PHYSICAL REVIEW B, VOLUME 63, 180504(R)

Magnetic ordering in Sr_2RuO_4 induced by nonmagnetic impurities

M. Minakata
Department of Physics, Kyoto University, Kyoto 606-8502, Japan

Y. Maeno
Department of Physics, Kyoto University, Kyoto 606-8502, Japan
and CREST, Japan Science and Technology Corporation, Japan

(Received 18 October 2000; revised manuscript received 5 January 2001; published 4 April 2001)

We report unusual effects of nonmagnetic impurities on the spin-triplet superconductor Sr_2RuO_4. The substitution of nonmagnetic Ti^{4+} for Ru^{4+} induces localized-moment magnetism characterized by unexpected Ising anisotropy with the easy axis along the interlayer c direction. Furthermore, for $x(\mathrm{Ti}) \geqslant 0.03$ magnetic ordering occurs in the metallic state with the remnant magnetization along the c axis. We argue that the localized moments are induced in the Ru^{4+} and/or oxygen ions surrounding Ti^{4+} and that the ordering is due to their interaction mediated by itinerant Ru-4d electrons with strong spin fluctuations.

DOI: 10.1103/PhysRevB.63.180504 PACS number(s): 74.70.−b, 74.62.Dh

The symmetry of unconventional superconductivity in Sr_2RuO_4 with $T_c = 1.5$ K has recently been identified as spin triplet.[1–3] The initial theoretical insight into the pairing symmetry in Sr_2RuO_4 was based on the similarity of its Fermi-liquid properties to those of liquid ^{3}He and of the ferromagnetic relative compound $SrRuO_3$.[4] Accordingly, it may seem that ferromagnetic spin fluctuation is the main origin of spin-triplet pairing. The investigation of the magnetic fluctuation spectrum by inelastic neutron scattering,[5] however, revealed a strong susceptibility peak at incommensurate wave number $q = Q_{\mathrm{ic}} \cong (2\pi/3a, 2\pi/3a, 0)$, which is attributable to nesting between two of the three Fermi-surface sheets.[6] Nevertheless, there is an important second component in the spin fluctuation spectrum: strongly enhanced paramagnetism extending in a wide q range, which is attributable to the correlation in the other Fermi-surface sheet.[7] Thus the roles of these band-specific spin fluctuations in the superconducting symmetry and mechanism are a subject of active theoretical investigations.[8,9]

In addition to metallic $SrRuO_3$ with ferromagnetic ordering below $T_c = 160$ K,[10] another relative compound $Sr_3Ru_2O_7$ has recently been shown to order ferromagnetically below $T_c = 100$ K under pressure.[11] Therefore, it may be possible to induce magnetic ordering also in Sr_2RuO_4 by appropriate modification of the compound. In fact, low-temperature transport properties of Sr_2RuO_4 under pressure suggest an important change in the electronic state above 1.5 GPa , although its details have not been clarified at present.[12] The characterization of the magnetic ordering, if induced, will add important information on the spin fluctuation.

Impurity ions substituting Cu have extensively been used as powerful probes to reveal the unconventional properties of high-T_c cuprates.[13] In particular, nonmagnetic Zn^{2+} is found to induce local moments and suppress T_c severely.[14–16] Here we report a corresponding remarkable effect of nonmagnetic impurities for Ru in Sr_2RuO_4. We select Ti^{4+} ($3d^0$), a closed-shell ion without d electrons, as a nonmagnetic impurity because it has the same oxidation number and coordination number as Ru^{4+} ($4d^4$), as well as a very similar ionic radius. In fact, the compound Sr_2TiO_4 is isostructural to Sr_2RuO_4 with very similar lattice parameters: the basal parameter a is longer by merely 0.4% and the interlayer parameter c is shorter by 1.0% than those of Sr_2RuO_4. We found that the nonmagnetic impurity induces a localized moment characterized by strong Ising anisotropy with the easy axis parallel to the interlayer c axis. Furthermore, we found that the magnetic ordering is induced while retaining the metallic state.

We used single crystals of $Sr_2Ru_{1-x}Ti_xO_4$ ($0 < x < 0.25$) grown by a floating zone method with an infrared image furnace (NEC Machinery, model SC-E15HD). To prepare a feed rod to be melted for the crystal growth, a mixture of $SrCO_3$, RuO_2, and TiO_2 powders with the molar ratio of $2:(1.15-x):x$ were reacted at 1250 °C for 24–48 h. For higher x, Sr_2TiO_4 was first synthesized and mixed with $SrCO_3$ and RuO_2. The excess Ru is to compensate for the active sublimation of RuO_2 during the crystal growth. The single phase of the K_2NiF_4-type tetragonal cell was confirmed by x-ray diffraction measurements on powdered crystals. The lattice parameter a increases and c decreases systematically with x at the rate of $da/dx = 0.15\%$ and $dc/dx = -1.9\%$ for $0 \leqslant x \leqslant 0.09$, consistent with the expected tendency for the Ru-Ti substitution. The high-resolution electron probe microanalysis (EPMA) revealed that the analyzed concentration x_a is related with the nominal x by $x_a = 0.95x$ for x up to 0.09.[17] All these clearly indicate that Ti is well substituted for Ru in the structure of Sr_2RuO_4. This is in sharp contrast with the Al doping case, in which the analyzed concentration is always much lower than the nominal one. We deduce that the trivalent Al ions are mainly introduced as lattice defects or interstitials, rather than directly replacing Ru, and their magnetic properties are quite different from those of Ti ions.[18] Nevertheless both kinds of impurities cause extremely strong depairing: with $x(\mathrm{Ti}) = 0.001$, the lowest x investigated in the present study, the superconductivity is already suppressed below 0.3 K, consistent with extreme sensitivity of T_c to impurities and defects.[18,19]

The dc magnetization and ac magnetic susceptibility were measured using a superconducting quantum interference de-

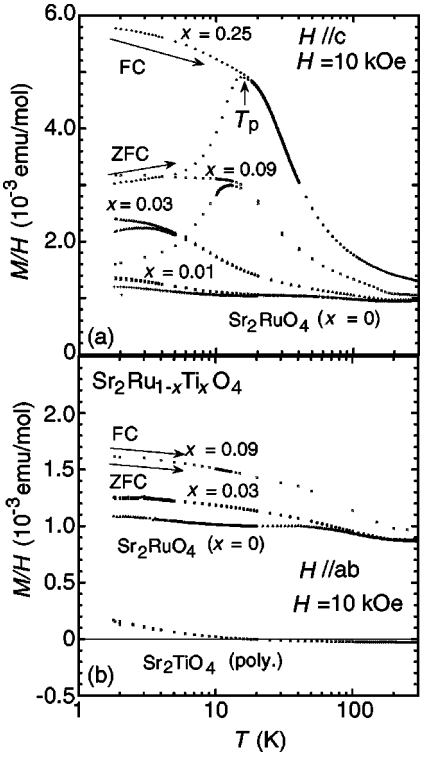

FIG. 1. Temperature dependence of the magnetization of $Sr_2Ru_{1-x}Ti_xO_4$ with the applied field (a) parallel to the c axis and (b) parallel to the ab plane. ZFC and FC denote zero-field-cooled and field-cooled data. Note that the scales of the figures differ by a factor of 2.

vice magnetometer (Quantum Design, model MPMS). Figure 1 shows dc magnetization M/H at $H=10$ kOe. The normal state of pure Sr_2RuO_4 shows almost isotropic magnetization with weak temperature dependence, characterized by enhanced Pauli paramagnetism due to hybridized Ru^{4+} and O^{2-} electrons.[20] In contrast, insulating Sr_2TiO_4 shows a negative value at high temperatures representing the diamagnetism of the ion cores. At low temperatures, a weak Curie term attributable to impurity ions is visible. When Ti^{4+} is introduced in Sr_2RuO_4, however, the magnetization becomes greater than those of both end members. It shows a growing Curie-Weiss-like term with increasing x, indicating that the localized moments are induced by the substitution of nonmagnetic Ti^{4+} for Ru^{4+}. The effective magnetic moment $p_{\rm eff}$ estimated from the Curie-Weiss fitting between 150 and 300 K is somewhat smaller than $0.5\mu_B$/Ti for $0<x<0.25$. As shown in Fig. 1, the induced moment exhibits strong Ising anisotropy with the easy axis along the c axis. This anisotropy was quite unexpected considering that the magnetization of Sr_2RuO_4 and $Ca_{2-x}Sr_xRuO_4$ with x close to 2 is nearly isotropic[21] and that the moments in the antiferromagnetic ground state of the relative Mott insulator Ca_2RuO_4 are lying in the ab plane.[22]

As the main feature in Fig. 1(a), magnetic ordering is induced for $x\geqslant 0.03$. With H parallel to the c axis hysteresis occurs between zero-field-cooled (ZFC) and field-cooled (FC) magnetization for $x\geqslant 0.03$, and a peak appears in the ZFC magnetization at T_p. To confirm the onset of magnetic

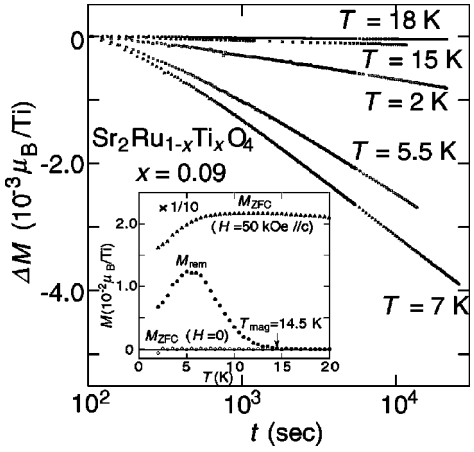

FIG. 2. Inset: Temperature dependence of the remnant magnetization $M_{\rm rem}$ of $Sr_2Ru_{1-x}Ti_xO_4$ ($x=0.09$) with the applied field parallel to the c axis. After zero field cooling at each temperature (bottom), the field was increased to 50 kOe (top). The remnant magnetization was measured 2 min after the field was decreased to zero (middle). A small, temperature-independent contribution of ca. $0.032\mu_B$/Ti, identified as the contribution from the $SrRuO_3$ impurity, has been subtracted. Main frame: Relaxation of the remnant magnetization, $\Delta M=M_{\rm rem}(t)-M_{\rm rem}(t_0)$, for which $M_{\rm rem}(t_0)$ is shown in the inset as $M_{\rm rem}$.

order, we performed M-H sequences with the results shown in the inset of Fig. 2. At each temperature, the crystal ($x=0.09$) was first cooled from 20 K in zero field (bottom). The field was then increased to 50 kOe (top) to allow the magnetization to develop, and subsequently decreased to zero again (middle). The remnant magnetization obtained in this sequence clearly disappears above $T_{\rm mag}=14.5$ K, indicating the magnetic ordering below this temperature. Thus, although $T_p=12.5$ K somewhat underestimates the ordering temperature, it serves as a good measure of it. As shown in Fig. 3, T_p increases linearly with x for $0.03\leqslant x\leqslant 0.09$ and tends to saturate beyond $x\simeq 0.1$.

With H parallel to the ab plane, there is no corresponding reduction or hysteresis in the M/H-vs-T curves. Further-

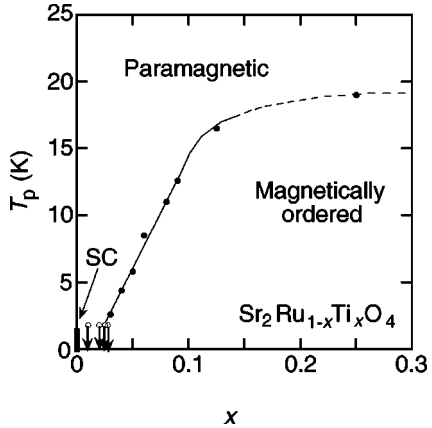

FIG. 3. Phase diagram of $Sr_2Ru_{1-x}Ti_xO_4$ with the applied field of $\mu_0H=10$ kOe. The open circles indicate that no peak of ZFC magnetization is seen at $T>1.8$ K. The dotted line is a guide to the eye.

more, magnetization with $H\|ab$ exhibits no in-plane anisotropy at 1.8−300 K for $x=0.09$, indicating the absence of an easy axis in the plane. The ac susceptibility also clearly shows the Ising anisotropy. Therefore, we conclude that the moment points in the c direction in the ordered state. The moments reside most probably on Ru^{4+} ions, which surround randomly distributed Ti^{4+}. But they may partially reside on the neighboring O^{2-} ions as well.

As shown in Fig. 2, the remnant magnetization exhibits a very slow relaxation with the $\ln t$ dependence, characteristic of a glassy state. The magnitudes of both ΔM and $M_{\rm rem}$ are peaked at 5–7 K and suggest at least a quantitative change at lower-temperatures in the ordered state. To further characterize this low-temperature behavior, investigations by neutron scattering and NMR may be useful.

The field and frequency dependence of the ordering is also consistent with the spin-glass formation. The magnetization in a wider range of fields (10 Oe $<H<$ 50 kOe) shows that with decreasing field the peak of ZFC magnetization becomes sharper and $T_{\rm p}$ increases. The peak temperature in the ac susceptibility weakly increases with increasing frequency (1–100 Hz). As we will show below, the in-plane conduction is maintained in the ordered phase. Moreover, the interlayer transport is respectably maintained, although weakly nonmetallic: the resistivity value at 4.2 K is two orders of magnitude smaller than that of the spin-glass phase of the high-$T_{\rm c}$ cuprate $La_{2-x}Sr_xCuO_4$ with $x=0.04$.[23] Thus the magnetism of the present system is consistent with Ising spin glass formed by Ruderman-Kittel-Kasuya-Yosida (RKKY)-type interaction among localized moments.

In contrast with the clear Ising anisotropy at low temperatures, the increase in the magnetization at 300 K is precisely isotropic: $d(M/H)/dx=1.05\times10^{-3}$ emu/mol for both $H\|c$ and $H\|ab$. Since the number of d electrons per mol decreases with increasing x, this indicates that the Pauli component arising from itinerant electrons is also enhanced with x, implying an approach to Fermi surface instability.

Electrical resistivity $\rho(T)$ was measured down to 4.2 K by a standard dc four-probe method. As shown in Fig. 4(a), the interlayer resistivity ρ_c of pure Sr_2RuO_4 shows metallic behavior below 130 K and nonmetallic $d\rho_c/dT<0$ at higher temperatures. The metal-nonmetal crossover temperature (at which $d\rho_c/dT=0$) decreases with increasing x. The appearance of the low-temperature upturn corresponds to the value of ρ_c exceeding 30–40 mΩ cm. In contrast, the in-plane resistivity ρ_{ab} retains metallic conduction at high temperatures at least up to $x=0.09$. Figure 4(b) shows the x dependence of $\rho_{ab}(T)$, which suggests that Ti impurities can be treated as strong potential scatterers, while they do not seriously affect the inelastic part. A metal-insulator transition is expected to occur if the universal value to sustain two-dimensional metallic conduction $h/4e^2=6.5$ kΩ/square per RuO_2 plane is exceeded. This value corresponds to $\rho_{ab}(0)\cong400$ $\mu\Omega$ cm for Sr_2RuO_4, and is not reached for $x\leqslant0.09$. The temperature of the minimum in ρ_{ab} neither corresponds to the magnetic ordering.

Let us discuss now why the moments induced by Ti^{4+} exhibit strong Ising anisotropy. Since the Pauli component remains isotropic, the induced Curie-Weiss component is ascribable to the local moments. For a localized state, the cluster calculation of the atomic orbits of RuO_6 indicates that the orbital moment aligns along the c axis if the RuO_6 octahedron is undistorted or elongated along the c direction, while it is in the plane if the octahedron is flattened.[24] In the presence of the interaction of the atomic orbits with spins, this explains why the moments in the Mott insulator Ca_2RuO_4 with flattened octahedra lie in the ab plane. Since the octahedron is elongated in the present system, the Ising anisotropy along the c axis is reasonable as long as the localized picture applies.

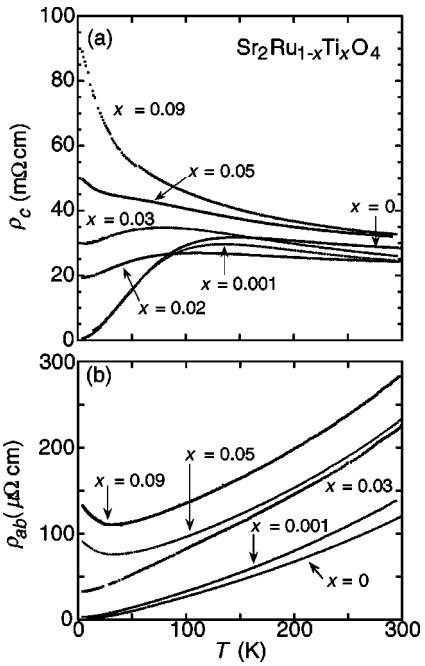

FIG. 4. Temperature dependence of (a) the interlayer and (b) the in-plane resistivity of $Sr_2Ru_{1-x}Ti_xO_4$.

The magnitude of the induced local moment, $p_{\rm eff}\lesssim0.5\mu_{\rm B}$ per Ti, is substantially smaller than the $2.82\mu_{\rm B}$ expected for the localized moment of Ru^{4+} in the low-spin configuration with $S=1$. Besides, there are four Ru sites adjacent to each Ti in the RuO_2 plane. Such small moment is also induced by Zn^{2+} in the cuprates: $\sim0.8\mu_{\rm B}$ in the underdoped region and $\sim0.2\mu_{\rm B}$ in the highly doped region.[16] These small moments may be due to the partially itinerant character of the d electrons of Ru and Cu. In the present case, one of the three t_{2g} orbitals of the Ru^{4+} ion in the Ru-O-Ti units does not involve bonding to the Ti site. Thus, such an orbital should be relatively unaffected by the absence of the d electron at the Ti site and retain itinerant character.

In the cuprates, *magnetic* ions such as Ni^{2+} are known to exhibit smaller moments as well as a weaker depairing effect than nonmagnetic ions.[14] A suitable magnetic impurity ion for Sr_2RuO_4 is Ir^{4+} ($5d^5$). According to the report on polycrystalline $Sr_2(Ru,Ir)O_4$, the Pauli component of the susceptibility decreases with slight Ir substitution and the Curie moment is induced with $p_{\rm eff}\sim0.3\mu_{\rm B}$/f.u. at $x({\rm Ir})=0.1$, corresponding to a large value: $\sim3\mu_{\rm B}$/Ir.[25] Considering the strong anisotropy found with Ti substitution, it is well worth repeating the investigation with single crystals.

Concerning the origin of the magnetic ordering, we discussed why it is ascribable to the spin glass formation of the induced moments by RKKY-type interaction. Here, it should be noted that the itinerant electron system mediating the interaction has a strongly q-dependent susceptibility, especially a strong peak at $q=Q_{ic}$. A recent tight-binding calculation including the spin-orbit interaction suggests that the susceptibility at Q_{ic} has an enhanced component along the c axis.[26] The characteristic length corresponding to Q_{ic} is $\lambda_{ic} \cong 3a/\sqrt{2}=0.82$ nm. This is to be compared with the mean Ti-Ti distance d_{ab} within the plane, $d_{ab}=a/\sqrt{x}$ on the assumption of random distribution of Ti ions. The threshold concentration for the magnetic ordering, $x_c \cong 0.025$, corresponds to $d=6.3a$, three times longer than λ_{ic}. We have not observed any indication that the magnetic phase becomes particularly stable at a special concentration, possibly related to λ_{ic}. We also note that the incommensurate antiferromagnetic ordering alone cannot explain the remnant moment, because the observed tetragonal structure (confirmed by neutron scattering at low temperatures[27]) does not allow a ferromagnetic component associated with spin canting. Nevertheless, it is quite important to investigate how the spin fluctuation at Q_{ic} is modified by the Ti substitution and by the resulting magnetic ordering at low temperatures.

In conclusion, we have shown that nonmagnetic impurities on the Ru site serve as a very effective probe of spin fluctuation in Sr_2RuO_4. Although the nonmagnetic impurities in both Sr_2RuO_4 and high-T_c cuprates induce local moments and severely suppress T_c, the anisotropy of the induced moments as well as their interaction appear substantially different, and result in the magnetic ordering in Sr_2RuO_4.

The authors acknowledge A. P. Mackenzie and M. Braden for important collaborations and N. Kikugawa and T. Iwamoto for their contribution. They are grateful to T. Ishiguro for his support, to Z. Q. Mao, S. NishiZaki, S. Nakatsuji, H. Fukazawa, and K. Deguchi for their technical support and useful discussions, and to M. Sigrist, T. Mizokawa, Kosaku Yamada, Kazuyoshi Yamada, K. Ishida, and N. Nagaosa for valuable discussions.

[1] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J.G. Bednorz, and F. Lichtenberg, Nature (London) **372**, 532 (1994).

[2] K. Ishida, H. Mukuda, Y. Kitaoka, K. Asayama, Z.Q. Mao, Y. Mori, and Y. Maeno, Nature (London) **396**, 658 (1998).

[3] For recent reviews, Y. Maeno, Physica B **281&282**, 865 (2000); A.P. Mackenzie and Y. Maeno, Physica B **280**, 148 (2000).

[4] T.M. Rice and M. Sigrist, J. Phys.: Condens. Matter **7**, L643 (1995).

[5] Y. Sidis, M. Braden, P. Bourges, B. Hennion, S. NishiZaki, Y. Maeno, and Y. Mori, Phys. Rev. Lett. **83**, 3320 (1999).

[6] I.I. Mazin and D.J. Singh, Phys. Rev. Lett. **82**, 4324 (1999).

[7] H. Mukuda, K. Ishida, Y. Kitaoka, K. Asayama, Z.Q. Mao, Y. Mori, and Y. Maeno, J. Phys. Soc. Jpn. **67**, 3945 (1998); T. Imai, A.W. Hunt, K.R. Thurber, and F.C. Chou, Phys. Rev. Lett. **81**, 3006 (1998).

[8] M. Sato and M. Kohmoto, J. Phys. Soc. Jpn. **69**, 3505 (2000); T. Kuwabara and M. Ogata, Phys. Rev. Lett. **85**, 4586 (2001); K-K. Ng and M. Sigrist, Europhys. Lett. **49**, 473 (2000).

[9] T. Nomura and K. Yamada, J. Phys. Soc. Jpn. **69**, 3678 (2000).

[10] A. Kanbayashi, J. Phys. Soc. Jpn. **41**, 1876 (1976).

[11] S. Ikeda, Y. Maeno, S. Nakatsuji, M. Kosaka, and Y. Uwatoko, Phys. Rev. B **62**, R6089 (2000).

[12] K. Yoshida, F. Nakamura, T. Goko, T. Fujita, Y. Maeno, Y. Mori, and S. NishiZaki, Phys. Rev. B **58**, 15 062 (1998).

[13] For early work, Y. Maeno, T. Tomita, M. Kyogoku, S. Awaji, Y. Aoki, K. Hoshino, A. Minami, and T. Fujita, Nature (London) **328**, 512 (1987); J.M. Tarascon, L.H. Greene, P. Barboux, W.R. McKinnon, G.W. Hull, T.P. Orlando, K.A. Delin, S. Foner, and E.J. McNiff, Jr., Phys. Rev. B **36**, 8393 (1987).

[14] G. Xiao, M.Z. Cieplak, J.Q. Xiao, and C.L. Chien, Phys. Rev. B **42**, 8752 (1990).

[15] K. Ishida, Y. Kitaoka, K. Yamazoe, K. Asayama, and Y. Yamada, Phys. Rev. Lett. **76**, 531 (1996); M.-H. Julien, T. Fehér, M. Horvatić, C. Berthier, O.N. Bakharev, P. Ségransan, G. Collin, and J.-F. Marucco, *ibid.* **84**, 3422 (2000).

[16] Y. Fukuzumi, K. Mizuhashi, K. Takenaka, and S. Uchida, Phys. Rev. Lett. **76**, 684 (1996); Y. Fukuzumi, K. Mizuhashi, and S. Uchida, Phys. Rev. B **61**, 627 (2000).

[17] EPMA was performed by A.P. Mackenzie using the facility at the University of Cambridge.

[18] A.P. Mackenzie, R.K.W. Haselwimmer, A.W. Tyler, G.G. Lonzarich, Y. Mori, S. Nishizaki, and Y. Maeno, Phys. Rev. Lett. **80**, 161 (1998); **80**, 3890(E) (1998).

[19] Z.Q. Mao, Y. Mori, and Y. Maeno, Phys. Rev. B **60**, 610 (1999).

[20] Y. Maeno, K. Yoshida, H. Hashimoto, S. Nishizaki, S. Ikeda, M. Nohara, T. Fujita, A.P. Mackenzie, N.E. Hussey, J.G. Bednorz, and F. Lichtenberg, J. Phys. Soc. Jpn. **66**, 1405 (1997).

[21] S. Nakatsuji and Y. Maeno, Phys. Rev. Lett. **84**, 2666 (2000); Phys. Rev. B **62**, 6458 (2000).

[22] M. Braden, G. André, S. Nakatsuji, and Y. Maeno, Phys. Rev. B **58**, 847 (1998).

[23] F.C. Chou, N.R. Belk, M.A. Kastner, R.J. Birgeneau, and A. Aharony, Phys. Rev. Lett. **75**, 2204 (1995); N. Kikugawa (private communication).

[24] T. Mizokawa, L.H. Tjeng, G.A. Sawatzky, G. Ghiringhelli, O. Tjernberg, N.B. Brookes, H. Fukazawa, S. Nakatsuji, and Y. Maeno (unpublished).

[25] R.J. Cava, B. Batlogg, K. Kiyono, H. Takagi, J.J. Krajewski, W.F. Peck, Jr., L.W. Rupp, Jr., and C. H. Chen, Phys. Rev. B **49**, 11 890 (1994).

[26] K.-K. Ng and M. Sigrist, J. Phys. Soc. Jpn. **69**, 3764 (2000).

[27] M. Braden (private communication).