^{17}O NMR Observation of Universal Behavior of Ferromagnetic Spin Fluctuations in the Itinerant Magnetic System $Sr_{1-x}Ca_xRuO_3$

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We report the first ^{17}O NMR study of spin dynamics in itinerant ferromagnet $SrRuO_3$ ($T_C = 160$ K) and Ca-doped variant $Sr_{1-x}Ca_xRuO_3$ for $x = 0.6$ ($T_C = 24$ K) and $x = 1$ (exchange enhanced paramagnet). We observed robust ferromagnetic spin fluctuations for all concentrations including $CaRuO_3$, even though the sign of Weiss temperature crosses over from positive to negative above $x \sim 0.7$. At elevated temperatures, ferromagnetic spin fluctuations exhibit a universal behavior.

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The Ruddlesden-Popper series of layered ruthenium oxides $(Sr, Ca)_{n+1}Ru_nO_{3n+1}$ are so-called *bad metals* [1], whose electrical resisitivity 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 Sr_2RuO_4 [3]. A unique feature of the ruthenates is that one can control the electronic properties by substitution of smaller Ca^{2+} ions into the Sr^{2+} sites. Moreover, one can change the dimension of the electronic states from 2D to 3D by varying n from 1 to ∞. The $n = \infty$ end member of the series, $SrRuO_3$, is a three dimensional itinerant ferromagnet (Curie temperature $T_C = 160$ K) with distorted cubic perovskite structure [16]. Ca substitution into $SrRuO_3$ does not change significantly the effective moment p_{eff} estimated from the Curie-Weiss fit of uniform susceptibility $\chi(T)$ between $SrRuO_3$ ($p_{\text{eff}} = 2.8\mu_B$) and $CaRuO_3$ ($p_{\text{eff}} = 3.4\mu_B$ 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 $Sr_{1-x}Ca_xRuO_3$ gradually to zero at $x \sim 0.7$, and changes the sign of the Weiss temperature θ 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 θ [18–20]. In the past few years, new experimental techniques have been applied to achieve better understanding of the physical properties of $Sr_{1-x}Ca_xRuO_3$. 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 *there has been no experimental report on spin dynamics* in $Sr_{1-x}Ca_xRuO_3$ 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 $Sr_{1-x}Ca_xRuO_3$ 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].

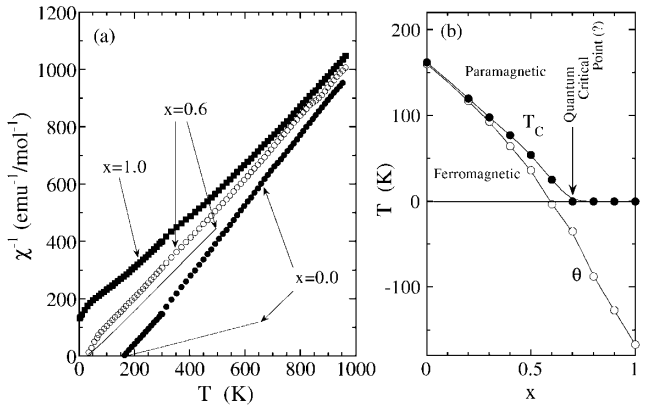

FIG. 1. (a) Temperature dependence of the inverse spin susceptibility $\chi(T)^{-1}$ for $x = 0$ (●), $x = 0.6$ (○), and $x = 1$ (■). Solid lines represent theoretically calculated $\chi(T)^{-1}$ based on Moriya's SCR theory for weakly ferromagnetic metals utilizing experimental spin fluctuation parameters. (b) Phase diagram of $Sr_{1-x}Ca_xRuO_3$. Solid and open circles represent the Curie temperature T_C and the Weiss temperature θ, respectively.

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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 $Sr_{1-x}Ca_xRuO_3$. In this Letter, we report successful ^{17}O NMR measurements of $1/T_1$ in ^{17}O isotope enriched $Sr_{1-x}Ca_xRuO_3$ and present two surprising findings. First, we show that a *ferromagnetic* dynamical scaling law holds for all samples including $CaRuO_3$, even though the Weiss temperature for $CaRuO_3$ is negative, $\theta = -150$ K. This finding casts serious doubt on the intuitive picture that $CaRuO_3$ is an antiferromagnetically correlated metal, but is consistent with a viewpoint that $CaRuO_3$ 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 $SrRuO_3$ ($T_C = 160$ K), $Sr_{0.4}Ca_{0.6}RuO_3$ ($T_C = 24$ K), and $CaRuO_3$ ($T_C = 0$ K) with ^{17}O isotope by annealing in $^{17}O_2$ 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 $^{17}\nu_Q \sim 0.95$ MHz convoluted by anisotropic Knight shifts. The line width Δf for the $I_z = 1/2$ to $-1/2$ central transition ($\Delta f \sim$ 150 KHz at 500 K in $SrRuO_3$) 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 ~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 $2p$ orbitals is zero, we attribute the large isotropic shifts to the Fermi's contact interaction caused by admixture of O $2s$ electrons at the Fermi level. We note that a sizable $2s$ contribution was previously observed also in Sr_2RuO_4 [15], suggesting strong hybridization between Ru $4d$ and O $2s$ orbitals in ruthenates. On general ground, one can

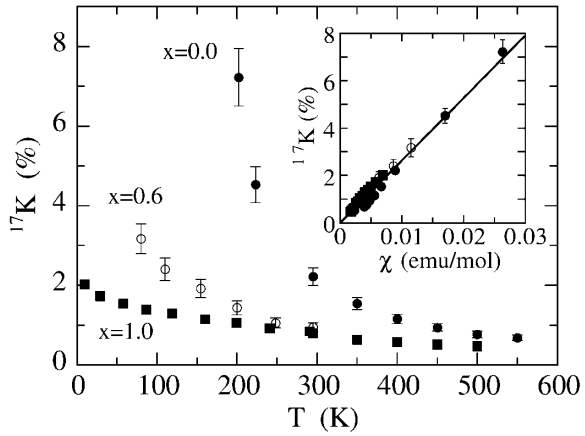

FIG. 2. Temperature dependence of ^{17}O NMR Knight shift ^{17}K in $Sr_{1-x}Ca_xRuO_3$ with $x = 0$ (●), 0.6 (○), and 1 (■). Inset: ^{17}K vs $\chi(T)$ with temperature T as the implicit parameter. Solid line is the best fit to Eq. (1) with $A_{HF} = +16$ kOe/μ_B.

write ^{17}K as [24]

$$^{17}K = \frac{A_{HF}}{N_A \mu_B}\chi(T), \qquad (1)$$

where A_{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 $A_{HF} = +16 \pm 1$ kOe/μ_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],

$$\frac{1}{T_1} = \frac{(^{17}\gamma_n)^2}{\mu_B^2 \hbar} k_B T \sum_{\mathbf{q}} |A_{HF}(\mathbf{q})|^2 \frac{\chi''(\mathbf{q}, \omega_n)}{\omega_n}, \qquad (2)$$

where $\chi''(\mathbf{q}, \omega_n)$ is dynamical electron spin susceptibility, $|A_{HF}(\mathbf{q})|^2 \sim 2A_{HF}^2 \cos^2(q_x/2)$ is the hyperfine form factor (we take the Ru-O-Ru bond direction as the x axis), $^{17}\gamma_n$ is the ^{17}O nuclear gyromagnetic ratio (5.772 MHz/T), $\mathbf{q}$ is the wave vector, ω_n is the NMR frequency (~52 MHz), and the summation is taken over the first Brillouin zone. The hyperfine form factor $|A_{HF}(\mathbf{q})|^2$ 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 $|A_{HF}(\mathbf{q})|^2$ at the ferromagnetic wave vector $\mathbf{q} = \mathbf{0}$, 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

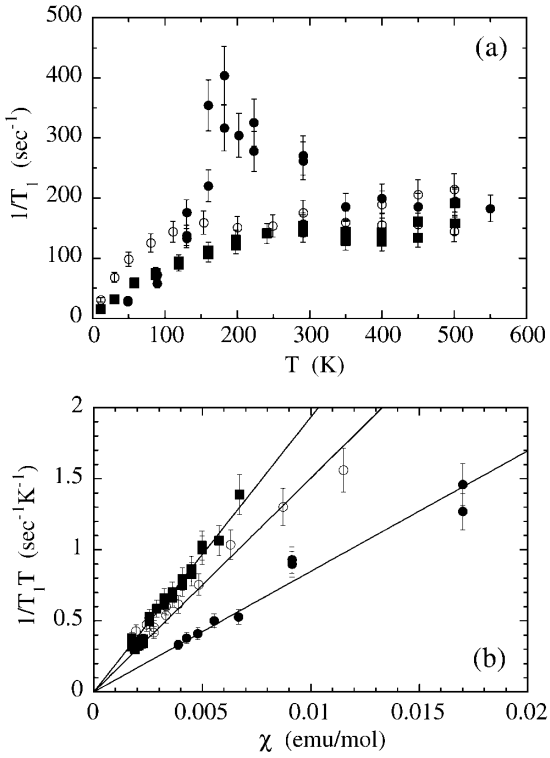

FIG. 3. (a) Temperature dependence of ^{17}O nuclear spin-lattice relaxation rate $1/T_1$ in $Sr_{1-x}Ca_xRuO_3$ with $x = 0$ (●), 0.6 (○), and 1 (■). (b) Plots of $1/T_1T$ vs $\chi(T)$. Solid linear lines show the linear relation between $1/T_1T$ and $\chi(T)$.

results in $|A_{\mathrm{HF}}(q_x \sim \pi)|^2 = 0$, hence $1/T_1$ is insensitive to commensurate antiferromagnetic spin fluctuations.

For $SrRuO_3$, $1/T_1$ shows divergent behavior near $T_C = 160$ K due to critical slowing down of ferromagnetic spin fluctuations. At higher temperatures, $1/T_1$ levels off at ~ 160 sec^{-1}. On the other hand, $1/T_1$ for $Sr_{0.4}Ca_{0.6}RuO_3$ increases monotonically with temperature and saturates to the same value as $SrRuO_3$. We attribute suppression of critical divergence of $1/T_1$ at $T_C = 24$ K to the application of 9 T of magnetic field [23]. Weak signal intensity has made measurements of $1/T_1$ at low magnetic fields impractical. Surprisingly, we found that $CaRuO_3$ also exhibits semiquantitatively the same behavior as $Sr_{0.4}Ca_{0.6}RuO_3$, and $1/T_1$ saturates at the same value. Moreover, $1/T_1T$ is proportional to uniform spin susceptibility $\chi(T)$ for all the samples as shown in Fig. 3(b). Recalling that $\chi(T) = \chi'(\mathbf{q} = \mathbf{0}, \omega = 0)$ measures the ferromagnetic $\mathbf{q} = \mathbf{0}$ component of static spin susceptibility, and that $1/T_1T$ probes primarily the ferromagnetic components of spin fluctuations, the linearity in Fig. 3(b) indicates that ferromagnetic *dynamical scaling* [26], $\chi''(\mathbf{q}, \omega_n)/\omega_n \propto \chi(T)/\Gamma$, holds for all concentrations of $Sr_{1-x}Ca_xRuO_3$ near $\mathbf{q} = \mathbf{0}$, where Γ is an energy scale of ferromagnetic spin fluctuations. The larger slope of the plot of $1/T_1T$ vs $\chi(T)$ for larger x in Fig. 3(b) implies that spin fluctuation energy scale Γ is smaller in $CaRuO_3$ than in $SrRuO_3$. The smaller energy scale of spin fluctuations in $CaRuO_3$ is consistent with the fact that Ca substitution enhances the buckling of the Ru-O-Ru bond angle, hence narrowing the electronic bandwidth as observed by angle-resolved photoemission spectroscopy measurements [10]. We note that insensitivity of $1/T_1T$ to antiferromagnetic modes of 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],

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

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

$$\Gamma(\mathbf{q}) \sim \Gamma q(q^2 + \kappa^2), \tag{3c}$$

where κ is the inverse correlation length and $\Gamma(\mathbf{q})$ 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 by Millis supports the validity of the SCR approach [20]. Equation (3) leads to ferromagnetic dynamical scaling $1/T_1T \sim \chi(T)/\Gamma$ [19,23] as required for the present case, and we deduced the spin fluctuation energy scale as $\Gamma \cong 1.2 \times 10^3$ K, 0.98×10^3 K, and 0.73×10^3 K for $x = 0$, 0.6, and 1, respectively. Using Γ 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 $Sr_{0.4}Ca_{0.6}RuO_3$ 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 $p_{\rm eff} \sim 2\sqrt{2}\,\mu_B(S = 1)$, and that the ratio $p_{\rm eff}/\sqrt{p_s(p_s + 2)}$ approaches unity with $x \to 0$, the spin degree of freedom in $SrRuO_3$ seems to have more localized character than heavily Ca doped $Sr_{1-x}Ca_xRuO_3$. To summarize the quantitative SCR analysis, we can infer that $Sr_{1-x}Ca_xRuO_3$ 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 $Sr_{1-x}Ca_xRuO_3$ 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 $A_{\rm HF}(\mathbf{q})$, 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 θ. 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 $Sr_{1-x}Ca_xRuO_3$ 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 $Sr_{1-x}Ca_xRuO_3$ 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.

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[1] V. J. Emery and S. A. Kivelson, Phys. Rev. Lett. **74**, 3253 (1995).
[2] R. J. Cava *et al.*, Phys. Rev. B **49**, 11 890 (1994).
[3] Y. Maeno *et al.*, Nature (London) **372**, 532 (1994).
[4] L. Klein *et al.*, Phys. Rev. Lett. **77**, 2774 (1996).
[5] P. B. Allen *et al.*, Phys. Rev. B **53**, 4393 (1996).
[6] K. Fujioka *et al.*, Phys. Rev. B **56**, 6380 (1997).
[7] T. Kiyama *et al.*, Phys. Rev. B **54**, R756 (1996).
[8] T. Kiyama *et al.*, J. Phys. Soc. Jpn. **67**, 307 (1998).
[9] G. Cao *et al.*, Phys. Rev. B **56**, 321 (1997).
[10] A. V. Puchkov *et al.*, Phys. Rev. Lett. **81**, 2747 (1998).
[11] P. Kostic *et al.*, Phys. Rev. Lett. **81**, 2498 (1998).
[12] D. J. Singh, Appl. Phys. Lett. **79**, 4818 (1996).
[13] S. Ikeda *et al.*, Phys. Rev. B **57**, 978 (1998).
[14] G. Cao *et al.*, Phys. Rev. Lett. **78**, 1751 (1997).
[15] T. Imai *et al.*, Phys. Rev. Lett. **81**, 3006 (1998).
[16] J. M. Longo *et al.*, J. Appl. Phys. **39**, 1327 (1968).
[17] A. Kanbayashi, J. Phys. Soc. Jpn. **44**, 108 (1978).
[18] K. K. Murata and S. Doniach, Phys. Rev. Lett. **29**, 285 (1972).
[19] T. Moriya, *Spin Fluctuations in Itinerant Electron Magnetism* (Springer-Verlag, New York, 1985).
[20] A. J. Millis, Phys. Rev. B **48**, 7183 (1993).
[21] S. Sachdev (unpublished).
[22] K. Yoshimura *et al.*, Phys. Rev. B **37**, 3593 (1988).
[23] A. Ishigaki and T. Moriya, J. Phys. Soc. Jpn. **65**, 3402 (1996).
[24] V. Jaccarino, in *Theory of Magnetism in Transition Metals*, Proceedings of the International School of Physics "Enrico Fermi," Course XXXVII (Academic Press, New York, 1967).
[25] T. Moriya, J. Phys. Soc. Jpn. **18**, 516 (1963).
[26] B. I. Halperin and P. C. Hohenberg, Phys. Rev. **177**, 952 (1969).
[27] Y. Ishikawa *et al.*, Phys. Rev. B **31**, 5884 (1985).
[28] G. G. Lonzarch and L. Taillefer, J. Phys. C **18**, 4339 (1985); Y. Takahashi and T. Moriya, J. Phys. Soc. Jpn. **54**, 1592 (1985).
[29] A. V. Chubukov and S. Sachdev, Phys. Rev. Lett. **71**, 169 (1993). Also see T. Imai *et al.*, Phys. Rev. Lett. **70**, 1002 (1993); S. Chakravarty and R. Orbach, Phys. Rev. Lett. **64**, 224 (1999).