x$ dependences of $1/T_1$ should not be affected by the powder average.

In Fig. 2, we show the temperature dependence of the $^{17}$O NMR Knight shift $^{17}K$. The entire NMR line shape shows large, temperature dependent NMR frequency shifts with positive sign. Since the powder average of the dipole hyperfine fields from the O 2$p$ orbitals is zero, we attribute the large isotropic shifts to the Fermi’s contact interaction caused by admixture of O 2$s$ electrons at the Fermi level. We note that a sizable 2$s$ contribution was previously observed also in $\text{Sr}_2\text{RuO}_4$ [15], suggesting strong hybridization between Ru 4$d$ and O 2$s$ orbitals in ruthenates. On general ground, one can write $^{17}K$ as [24]

$$^{17}K = \frac{A_{\text{HF}}}{N_A \mu_B} \chi(T),$$

where $A_{\text{HF}}$ is the powder average of the hyperfine coupling constant. We ignored the orbital contribution in Eq. (1), because it is orders of magnitude smaller than observed results of $^{17}K$. In the inset of Fig. 2, we plot $^{17}K$ vs $\chi(T)$ with temperature $T$ as the implicit parameter. From the observed linear relation, we find that $A_{\text{HF}} = +16 \pm 1$ kOe/$\mu_B$ is independent of the Ca concentration $x$.

In Fig. 3(a), we present the main result of the present work, temperature dependence of the $^{17}$O nuclear spin-lattice relaxation rate $1/T_1$ [25],

$$\frac{1}{T_1} = \frac{(^{17}I_n)^2}{\mu_B^2} \frac{k_B T}{h} \sum_q |A_{\text{HF}}(q)|^2 \frac{\chi''(q, \omega_n)}{\omega_n},$$

where $\chi''(q, \omega_n)$ is dynamical electron spin susceptibility, $|A_{\text{HF}}(q)|^2 \sim 2A_{\text{HF}}^2 \cos^2(q_0/2)$ is the hyperfine form factor (we take the Ru-O-Ru bond direction as the $x$ axis), $^{17}I_n$ is the $^{17}$O nuclear gyromagnetic ratio (5.772 MHz/T), $q$ is the wave vector, $\omega_n$ is the NMR frequency ($\sim 52$ MHz), and the summation is taken over the first Brillouin zone. The hyperfine form factor $|A_{\text{HF}}(q)|^2$ arises from geometrical effects [25]. If polarization of the spin density at two neighboring Ru sites points to the same direction (i.e., ferromagnetic spin correlations), covalency effects polarize electron spins to the same direction at the O site located between the two Ru sites. This situation is reflected in the finite value of $|A_{\text{HF}}(q)|^2$ at the ferromagnetic wave vector $q = 0$, therefore $1/T_1$ is sensitive to ferromagnetic spin fluctuations. On the other hand, when Ru spin density has commensurate antiferromagnetic configuration, the net spin polarization is canceled at the O sites in the middle of the two Ru sites.

![Figure 2](image_url)

**FIG. 2.** Temperature dependence of $^{17}$O NMR Knight shift $^{17}K$ in $\text{Sr}_{1-x}\text{Ca}_x\text{RuO}_3$ with $x = 0$ (●), 0.6 (○), and 1 (■). Inset: $^{17}K$ vs $\chi(T)$ with temperature $T$ as the implicit parameter. Solid line is the best fit to Eq. (1) with $A_{\text{HF}} = +16$ kOe/$\mu_B$. 

![Figure 3(a)](image_url)

In Fig. 3(a), we present the main result of the present work, temperature dependence of the $^{17}$O nuclear spin-lattice relaxation rate $1/T_1$ [25],

$$\frac{1}{T_1} = \frac{(^{17}I_n)^2}{\mu_B^2} \frac{k_B T}{h} \sum_q |A_{\text{HF}}(q)|^2 \frac{\chi''(q, \omega_n)}{\omega_n},$$

where $\chi''(q, \omega_n)$ is dynamical electron spin susceptibility, $|A_{\text{HF}}(q)|^2 \sim 2A_{\text{HF}}^2 \cos^2(q_0/2)$ is the hyperfine form factor (we take the Ru-O-Ru bond direction as the $x$ axis), $^{17}I_n$ is the $^{17}$O nuclear gyromagnetic ratio (5.772 MHz/T), $q$ is the wave vector, $\omega_n$ is the NMR frequency ($\sim 52$ MHz), and the summation is taken over the first Brillouin zone. The hyperfine form factor $|A_{\text{HF}}(q)|^2$ arises from geometrical effects [25]. If polarization of the spin density at two neighboring Ru sites points to the same direction (i.e., ferromagnetic spin correlations), covalency effects polarize electron spins to the same direction at the O site located between the two Ru sites. This situation is reflected in the finite value of $|A_{\text{HF}}(q)|^2$ at the ferromagnetic wave vector $q = 0$, therefore $1/T_1$ is sensitive to ferromagnetic spin fluctuations. On the other hand, when Ru spin density has commensurate antiferromagnetic configuration, the net spin polarization is canceled at the O sites in the middle of the two Ru sites. This
implies that spin intensity has made measurements of fields impractical. Surprisingly, we found that CaRuO$_3$ also exhibits semiquantitatively the same behavior as SrRuO$_3$, increases monotonically with temperature and saturates to the same value as SrRuO$_3$. We attribute suppression of antiferromagnetic spin fluctuations does not allow us to rule out the possibility of their coexistence with ferromagnetic modes of spin fluctuations in CaRuO$_3$. However, very strong enhancement of antiferromagnetic spin fluctuations seems unlikely, because the total moment sum rule [25] must hold at elevated temperatures where the ferromagnetic contribution to $1/T_1$ is very similar for all three compositions.

In order to gain insight into the quantitative aspect of the ferromagnetic component of spin fluctuations, we need to analyze the data assuming certain wave vector and energy dependences of dynamical spin susceptibility. In what follows, we take a standard form derived by Moriya for overdamped magnons in ferromagnetically correlated 3D electron gas based on his SCR (self-consistent renormalization) theory for itinerant ferromagnets [19],

$$\chi(q, \omega) = \frac{\chi(0)}{1 - i \omega/\Gamma(q)},$$  
(3a)

$$\chi(q) = \frac{\chi(0)}{1 + q^2/\kappa^2},$$  
(3b)

$$\Gamma(q) \sim \Gamma q(q^2 + \kappa^2),$$  
(3c)

where $\kappa$ is the inverse correlation length and $\Gamma(q)$ is magnon damping. We emphasize that these SCR expressions have been verified experimentally based on inelastic neutron scattering in MnSi [27], and are known to fit many itinerant magnets beautifully [22,28]. In addition, recent renormalization group analysis byMillis supports the validity of the SCR approach [20]. Equation (3) leads to ferromagnetic dynamical scaling $1/T_1 T \sim \chi(T)/\Gamma$ [19,23] as required for the present case, and we deduced the spin fluctuation energy scale as $\Gamma \approx 1.2 \times 10^3$ K, $0.98 \times 10^3$ K, and $0.73 \times 10^3$ K for $x = 0$, 0.6, and 1, respectively. Using $\Gamma$ and other thermodynamic parameters such as $T_C$, one can calculate the inverse spin susceptibility $\chi(T)^{-1}$ for $x = 0$ and 0.6 as shown by solid lines in Fig. 1(a) within the same SCR framework (for details of the calculation method, see [19,22]). The agreement with the SCR fit is reasonable for the case of $x = 0.6$, suggesting that $Sr_{1-x}Ca_{x}RuO_3$ belongs to the category of weak ferromagnets. Lack of ferromagnetic transition ($T_C$) in $x = 1$ does not allow us to have enough thermodynamic constraints to calculate $\chi(T)^{-1}$ for CaRuO$_3$. However, earlier analysis of the specific heat data indicates that one can understand the thermodynamic properties of CaRuO$_3$ quite well as an exchange enhanced paramagnet [8,9], i.e., both spin dynamics probed by $1/T_1$ and thermodynamic properties of CaRuO$_3$ can be accounted for as a nearly ferromagnetic metal. On the other hand,
agreement is very poor for SrRuO$_3$ between the calculated and measured results of $\chi(T)^{-1}$, suggesting the breakdown of the itinerant limit dealt by the SCR theory. Given the fact that $p_{\text{eff}} \sim 2\sqrt{2}\mu_B(S = 1)$, and that the ratio $p_{\text{eff}}/\sqrt{p_{\text{eff}}(p_{\text{eff}} + 2)}$ approaches unity with $x \to 0$, the spin degree of freedom in SrRuO$_3$ seems to have more localized character than heavily Ca doped Sr$_{1-x}$Ca$_x$RuO$_3$. To summarize the quantitative SCR analysis, we can infer that Sr$_{1-x}$Ca$_x$RuO$_3$ shows a crossover from the robust local moment regime for SrRuO$_3$ to the weakly itinerant ferromagnetic regime for Sr$_{0.4}$Ca$_{0.6}$RuO$_3$, then finally to the nearly ferromagnetic metallic regime for CaRuO$_3$.

To conclude, we successfully probed ferromagnetic components of spin dynamics in Sr$_{1-x}$Ca$_x$RuO$_3$ for the first time in a broad temperature range and across the zero-temperature phase boundary at $x \sim 0.7$ between ferromagnetic SrRuO$_3$ and paramagnetic CaRuO$_3$. Utilizing the wave-vector dependence of the hyperfine form factor $A_{\text{hf}}(q)$, we showed the presence of strong ferromagnetic spin fluctuations in all compositions including CaRuO$_3$. Even though we cannot rule out the coexistence of the modest enhancement of antiferromagnetic spin fluctuations in CaRuO$_3$, to which our method is insensitive, our observation overturns the frequently quoted viewpoint that electronic correlations in CaRuO$_3$ are entirely antiferromagnetic because of the negative value of $\theta$. Our observation of ferromagnetic dynamic scaling and a universal relaxation rate at elevated temperatures for all Ca concentration $x$ indicates that a universal description of spin fluctuation properties ought to be possible for Sr$_{1-x}$Ca$_x$RuO$_3$ based on one form of dynamical spin susceptibility. Recalling that quantum criticality in correlated metals is known to result in a universal behavior of $1/T_1$ both in 3D ferromagnetic metals [21,23] and 2D antiferromagnetic metals [29], it is natural to speculate that our observation of a universal behavior in Sr$_{1-x}$Ca$_x$RuO$_3$ indicates the presence of a quantum critical point at $x \sim 0.7$. On the other hand, the discrepancy from the predicted form of the universal temperature dependence for 3D itinerant ferromagnetic systems ($1/T_1 \sim T^{-3/4}$), together with the difficulty reproducing $\chi(T)$ quantitatively for SrRuO$_3$ within the itinerant limit, suggests that the regime near $x = 0$ is certainly beyond the reach of existing theoretical models.

We are grateful for useful discussions with T. Moriya, Y. Takahashi, M. Kato, Y. Itoh, M. Beaseley, T. Geballe, Z. Schlesinger, Z.X. Shen, G. Cao, A.P. Mackenzie, A. Chubukov, S. Sachdev, A.J. Millis, and S. Kivelson. The work at MIT was supported by the NSF DMR 96-23858 and the A.P. Sloan Foundation. The extended visit by K.Y. to MIT was made possible by the financial support provided to MIT by the Mitsui Foundation. The work at Kyoto was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan (09440241).

*Permanent address: Kyoto University, Kyoto, Japan.