Effect of Mn impurities on the superconductivity in $Na_xCoO_2 \cdot yH_2O$

Y.-J. Chen,[1,4] C.-J. Liu,[2] J.-S. Wang,[2] J.-Y. Lin,[1] C. P. Sun,[3] S. W. Huang,[4] J. M. Lee,[5] J. M. Chen,[5] J. F. Lee,[5] D. G. Liu,[5] and H. D. Yang[3]

[1]*Institute of Physics, National Chiao Tung University, Hsinchu 300, Taiwan*

[2]*Department of Physics, National Changhua University of Education, Changhua 50007, Taiwan*

[3]*Department of Physics, Center of Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung 804, Taiwan*

[4]*Department of Electrophysics, National Chiao Tung University, Hsinchu 300, Taiwan*

[5]*National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan*

(Received 26 May 2007; published 5 September 2007)

To shed light on the symmetry of the superconducting order parameter in $Na_xCoO_2 \cdot yH_2O$, the Mn doping effects are studied. X-ray absorption spectroscopy verifies that the doped Mn impurities occupy the Co sites and are with a valance close to +4. Impurity scattering by Mn is in the unitary limit that, however, does not lead to strong T_c suppression. This absence of the strong impurity effects on T_c is inconsistent with the simple picture of a sign-changing order parameter. Coexistence of the *s*-wave superconducting order parameter and the nodal one is proposed to reconcile all the existing experiments and has been implied by the specific heat experiments.

DOI: 10.1103/PhysRevB.76.092501 PACS number(s): 74.62.Dh, 74.20.−z, 74.70.−b

$Na_xCoO_2 \cdot yH_2O$ has stimulated researchers due to its exotic superconductivity, the electronic frustration on the triangular Co lattice, and the characters of the strongly correlated electron systems.[1–3] There is no doubt that $Na_xCoO_2 \cdot yH_2O$ has been recognized as one of the most interesting superconductors since the high-T_c superconductor era. Compared with MgB_2 in which the two-gap feature was concluded within one year of its discovery,[4] $Na_xCoO_2 \cdot yH_2O$ appears to be more exotic judged by, for example, the proposed models of its superconductivity (Refs. 5–8 and references therein). The superconducting order parameter of $Na_xCoO_2 \cdot yH_2O$ has remained elusive. On the one hand, almost all the relevant experiments agree on the existence of the nodal lines in the order parameter favoring *p*- or *f*-wave pairing, if the crystal and time reversal symmetries are further considered.[9–13] On the other hand, the decrease in the Knight shift below T_c is a strong advocate of *s*- or *d*-wave pairing.[12,13] To gain more insights into the nature of the superconductivity in $Na_xCoO_2 \cdot yH_2O$, the impurity scattering effects could provide one useful venue. Impurity effects on T_c have revealed indispensable information about superconductivity in many novel superconductors such as cuprates[14–21] and Sr_2RuO_4.[22] The general idea is that impurity potential scattering breaks Cooper pairs in the superconductors with a sign-changing order parameter, while it rarely affects T_c of those with a fully gapped *s*-wave order parameter if the impurity doping does not change the carrier density significantly. To shed light on the crucial issue of the order parameter symmetry, $Na_{0.7}Co_{1-z}Mn_zO_2 \cdot yH_2O$ samples were prepared. For the first time, x-ray absorption spectroscopy (XAS) shows that the doped Mn ions indeed occupy the Co sites. However, the unitary impurity scattering by Mn does not lead to strong T_c suppression. To reconcile the weak T_c suppression by impurities with other experiments, coexistence of *s*-wave and the unconventional pairings is proposed. This model is further supported by the direct observation from the specific heat $C(T)$ experiments.

Polycrystalline parent compounds of sodium cobalt oxides γ-$Na_{0.7}Co_{1-z}Mn_zO_2$ (z=0–0.03) were prepared using a rapid heat-up procedure. High purity powders of Na_2CO_3, Mn_2O_3, and CoO were *thoroughly* mixed, ground, and calcined. The resulting powders were immersed in the 3*M* Br_2/CH_3CN solution for five days, followed by filtering and thorough washing with CH_3CN and de-ionized water. X-ray diffraction (XRD) patterns indicated that all parent and hydrated samples were of single phase. To further characterize the samples, XAS [including x-ray absorption near-edge spectroscopy (XANES) and extended x-ray absorption fine structure (EXAFS)] was carried out for Mn *K* and *L* edges as well as Co *K* edge. Details of XAS experiments can be found in Refs. 23 and 24. To ensure the accurate results, T_c measurements were carried out, respectively, in two systems (MPMS and PPMS of Quantum Design). Results from two measurement systems and two different batches of samples were all consistent. Resistivity ρ was measured by the standard four-probe method.[25] $C(T)$ was further measured to explore the phase transition at very low temperatures. A detailed description of the $C(T)$ measurements can be found in Ref. 15.

Indeed, there was at least one report on the Ir and Ga impurity effects in $Na_xCoO_2 \cdot yH_2O$.[26] However, whether Ir or Ga impurities occupied the Co sites was not carefully examined. To explore the impurity effects in cobaltates, $Na_xCo_{1-z}Mn_zO_2 \cdot yH_2O$ seems a natural choice. Layered $Alk_xMnO_2 \cdot yH_2O$ (Alk=Li,Na,K) with the triangular MnO_2 planes was successfully synthesized more than a decade ago.[27,28] This indicates that the doped Mn ions would favor the Co sites in $Na_xCoO_2 \cdot yH_2O$ and do not alter the crystal symmetry, as suggested by XRD. For further characterizations of the doped Mn ions, Fig. 1(a) shows Mn *L*-edge XANES spectra of $Na_xCo_{1-z}Mn_zO_2 \cdot yH_2O$ together with those of MnO_2, Mn_2O_3, and MnO. It is clear that all the Mn-doped samples have similar spectra distinct from those of the starting material Mn_2O_3 and two other common manganese oxides. Moreover, judged by the edge energy around 6550 eV in Fig. 1(b), Mn ions in all the doped samples, hydrated or not, have a valence close to +4. The Mn^{4+} state is consistent with the previous suggestion that the valence of Mn in nominal $Alk_xMnO_2 \cdot yH_2O$ is close to +4 by the extraction reactions.[27] The first spectroscopic evidence of Mn^{4+}

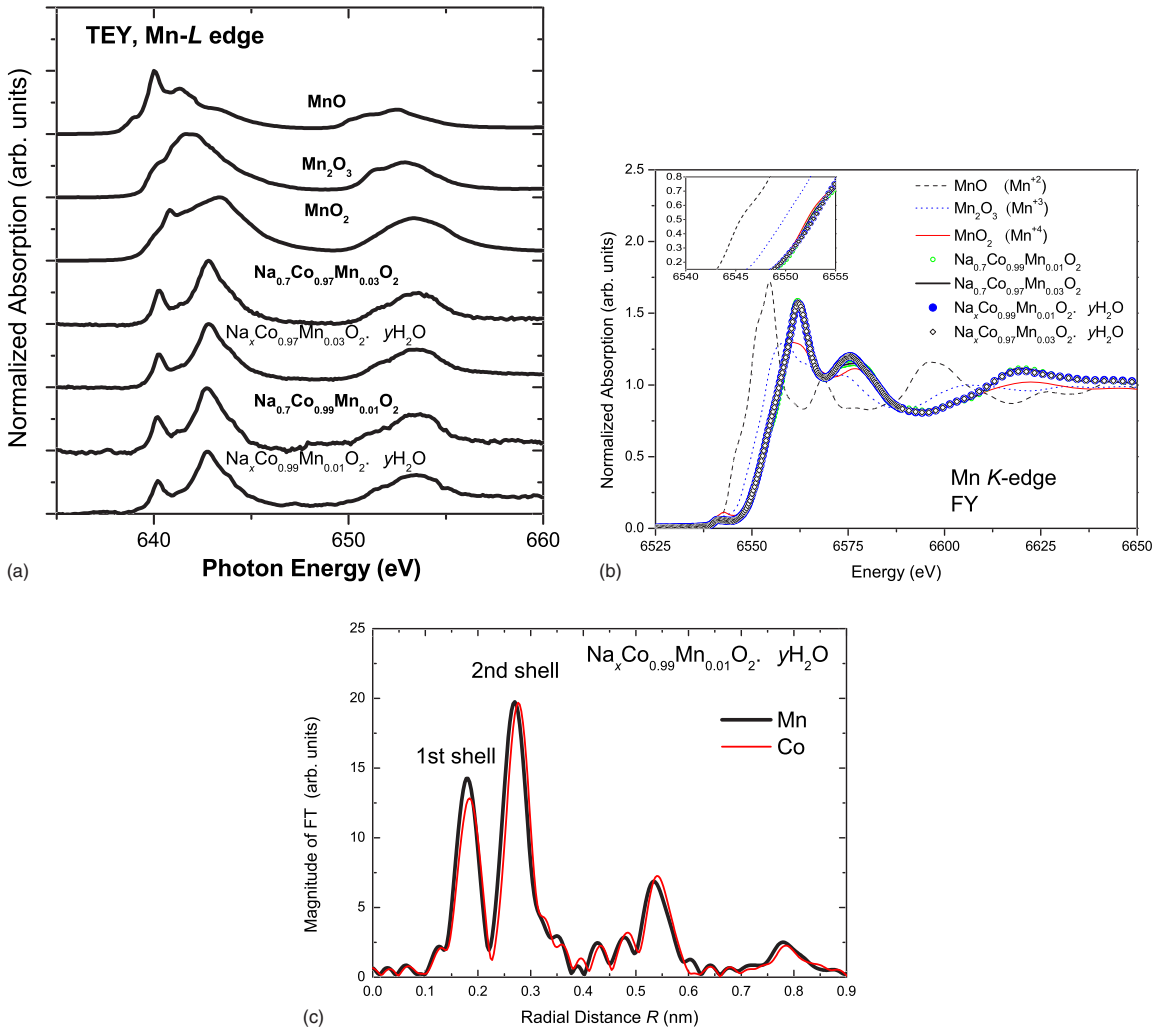

FIG. 1. (Color online) Mn (a) L-edge and (b) K-edge XANES of $Na_xCo_{1-z}Mn_zO_2 \cdot yH_2O$ and the standard samples; (c) FT magnitudes with phase correction of the k^3-weighted EXAFS data at Mn K edge. Inset of (b) shows the enlarged edge region. All the Mn-doped samples have similar spectra in (a) and (b).

is provided here for Mn ions on the triangular lattice. Figure 1(c) shows the Fourier transform (FT) amplitudes and profiles of EXAFS data at Co and Mn K edges for $Na_xCo_{0.99}Mn_{0.01}O_2 \cdot yH_2O$. FT amplitudes and profiles of EXAFS for both Co and Mn show identical features, indicating that Mn ions are in the same environment as Co ions and no other local structure of any second phase is present. FT peak position for the first shell of Co is 0.187 nm [Fig. 1(c)], identical to the Co-O bond length of $Na_xCoO_2 \cdot yH_2O$ from the neutron diffraction.[29,30] Also shown in Fig. 2(c), the Mn-O bond length is found to be 0.181 nm. This implies that the Mn^{4+} ionic radius (r_I) of 0.052 nm might be smaller than that of the Co ions which valence is between +3.3 and +3.4 (r_I=0.065 nm for Co^{3+}; r_I for Co^{4+} not available).[31,32]

With the characterizations verifying that *the doped Mn impurities occupy the Co sites in* CoO_2 *planes*, one is ready to study the impurity effects on T_c of $Na_xCo_{1-z}Mn_zO_2 \cdot yH_2O$. Figure 2 shows M vs T below 6 K for samples of the first batch. The inset demonstrates the Meissner effect of the undoped $Na_xCoO_2 \cdot yH_2O$, as pronounced as those of the best polycrystalline samples in the literature. T_c is defined as the onset of the Meissner effect. The doping dependence of T_c for two respective batches is depicted in Fig. 3. T_c suppression rate dT_c/dz=0.64 K/1% is determined by fitting data of all samples in Fig. 2. For samples with $z>0.02$, albeit with a small drop in the M-T curve, the signal is too small to well determine T_c as discussed later.

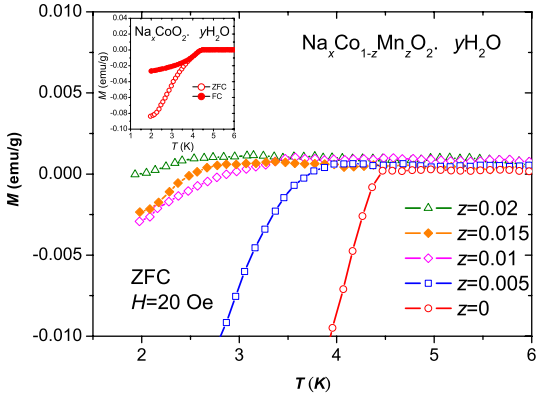

FIG. 2. (Color online) M vs T of $Na_xCo_{1-z}Mn_zO_2 \cdot yH_2O$ samples. Inset shows zero-field-cooled and field-cooled data of undoped $Na_xCoO_2 \cdot yH_2O$.

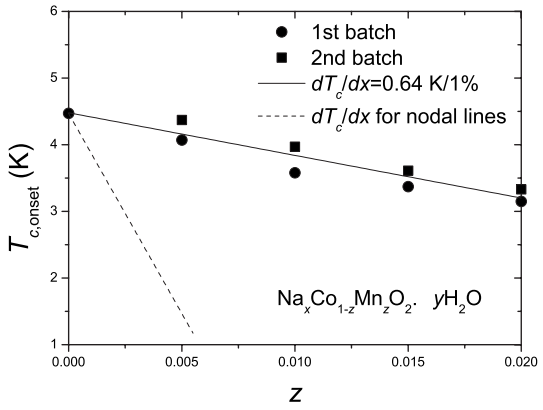

FIG. 3. T_c suppression by Mn impurities. The solid line is the linear fit of all data. The observed T_c suppression rate is much smaller than that (the dashed line) of a superconductor with line nodes (see text).

The results in Fig. 3 are surprising. Previously, the nodal order parameter was detected in $Na_xCoO_2 \cdot yH_2O$.[9–13] Therefore, T_c should have been strongly suppressed by impurity scattering as in the cases of cuprates and Sr_2RuO_4. For example, dT_c/dz=12 K/1% in $YBa_2(Cu_{1-z}Zn_z)3O_{6.93}$.[15–18] One might suggest that, by scaling with T_{c0}'s of the undoped sample in YBCO (T_{c0}=92 K) and $Na_xCoO_2 \cdot yH_2O$ (T_{c0} =4.5 K), the 20 times smaller dT_c/dz is reasonable in the context of the line nodal order parameter. However, considering the potential pair breaking with isotropic impurity scattering rate τ_{imp}^{-1}, $(T_{c0}-T_c) \equiv \Delta T_c = \tau_{imp}^{-1}/8$ for small z. That is, ΔT_c mainly depends on τ_{imp}^{-1}, and T_{c0} is not an important parameter for T_c suppression rate. To discuss the impurity scattering in a more quantitative way, $\rho(T=10\ \mathrm{K}) \equiv \rho_0$ vs z can be seen in the inset of Fig. 4. Taking $d\rho_0/dz$ =314 $\mu\Omega$ cm/1%, the increase in the sheet resistance R of the CoO_2 planes due to the impurities can be obtained by

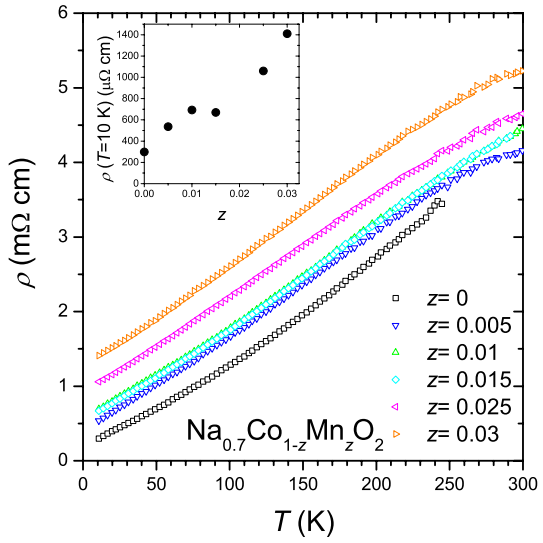

FIG. 4. (Color online) $\rho(T)$ for $Na_xCo_{1-z}Mn_zO_2$ indicate an increase in τ_{imp}^{-1} due to Mn doping. Data of z=0.01, 0.015, 0.025 are adjusted within a factor of 25% to simulate Matthiessen's rule. Inset shows an increase in $\rho(T=10\ \mathrm{K})$ with z.

$R=\rho/(c/2)$, where c=0.55 nm is the c axis of $Na_{0.7}CoO_2$. However, for polycrystalline samples, ρ does not necessarily represent the intrinsic value due to the complex current flow paths, grain boundaries, and other effects. Indeed, $\rho(T)$ of $Na_{0.7}CoO_2$ shown in Fig. 4 has a similar T dependence compared to that of the single crystal with the same composition, but with a five-time larger magnitude.[2] Taking this factor of 5, $d\rho_0/dz$=63 $\mu\Omega$ cm/1% is the normalized value for $Na_{0.7}Co_{1-z}Mn_zO_2$, and consequently dR_0/dz=1100 Ω/1%. For two dimensional isotropic scattering, $R_0=4(\hbar/e^2) \times (z/n)\sin^2 \delta_0$, where n is the carrier number and δ_0 is the phase shift. In the unitary limit, dR_0/dz=545 Ω/1% with a conservative value of n=0.3 per CoO_2 plane. Therefore, Mn impurities in CoO_2 planes indeed scatter carriers in the unitary limit. To compare to the Zn impurity scattering (usually considered as a case of the unitary limit) in $YBa_2(Cu_{1-z}Zn_z)_3O_{6.93}$, $d\rho_0/dz$=45 $\mu\Omega$ cm/1% from Ref. 15. Assuming that all Zn impurities go to the planes, dR_0/dz=528 Ω/1%, and the theoretical unitary limit is dR_0/dz=1020 Ω/1% with n=0.16 per CuO_2 plane. T_c suppression rate for a two dimensional line nodal superconductor due to unitary scattering was calculated to be $dT_c/dz \approx 6$ K/1% and plotted in Fig. 3 as the dashed line.[14]

The slow T_c suppression due to impurity scattering shown in Fig. 3 naively suggests a fully gapped s-wave superconductivity in $Na_xCoO_2 \cdot yH_2O$. However, the existence of the nodal order parameter by other experiments hinders a simple s-wave scenario. There are proposals such as the triplet s-wave[6] and the extended s-wave[8] scenarios to reconcile with the observed weak T_c suppression. With further consideration of the possible existence of the singlet state from NMR results, we propose that two superconducting order parameters coexist in $Na_xCoO_2 \cdot yH_2O$, which happen to have about the same T_c. It is likely that the s, d, f waves all have similar pairing strength, as in the calculations for a certain range of parameters.[8] In this coexistence model, the Mn impurities strongly suppress superconductivity with the nodal order parameter, while the s-wave component remains relatively robust. This model, though seemingly exotic, is one of the few that reconcile all three major facts: the existence of the nodal lines, that of the singlet state, and the weak T_c suppression due to impurity scattering. Actually, specific heat data in Ref. 11, with further analysis, could accommodate the coexistence of a fully gapped (presumably s wave) and a nodal order parameter with up to 60% of the Fermi surface gapped.[33] The minor T_c suppression of the s-wave component by Mn impurities could be due to the change of the Co valance, which is known to have influence on T_c and likely to be affected by doped Mn^{4+} ions. Another possibility is the magnetic pair breaking by the spin-flip scattering rate τ_s^{-1} from the local moment of Mn^{4+}, which usually is 1 order of magnitude smaller than τ_{imp}^{-1}.[34] The signal of the Meissner effect becomes substantially weak for $z \geqslant 0.01$. This could be partly due to the suppression of superconductivity in the volume of the nodal order parameter. Moreover, impurities may perturb and remove the energy degeneracy of the two order parameters and the samples with increasing z become favoring the nodal order parameter. The present results might actually be consistent with a recent intriguing phase diagram

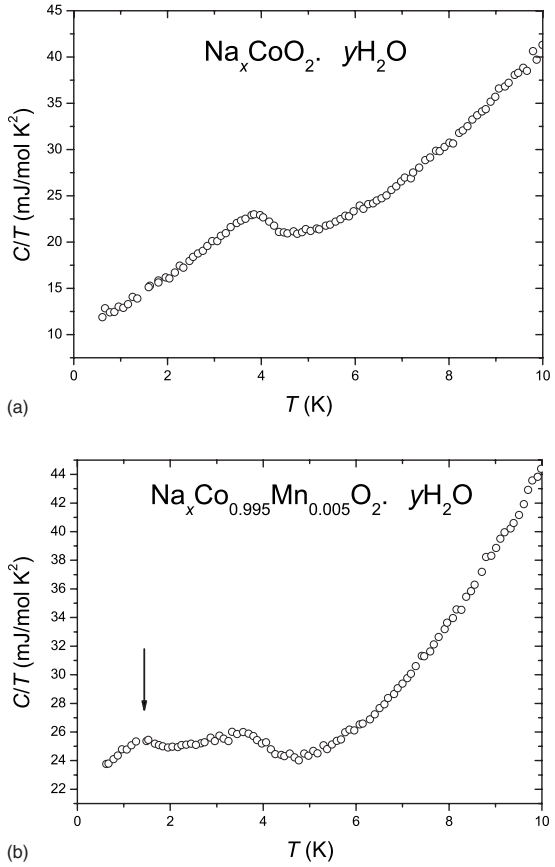

FIG. 5. $C(T)/T$ of (a) $Na_xCoO_2\cdot yH_2O$ and (b) $Na_xCo_{0.995}Mn_{0.005}O_2\cdot yH_2O$. The arrow indicates the lower temperature phase transition in addition to that associated with T_c by the M measurements.

that two superconducting regimes are separated by a magnetic ordering phase with respect to the Co NQR frequency.[35–37] These two superconducting phases are suggested to have distinct order parameters.[38] Unless with the well-specified conditions during the process as in Ref. 35, most $Na_xCoO_2\cdot yH_2O$ samples could have two superconducting phases mixed together, manifested by the experiments of the present work. Recently, there have been more theoretical works discussing the multiorder parameters and the related subjects.[38,39]

Finally, $C(T)$ experiments reveal persuasive evidence supporting the coexistence model. In Fig. 5(a), $C(T)/T$ of $Na_xCoO_2\cdot yH_2O$ is similar to that of Ref. 11 and the anomaly manifests the superconducting phase transition around 4.5 K. In Fig. 5(b), $C(T)/T$ of the doped sample $Na_xCo_{0.995}Mn_{0.005}O_2\cdot yH_2O$ has a well defined anomaly consistent with T_c measured by the M measurements. More strikingly, there occurs another anomaly at lower T (indicated by the arrow) which can be attributed to the second transition due to the nodal order parameter. It is noted that the transition temperature of this anomaly below 2 K is in quantitative agreement with the potential pair-breaking model, as denoted by the dashed line in Fig. 3.

To summarize, Mn impurities have been successfully doped into CoO_2 planes in $Na_xCo_{1-z}Mn_zO_2\cdot yH_2O$. Spectroscopy evidence indicates that the doped Mn ions are located on the Co sites. The absence of the strong impurity effects on T_c is *inconsistent* with the simple picture of a sign-changing order parameter. The model of coexistence of s-wave superconducting order parameter and the nodal one is proposed as one of the possible scenarios to reconcile the observed T_c suppression rate and the results from other experiments. Cautions should be taken due to the reduction of the superconducting volume in Mn-doped samples.

We are grateful to H. Sakurai and M. Ogata for indispensable discussions. This work was supported by MOE-ATU and the National Science Council of Taiwan, under Grant Nos. NSC 94-2112-M-009-006, 94-2112-M-018-001, and 94-2112-M-110-010.

[1] K. Takada *et al.*, Nature (London) **422**, 53 (2003).
[2] M. L. Foo *et al.*, Phys. Rev. Lett. **92**, 247001 (2004).
[3] I. I. Mazin and M. D. Johannes, Nat. Phys. **1**, 91 (2005).
[4] H. D. Yang *et al.*, Phys. Rev. Lett. **87**, 167003 (2001).
[5] H. Ikeda *et al.*, J. Phys. Soc. Jpn. **73**, 17 (2004).
[6] M. D. Johannes *et al.*, Phys. Rev. Lett. **93**, 097005 (2004).
[7] M. Mochizuki *et al.*, Phys. Rev. Lett. **94**, 147005 (2005).
[8] K. Kuroki *et al.*, Phys. Rev. B **73**, 184503 (2006).
[9] K. Ishida *et al.*, J. Phys. Soc. Jpn. **72**, 3041 (2003).
[10] A. Kanigel *et al.*, Phys. Rev. Lett. **92**, 257007 (2004).
[11] H. D. Yang *et al.*, Phys. Rev. B **71**, 020504(R) (2005).
[12] Y. Kobayashi *et al.*, J. Phys. Soc. Jpn. **74**, 1800 (2005).
[13] Y. Ihara *et al.*, J. Phys. Soc. Jpn. **74**, 2177 (2005).
[14] P. Monthoux and D. Pines, Phys. Rev. B **49**, 4261 (1994).
[15] K. Mizuhashi *et al.*, Phys. Rev. B **52**, R3884 (1995).
[16] S. K. Tolpygo *et al.*, Phys. Rev. B **53**, 12454 (1996).
[17] S. K. Tolpygo *et al.*, Phys. Rev. B **53**, 12462 (1996).
[18] J.-Y. Lin *et al.*, Phys. Rev. B **59**, 6047 (1999).
[19] G. Haran and A. D. S. Nagi, Phys. Rev. B **63**, 012503 (2000).
[20] W. A. Atkinson *et al.*, Phys. Rev. Lett. **85**, 3926 (2000).
[21] J.-Y. Lin and H. D. Yang, Phys. Rev. B **65**, 216502 (2002).
[22] A. P. Mackenzie *et al.*, Phys. Rev. Lett. **80**, 161 (1998).
[23] I. P. Hong *et al.*, Europhys. Lett. **58**, 126 (2002); H. D. Yang *et al.*, Phys. Rev. B **68**, 092505 (2003).
[24] Li-Shing Hsu *et al.*, Phys. Rev. B **72**, 115115 (2005).
[25] H. D. Yang *et al.*, Phys. Rev. Lett. **87**, 167003 (2001).
[26] M. Yokoi *et al.*, J. Phys. Soc. Jpn. **73**, 1297 (2004).
[27] Q. Feng *et al.*, Chem. Mater. **7**, 1226 (1995).
[28] Rongji Chen *et al.*, Chem. Mater. **8**, 1275 (1996).
[29] J. W. Lynn *et al.*, Phys. Rev. B **68**, 214516 (2003).
[30] J. D. Jorgensen *et al.*, Phys. Rev. B **68**, 214517 (2003).
[31] K. Takada *et al.*, J. Mater. Chem. **14**, 1448 (2004).
[32] C. J. Milne *et al.*, Phys. Rev. Lett. **93**, 247007 (2004).
[33] J.-Y. Lin *et al.* (unpublished).
[34] A. A. Abrikosov, *Fundamentals of the Theory of Metals* (North-Holland, Amsterdam, 1988).
[35] H. Sakurai *et al.*, Phys. Rev. B **74**, 092502 (2006).
[36] Y. Kobayashi *et al.*, J. Phys. Soc. Jpn. **75**, 074717 (2006).
[37] Y. Ihara *et al.*, J. Phys. Soc. Jpn. **75**, 124714 (2006).
[38] M. Mochizuki, *et al.*, J. Phys. Soc. Jpn. **76**, 023702 (2007).
[39] J. T. Kao *et al.*, Phys. Rev. B **75**, 012503 (2007).