Spin-gap behavior in underdoped $TlSr_2(Lu_{0.7}Ca_{0.3})Cu_2O_y$: ^{63}Cu and ^{205}Tl NMR studies

K. Magishi, Y. Kitaoka, G.-q. Zheng, and K. Asayama
Department of Material Physics, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

T. Kondo, Y. Shimakawa, T. Manako, and Y. Kubo
Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba 305, Japan

(Received 11 March 1996)

Measurements of the Knight shift of ^{63}Cu and the nuclear spin-lattice relaxation rate of ^{205}Tl, $^{205}(1/T_1)$, have revealed that $TlSr_2(Lu_{0.7}Ca_{0.3})Cu_2O_y$ with T_c = 40 K consisting of the bi-CuO_2 layer without the CuO chain is in the underdoped regime with the spin pseudogap, which is evidenced by the significant decrease of $^{205}(1/T_1T)$ below 120 K far above T_c and the decrease of the ^{63}Cu spin Knight shift upon cooling. Although the disorder is introduced into the adjacent Ca layers to the CuO_2 plane by the substitution of Lu for Ca sites, the spin-gap behavior is presented not to be masked. From this result, it is suggested that the absence of the spin-gap behavior in $La_{2-x}Sr_xCuO_4$ is neither due to the disorder introduced into the adjacent LaO layers to the CuO_2 plane by the substitution of Sr for La sites nor the absence of the CuO chain. [S0163-1829(96)05629-9]

The normal state of high-T_c cuprates is unusual, exhibiting the T-linear resistivity and the anomalous T dependence of the Hall coefficient, etc.[1] In particular, the magnetic properties in underdoped $YBa_2Cu_3O_{6+x}$ ($YBCO_{6+x}$) (Refs. 2 and 3) and $YBa_2Cu_4O_8$ (Y124) (Ref. 4) with the pyramidal bi-CuO_2 layer are outstanding where the spin susceptibility, $\chi_s(T)$, decreases commonly upon cooling and the nuclear spin-lattice relaxation rate of ^{63}Cu divided by the temperature, $^{63}(1/T_1T)$, has a broad peak far above T_c. These magnetic anomalies, the so-called spin-gap behavior, have attracted a great interest, since it suggests a possible formation of the spin singlet far above T_c. Initiated by the RVB picture,[5] it was argued that the superconductivity would occur in the non-Fermi liquid state. In contrast to above compounds, it was shown from the nuclear relaxation[6] and the inelastic neutron scattering measurements[7] that $La_{2-x}Sr_xCuO_4$ (LSCO) with a smaller hole content did not exhibit any significant signature of the similar spin gap behavior. In $YBCO_{6+x}$, although the disorder is introduced into the CuO chain associated with the variation of the oxygen content, such effect takes place away from the CuO_2 plane. By contrast, in LSCO, the disorder is introduced into the adjacent LaO layers to the CuO_2 plane by the substitution of Sr for La sites. This may give a hint for the contrasting behavior in the magnetic excitation among LSCO and underdoped $YBCO_{6+x}$. Alternatively, a difference of the number of the CuO_2 plane may also be a possible reason for the contrasting magnetic excitations.

In Tl-based compounds such as $Tl_2Ba_2CuO_{6+\delta}$ (Tl2201) (Ref. 8) with a single CuO_2 layer, $Tl_2Ba_2CaCu_2O_{8-\delta}$ (Tl2212) (Ref. 9) and $TlSr_2CaCu_2O_{7-\delta}$ (Tl1212) (Ref. 10) with double CuO_2 layers and $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl2223) (Ref. 11) with triple CuO_2 layers, the shallow peak of $^{205}(1/T_1T)$ was observed above T_c. It might be then argued to be associated with the spin-gap behavior. However, the T dependence of the ^{205}Tl Knight shift could not give a firm and reliable evidence for the decrease of the spin susceptibility upon cooling, which is another signature of the spin-gap behavior, because of the dominance of the T independent chemical shift. As a matter of fact, from the T invariance of the ^{63}Cu Knight shift above T_c in Tl2201 and Tl1212 compounds, such shallow peak of $^{205}(1/T_1T)$ was suspected to do nothing with the spin-gap behavior, instead, these systems were characterized to belong to the overdoped regime. By contrast, both results of the Knight shift and T_1 of ^{63}Cu in Tl2223 were compatible with the presence of the spin-gap behavior. Furthermore, the ^{205}Tl NMR was suggested to be not a good probe for unraveling the magnetic properties in the CuO_2 plane, since Tl atoms are partially replaced into the Ca layers, which makes a situation complicated. Apparently, it is not fully established yet in Tl compounds with the same bilayer as in Y-based compounds but no CuO chain whether the spin-gap behavior is in the same category as in Y-based compounds or not.

In a series of $TlSr_2(Lu_{1-x}Ca_x)Cu_2O_y$ compounds (T_c = 90−0 K) with the pyramidal bilayer without the CuO chain, an overdoped regime is realized by reducing the oxygen content, while an underdoped regime by the substitution of Lu atoms for the Ca layers sandwiched by the bilayer. In three overdoped compounds with T_c=70 K, 52 K, and 10 K, the Knight shift was T invariant, whereas $^{63}(1/T_1T)$ had a shallow peak just above T_c, followed by the Curie-Weiss law,[10] which are analogous to the behavior in $YBa_2Cu_3O_7$.

In this paper, from the combined measurements of the Knight shift of ^{63}Cu and $1/T_1$ of ^{205}Tl in $TlSr_2(Lu_{0.7}Ca_{0.3})Cu_2O_y$ (Lu-doped Tl1212) with T_c=40 K, we report first unambiguous evidences of the spin-gap behavior in a Tl-based compound with a bilayer but no CuO chain. A cause for the absence of the spin-gap behavior in LSCO is suspected to be due to the disorder introduced into the adjacent LaO layers to the CuO_2 plane. Motivated also by this, the present system where the disorder is introduced into the adjacent Ca layers to the CuO_2 plane allows us to gain an insight into a relevance of the disorder effect to the spin-gap behavior.

The $TlSr_2(Lu_{0.7}Ca_{0.3})Cu_2O_y$ polycrystalline sample was prepared by the conventional solid-state reaction method and confirmed to be of almost single phase by the powder x-ray diffraction described elsewhere.[12] The pellet was pulverized into grains with size smaller than 20 μm in diameter for the NMR measurement. T_c was determined to be 40 K from the temperature where the diamagnetic signal appeared in the dc susceptibility. The NMR measurements were performed in a phase-coherent laboratory-built pulsed spectrometer by use of a superconducting magnet (12 T at 4.2 K). The NMR spectrum was obtained using a boxcar integrator with sweeping the magnetic field. The nuclear spin-lattice relaxation rate, $1/T_1$, was measured by the saturation recovery method. The Knight shift and $1/T_1$ measurements for ^{63}Cu ($^{63}\gamma_N/2\pi = 1.1285$ MHz/kOe) and ^{205}Tl ($^{205}\gamma_N/2\pi = 2.4567$ MHz/kOe) were made at $f = 125.1$ and 211.1 MHz, respectively, in a T range 4.2−300 K. Unfortunately, the powder sample was not aligned. So, the Knight shift perpendicular to the c axis, $^{63}K_\perp$, was determined from the peak of $\theta = 90°$ to the c axis of the powder pattern, whereas that parallel to the c axis, $^{63}K_\parallel$, was not determined.

When the external magnetic field, H, is perpendicular to the c axis, the observed shift consists of the Knight shift, $K_\perp$, and the second-order quadrupole shift. $K_\perp$ and the quadrupole frequency, ν_Q, of ^{63}Cu can be expressed for the central transition ($1/2 \leftrightarrow -1/2$) as follows:[13,14]

$$\frac{\omega-\gamma_N H_{\rm res}}{\gamma_N H_{\rm res}} = K_\perp + \frac{3\nu_Q^2}{16(1+K_\perp)(\gamma_N H_{\rm res})^2}, \qquad (1)$$

where $H_{\rm res}$ is the resonance field, γ_N the nuclear gyromagnetic ratio, and ω the NMR frequency, respectively. From a slope of $(\omega-\gamma_N H_{\rm res})/(\gamma_N H_{\rm res})$ vs $(\gamma_N H_{\rm res})^{-2}$ plots obtained from the ω dependence of $H_{\rm res}$, ν_Q is estimated to be ~ 19.0 MHz. This value is smaller than those in the overdoped compounds (21−26 MHz) (Ref. 10) and other underdoped compounds (30−40 MHz).[15] $K_\perp$ is determined from an extrapolation to zero of $(\gamma_N H_{\rm res})^{-2}$ for the same plots. Thus obtained T dependence of $^{63}K_\perp$ is displayed in Fig. 1 for the Lu-doped Tl1212 compound with $T_c = 40$ K together with the results for the overdoped Tl1212 with $T_c = 70$ K (Ref. 10) and the underdoped $YBCO_{6+x}$.[16] For the overdoped Tl1212, $^{63}K_\perp$ is T invariant in the normal state, while $^{63}K_\perp$ for the Lu-doped Tl1212 decreases upon cooling, coinciding with the data for the underdoped $YBCO_{6+x}$ compound.

The Knight shift, $K(T)$, in high-T_c cuprates consists of the T independent orbital part, $K_{\rm orb}$, and the T dependent spin part, $K_s(T)$, as

$$K_\alpha(T) = K_{{\rm orb},\alpha} + K_{s,\alpha}(T) \quad (\alpha=\perp,\parallel). \qquad (2)$$

According to the Mila-Rice model,[17] the ^{63}Cu spin Knight shift, $^{63}K_s$, in the CuO_2 plane is expressed as follows:

$$^{63}K_{s,\alpha}(T) = (A_\alpha + 4B)\chi_s(T) \quad (\alpha=\perp,\parallel) \qquad (3)$$

where A_α and B are the on-site and the supertransferred hyperfine fields of ^{63}Cu in the CuO_2 plane, respectively, and $\chi_s(T)$ is assumed to be isotropic. In the inset of Fig. 1, $^{63}K_\perp$ is plotted against $\chi(T)$ reported previously[12] with temperature as an implicit parameter above T_c. Since $^{63}K_{s,\perp}$ is expressed by Eq. (3) from the slope of $K_\perp(T)$ vs $\chi(T)$ plot, $A_\perp + 4B$ is estimated to be ~ 190 kOe/μ_B. If the on-site hyperfine field is assumed to be the same as that of other underdoped compounds ($A_\perp$~ 37 kOe/μ_B),[18–20] B is obtained as ~ 40 kOe/μ_B, which is nearly equal to those values for LSCO,[21] $YBCO_{6+x}$,[16] and Y124,[22] respectively, suggesting that the almost invariant B~ 40 kOe/μ_B is characteristic for the underdoped high-T_c cuprates regardless of the number of the CuO_2 layers and their different oxygen configuration.

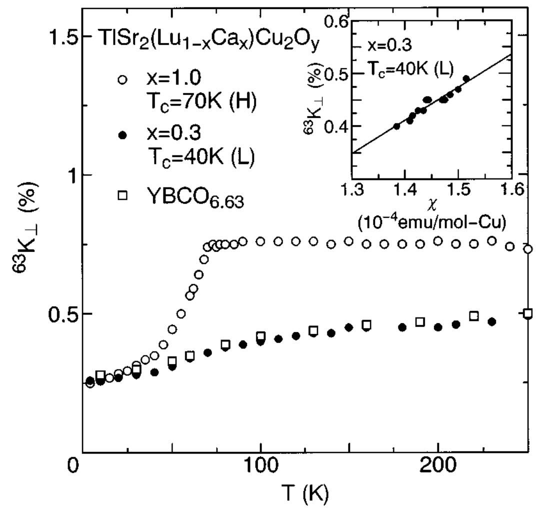

FIG. 1. T dependence of the ^{63}Cu Knight shift, $^{63}K_\perp$, perpendicular to the c axis for underdoped $TlSr_2(Lu_{0.7}Ca_{0.3})Cu_2O_y$ with T_c=40 K (●), together with the results for overdoped $TlSr_2CaCu_2O_{7-\delta}$ with T_c=70 K (○) (Ref. 10) and oxygen-deficient $YBa_2Cu_3O_{6.63}$ (□) (Ref. 16). Inset indicates $^{63}K_\perp$ vs the bulk susceptibility, χ, plots for $TlSr_2(Lu_{0.7}Ca_{0.3})Cu_2O_y$.

By contrast, ^{205}K dominated by the large chemical shift has exhibited only a small variation from 0.25±0.01% at 40 K to 0.27±0.01% at 250 K, pointing to very weak supertransferred hyperfine coupling with the CuO_2 plane via the apical oxygen. Thus, the ^{205}Tl Knight shift is not enough to extract any precise magnetic properties in the present compound.

Figure 2 shows the T dependences of $(1/T_1T)_\perp$ for ^{63}Cu and ^{205}Tl in the overdoped Tl1212 with $T_c = 70$ K. In the inset in Fig. 2, $^{63}(1/T_1)_\perp$ is plotted against $^{205}(1/T_1)_\perp$ with temperature as an implicit parameter. This scaling proves that T dependences of $^{63}(1/T_1)_\perp$ coincides with that of $^{205}(1/T_1)_\perp$ regardless of rather weak hyperfine coupling between Tl nuclei and the Cu d-spin polarization in the CuO_2 plane. The antiferromagnetic (AF) spin correlation in the CuO_2 plane is hence possible to be deduced from the relaxation behavior of ^{205}Tl. In Lu-doped Tl1212 compound, it was difficult to measure $^{63}(1/T_1)$ accurately, since the powder sample was not aligned and the NMR signal was not strong enough to measure $^{63}(1/T_1)$ accurately. Alternatively, the T dependence of $^{205}(1/T_1)$ was employed as a probe to unravel the nature of the spin correlation with the confirmation of the scaling between $^{205}(1/T_1)$ and $^{63}(1/T_1)$ in overdoped Tl1212 with the same structure.

In Fig. 3, a relaxation curve of ^{205}Tl, $R(t) = [M(\infty)-M(t)]/M(\infty)$, at $T = 60$ K and $f = 211.1$ MHz

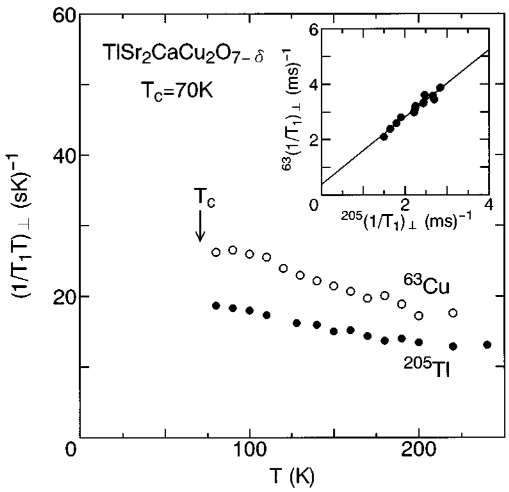

FIG. 2. T dependences of $(1/T_1T)_\perp$ for ^{63}Cu (○) and ^{205}Tl (●) in overdoped $TlSr_2CaCu_2O_{7-\delta}$ with $T_c=70$ K. The inset indicates $^{205}(1/T_1T)_\perp$ vs $^{63}(1/T_1T)_\perp$ plot with temperature as an implicit parameter.

is plotted against the time, t, after saturation pulses in Lu-doped Tl1212. Since ^{205}Tl has no quadrupole moment ($I=1/2$), the relaxation curve should be of single exponential type. As seen in the figure, the data were, however, not fitted with a single T_1 component. This is because the disorder is introduced into the CuO_2 plane by the substitution of Lu^{3+} for Ca^{2+} sites to control the hole content. Figure 4 shows the T dependences of $^{205}(1/T_1T)$, where solid (●) and open (○) circles indicate the short and the long component, $^{205}(1/T_1T)_S$ and $^{205}(1/T_1T)_L$, which is tentatively extracted from a fit (solid lines in Fig. 3) to the data of $R(t)$ larger than 0.5 and smaller than 0.1, respectively. A remarkable feature is that both $^{205}(1/T_1T)_S$ and $^{205}(1/T_1T)_L$ exhibit a broad peak around $T^*\sim$ 120 K far above $T_c=40$ K, confirming the spin-gap behavior similar to the underdoped $YBCO_{6+x}$ (Refs. 2 and 3) and Y124.[4] It is noteworthy that $^{205}(1/T_1T)$ reveals a Curie-Weiss-like behavior above T^*, demonstrating the presence of the AF spin fluctuation as well. These characteristic behaviors of $^{205}(1/T_1T)$ are considered to reflect those for $^{63}(1/T_1T)$. Although the shallow peak of $^{205}(1/T_1T)$ above T_c was already reported in Tl2212 compounds with the pyramidal bilayer,[9] no data on ^{63}Cu NMR were presented there either to make sure the scaling with the ^{63}Cu relaxation behavior or the decreasing behavior of the spin susceptibility upon cooling.

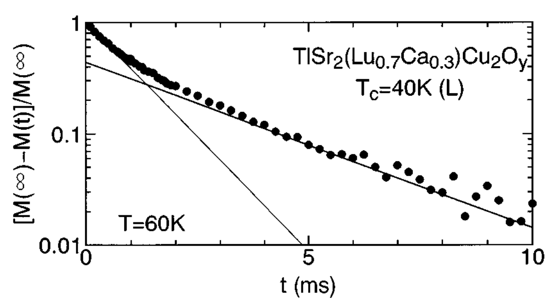

FIG. 3. NMR relaxation curve of ^{205}Tl, $R(t)=[M(\infty)-M(t)]/M(\infty)$, plotted against the time, t, after the saturation pulses in $TlSr_2(Lu_{0.7}Ca_{0.3})Cu_2O_y$ at T = 60 K and f = 211.1 MHz.

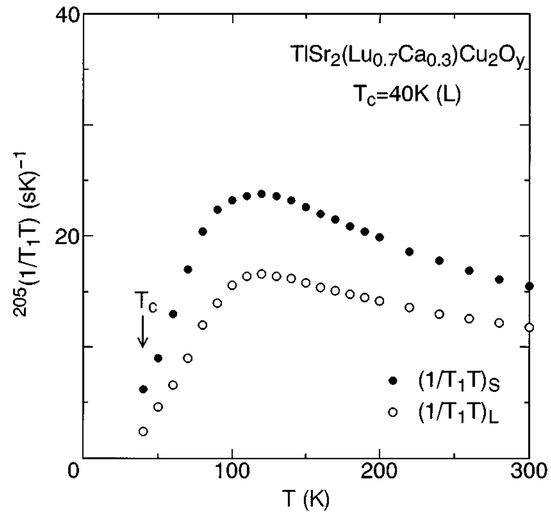

FIG. 4. T dependence of $^{205}(1/T_1T)$ in $TlSr_2(Lu_{0.7}Ca_{0.3})Cu_2O_y$ under the external magnetic field of $\sim$ 11 T. Solid (●) and open (○) circles indicate the short and the long components of $^{205}(1/T_1T)$, respectively.

Figure 5 shows the T dependences of $^{205}(1/T_1T)$ in a series of the Tl1212 compounds covering from an under- to overdoped region. As seen in the figure, $^{205}(1/T_1T)$ for Lu-doped Tl1212 compounds exhibit an appreciable decrease far above T_c, i.e., the spin-gap behavior in contrast to a gradual increase of $1/T_1T$ close to T_c for the overdoped compounds. The spin-gap behavior is thus reproducible for the underdoped compounds with the CuO_2 bilayer, neither affected by the disorder introduced into the Ca(Lu) layers controlling the hole content nor the absence of the CuO chain. This result suggests that the lack of the spin-gap behavior in LSCO is neither due to the disorder in La(Sr)O layer nor the absence

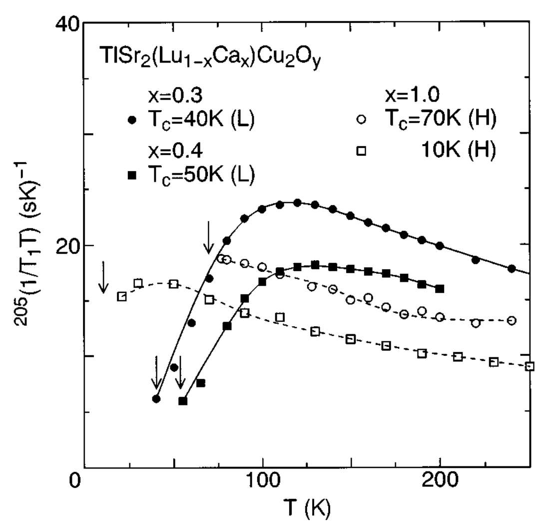

FIG. 5. T dependences of $^{205}(1/T_1T)$ in a series of Tl1212 compounds covering from the under- to overdoped region. The solid and dashed lines are a guide to the eyes.

of the CuO chain. In this sense, the spin-gap behavior may be associated with the bilayer exchange coupling along the c axis, as argued by several authors.[23,24]

In summary, ^{63}Cu and ^{205}Tl NMR measurements have been carried out in the underdoped $TlSr_2(Lu_{0.7}Ca_{0.3})Cu_2O_y$ ($T_c=40$ K) consisting of the pyramidal bilayer. The ^{63}Cu Knight shift, $^{63}K_{\perp}(T)$, perpendicular to the c axis decreases upon cooling as in the underdoped compounds such as $La_{2-x}Sr_xCuO_4$, $YBa_2Cu_3O_{6+x}$, and $YBa_2Cu_4O_8$. From the remarkable result that $^{205}(1/T_1T)$, which has verified to scale to the relaxation behavior of $^{63}(1/T_1T)$, has a broad peak around $T^*\sim$ 120 K far above T_c, the spin-gap behavior has been shown to be the common feature for the underdoped compounds with the pyramidal bilayer, which is neither masked by the disorder in the adjacent layers to the CuO_2 plane nor the absence of the CuO chain. By contrast, the decrease of the spin susceptibility upon cooling is rather universal regardless of the number of CuO_2 layers and the oxygen coordination. In this context, it is suggested that such a spin-gap behavior that $1/T_1T$ begins to decrease far above T_c could be absent in the LSCO systems composed of the single CuO_2 layer.

One of the authors (K.M.) would like to thank Dr. K. Ishida for valuable discussions. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas ''Anomalous Metallic Phase near Mott Transition'' from the Ministry of Education, Science of Culture.

[1] For a review, see for example, Physica C **235-240** (1994).
[2] W. W. Warren, Jr., *et al.*, Phys. Rev. Lett. **62**, 1193 (1989).
[3] H. Yasuoka, T. Imai, and T. Shimizu, *Strong Correlation and Superconductivity* (Springer-Verlag, Berlin, 1989), p. 254.
[4] H. Zimmerman *et al.*, Physica C **159**, 681 (1989); T. Machi *et al.*, *ibid.* **173**, 32 (1990).
[5] T. Tanamoto, K. Kohno, and H. Fukuyama, J. Phys. Soc. Jpn. **61**, 1886 (1992); **62**, 717 (1993); **62**, 1455 (1993); **63**, 2739 (1994).
[6] Y. Kitaoka *et al.*, Physica C **170**, 189 (1990); S. Ohsugi *et al.*, J. Phys. Soc. Jpn. **60**, 2351 (1991).
[7] J. Rossat-Mignod *et al.*, Physica B **169**, 58 (1991); Physica C **185-189**, 89 (1991); Physica B **186-188**, 1 (1993).
[8] Y. Kitaoka *et al.*, Physica C **179**, 107 (1991); K. Fujiwara *et al.*, *ibid.* **184**, 207 (1991).
[9] F. Hentsch *et al.*, Physica C **158**, 137 (1989); N. Winzek and M. Mehring, Appl. Magn. Res. **3**, 535 (1992).
[10] K. Magishi *et al.* (unpublished).
[11] G.-q. Zheng *et al.*, J. Phys. Soc. Jpn. **64**, 2524 (1995); Physica C **260**, 197 (1996).
[12] T. Kondo *et al.*, Phys. Rev. B **50**, 1244 (1994).
[13] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961).
[14] M. Takigawa *et al.*, Phys. Rev. B **39**, 300 (1989).
[15] G.-q. Zheng *et al.*, Physica C **208**, 339 (1993); K. Asayama *et al.*, Hyperfine Interact. **79**, 835 (1993).
[16] M. Takigawa *et al.*, Phys. Rev. B **43**, 247 (1991).
[17] F. Mila and T. M. Rice, Physica C **157**, 561 (1989); Phys. Rev. B **40**, 11 382 (1989).
[18] H. Monien, D. Pines, and M. Takigawa, Phys. Rev. B **43**, 258 (1991).
[19] H. Monien, P. Monthoux, and D. Pines, Phys. Rev. B **43**, 275 (1991).
[20] T. Imai, J. Phys. Soc. Jpn. **59**, 2508 (1990).
[21] S. Ohsugi *et al.*, J. Phys. Soc. Jpn. **63**, 700 (1994).
[22] H. Zimmermann *et al.*, Physica C **185-189**, 1145 (1991).
[23] A. J. Millis and H. Monien, Phys. Rev. Lett. **70**, 2810 (1993).
[24] M. U. Ubbens and P. A. Lee, Phys. Rev. B **50**, 438 (1994).