^{63}Cu NMR probe of superconducting properties in $HgBa_2Ca_2Cu_3O_{8+\delta}$: A possible reason for $T_c = 133$ K

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(Received 5 December 1995; revised manuscript received 19 January 1996)

Superconducting properties in $HgBa_2Ca_2Cu_3O_{8+\delta}$, with a transition temperature of T_c=133 K, have been investigated by measurements of the nuclear spin-lattice relaxation rate, $^{63}(1/T_1)$. It has been found that the T_1T=const behavior, observed well below T_c, arises from combined relaxation channels to vortex cores, as well as from a residual density of states (DOS), N_{res}, at the Fermi level associated with the gapless superconductivity. From the value of T_1T=const in the latter channel, the DOS fraction normalized by its value at T_c, N_{res}/N_{T_c}, has been deduced to be as small as $\sim$0.05. Based on the two-dimensional gapless d-wave model, the T_c reduction rate, $\Delta T_c/T_{c0}$, is estimated to be as small as 0.02 for $N_{res}/N_0\sim$0.05. It is pointed out that these measures of the quality of $HaBa_2Ca_2Cu_3O_{8+\delta}$ explain why T_c reaches such a high value.

Among the mercury-based homologous series of $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ (n=1,2,3,4) compounds, the n=3 member $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg1223) has drawn particular interest because of its high superconducting transition temperature, T_c = 133 K.[1] Furthermore, it is remarkable that T_c can be substantially enhanced to $\sim$ 150 K through the application of pressure.[2,3] It is well known that a key factor in increasing the value of T_c is to increase the number of CuO_2 layers from one to three. It is, however, not fully understood why T_c in Hg1223 is so much higher when compared with the Bi- and Tl-based compounds that also contain three CuO_2 layers. In previous papers,[4,5] in order to characterize the magnetic properties in the normal state of $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl2223) (Ref. 4) and Hg1223 (Ref. 5) with three CuO_2 layers, Zheng *et al.* and Magishi *et al.* reported extensive NMR results involving the Knight shift, K, the nuclear spin-lattice relaxation rate, $1/T_1$, and the transverse relaxation rate, $1/T_{2G}$, of ^{63}Cu. It was found that the product of the characteristic energy of the spin fluctuations, Γ_Q, and the staggered susceptibility, χ_Q, at $Q=(\pi/a,\pi/a)$, $\Gamma_Q\chi_Q$, for both Tl2223 and Hg1223 were markedly larger than that for $YBa_2Cu_3O_7$. The spin-fluctuation-induced superconductivity mechanism,[6,7] which predicts a higher T_c for larger $\Gamma_Q\chi_Q$, becomes increasingly promising with additional experimental suggestions[8] that the order parameter is of the d-wave-pairing type with $d_{x^2-y^2}$ symmetry; it naturally follows that a cause for the higher T_c in Tl2223 and Hg1223 than that in YBa_2Cu_3O, may be due to an enhancement of $\Gamma_Q\chi_Q$. Furthermore, from the T_1T=const behavior observed well below T_c in Tl2223, it was shown that the superconductivity was in the gapless regime where a finite density of state (DOS) was induced at the Fermi level by some imperfections. Since Tl atoms in Tl2223 compounds are reported to be partially substituted into the Ca layers sandwiched by pyramidal and square CuO_2 layers, such a partial disorder for the atomic arrangement was suggested to be a cause to suppress T_c down to 120 K in Tl2223, less than T_c=133 K in Hg1223.

In this paper, we focus on the relaxation behavior of ^{63}Cu for *both* the square (fourfold) and the pyramidal (fivefold) layers in the superconducting state for Hg1223. This is because the superconducting characteristics in Tl2223 differ between the fivefold and fourfold CuO_2 layers, namely, the latter pointed to a larger fraction of the residual DOS below T_c than the former.

Preparation of the Hg1223 compound was described elsewhere.[9] The sample was confirmed to be almost single-phase by x-ray-diffraction experiments.[9] The pellet was pulverized into grain sizes smaller than 20 μm in diameter, and was magnetically aligned along the c axis by use of the anisotropy of the normal-state susceptibility and fixed with the Stycast 1266 epoxy with an external magnetic field of 11 T. The value T_c was confirmed to be 133 K, below which the diamagnetic signal appeared in ac susceptibility. The ^{63}Cu NMR measurements were carried out in a temperature and magnetic-field range of 1.4–300 K and 6–11 T, respectively, using a conventional phase-coherent home-made pulsed spectrometer with a superconducting magnet (12 T at 4.2 K).

Figures 1(a) and 1(b) show the ^{63}Cu-NMR spectra at T = 140 K and f=125.1 MHz for the central transition ($\frac{1}{2}\leftrightarrow -\frac{1}{2}$) with the c axis parallel and perpendicular to the external magnetic field, H, respectively. The spectra were obtained, using a boxcar integrator, by sweeping the magnetic field. In Fig. 1(b) for $c\perp H$, there are two well resolved peaks corresponding to two different Cu sites in the pyramidal (fivefold) and the square (fourfold) CuO_2 plane. In this condition, the shift, $\Delta\nu$, is composed of the Knight shift, $K_\perp$, and the second order quadrupole shift as expressed by

$$\Delta\nu/\gamma_N H_{res} = K_\perp + 3\nu_Q^2/16(1+K_\perp)(\gamma_N H_{res})^2 \times(1-\cos^2\theta)(1-9\cos^2\theta), \quad (1)$$

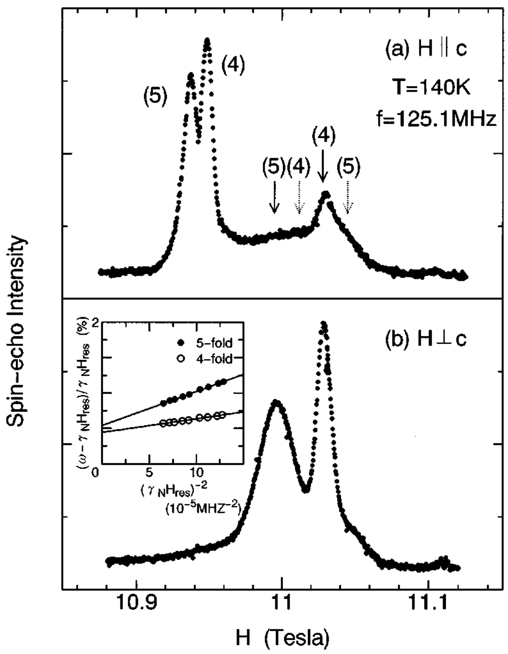

FIG. 1. ^{63}Cu-NMR spectra of $HgBa_2Ca_2Cu_3O_{8+\delta}$ with T_c=133 K at f = 125.1 MHz and T = 140 K. (a) and (b) correspond to the spectra with the c axis parallel and perpendicular to the external magnetic field, respectively. From the ratio of the integrated intensity of well-resolved two peaks for the oriented powders for $c \perp H$, it is determined that the lower and the higher field peaks originate from the fivefold and fourfold copper site, respectively. The solid and dash arrows indicate the positions of the peaks arising from grains with θ = 90° and 41.8° to the c axis for the unoriented powders.

with $\theta=\pi/2$, where $H_{\rm res}$ is the field where the resonance is observed and γ_N is the nuclear gyromagnetic ratio, respectively. From the above formula, confirmed experimentally as displayed in the inset of Fig. 1(b), the nuclear quadrupole frequency, ν_Q, is estimated to be $\sim$ 10.2 and $\sim$ 16.1 MHz for the fourfold and fivefold sites, respectively. In Fig. 1(a) for $c \| H$, two peaks in the lower field region arise from the oriented powder with the c axis parallel to the field, while the broad spectrum with a single peak in the higher field region is associated with the unoriented powder. This is because the spectrum for the unoriented powder is distributed with two peaks for each Cu site as denoted by arrows in Fig. 1(a), where solid and dash arrows correspond to the peaks arising from grains with θ = 90° and 41.8° to the c axis for the unoriented powder, respectively. As expected, the position of the single peak in the high field region in Fig. 1(a) coincides with the spectrum with the narrower linewidth in Fig. 1(b) for $c \perp H$. From the integrated intensity ratio of the spectra with the two peaks in the low field region to the broad spectrum with the single peak in the high field region, a fraction of the oriented powder with the c axis parallel to the field is anticipated to be $\sim$ 60% of the whole powder. For both the crystal directions, we note that the spectra in the lower field are broader than those in the higher field. The full-width at half-maximums are about $\sim$130 and $\sim$80 Oe for the lower and higher field spectrum for $c \| H$, whereas they are $\sim$300 and $\sim$140 Oe for $c \perp H$, respectively. In Fig. 1(b) for $c \perp H$, affected by the second order quadrupole effect, the spectrum broadens mainly due to an inhomogeneous distribution of ν_Q, and hence, the linewidth for the fivefold site with a larger ν_Q (16.1 MHz) is expected to be broader than that for the fourfold site with a smaller ν_Q (10.1 MHz). Furthermore, from a ratio of the integrated intensity of the well-resolved two peaks, i.e., of the sharp to broad NMR line being about $\frac{1}{2}$, the higher and the lower field peak is hence assigned to the fourfold and fivefold Cu sites, respectively, because the number of Cu site for the former is $\frac{1}{2}$ of that for the latter. In contrast, the intensity argument which is used to assign the spectrum to each Cu site, is not applied to the spectra in Fig. 1(a) for $c \| H$. This is because the separation between the two peaks for the spectra of the oriented powder is not large enough to allow us to estimate an intensity ratio reliably and we cannot rule out a possible asymmetry of the spectra associated with the presence of misoriented grains whose c axis is not exactly directed to the magnetic field, i.e., $\theta \neq 0$. For $c \| H$, moreover, it was not possible to measure T_1 for both Cu sites separately at low temperatures because the spectrum for one Cu site overlaps with another upon lowering the temperature below 60 K, due to nearly the same value of the Knight shift. Therefore, we are concerned with the T_1 measurements for $c \perp H$ below T_c. Thus, difficulties in distinguishing each spectrum for $c \| H$ does not prevent the separate investigation of the superconducting properties for the fourfold and fivefold sites in Hg1223.

For $c \perp H$, it is likely that the spectrum for each Cu site may slightly overlap the peak for θ=41.8° [dashed arrows in Fig. 1(a)] arising from the unoriented powder. However, since T_1 for $c \perp H$ has been determined with a single component as described below, the contribution of the unoriented powder to the spectrum is considered to be negligible, if there is any at all. Accordingly, we present the T dependence of $^{63}(1/T_{1\perp})$ below T_c for $H \perp c$.

$1/T_1$ was measured by the saturation recovery method. The nuclear relaxation function, $m(t)$, for the $(1/2 \leftrightarrow -1/2)$ central transition is expressed as follows:[10]

$$m(t)=[M(\infty)-M(t)]/M(\infty)$$
$$=0.9\exp(-6t/T_1)+0.1\exp(-t/T_1), \quad (2)$$

where $M(t)$ is the nuclear magnetization at time t after the saturation pulses.

Figures 2(a) and 2(b) display $m(t)$ for the square Cu site plotted against t at T = 40 and 10 K, respectively. The solid line in Fig. 2(a) indicates a best fit with a single T_1 component of Eq. (2). On the other hand, short T_1 components become appreciable in $T \leqslant 30$ K as seen in Fig. 2(b), associated with the presence of vortex cores. A prominent finding is, however, that all T_1 components follow the T_1T=const law below 7 K as proven from the results that $m(t)$ plotted against the time (t) multiplied by the temperature, tT, is on a single curve as indicated in the inset of Fig. 2(b). To display an overall T dependence of $^{63}(1/T_{1\perp})$ below T_c, a long component of $^{63}(1/T_{1\perp})$ below 30 K is tentatively extracted from a fit of Eq. (2) to the data of $m(t)$ smaller than 0.5 as indicated by the solid line in Fig. 2(b).

Figures 3(a) and 3(b) show the T dependence of $^{63}(1/T_{1\perp})$ (○) below T_c for the fourfold and fivefold sites, respectively, under a magnetic field of $\sim$ 11 T. The magni-

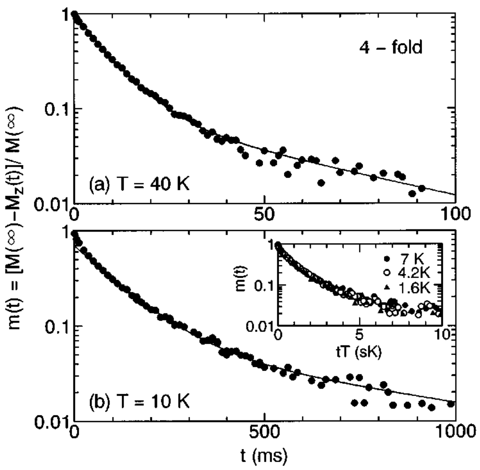

FIG. 2. Examples of ^{63}Cu-NMR relaxation curves, $m(t)$, plotted against t at (a) $T=$ 40 K and (b) 10 K, respectively. Solid lines are the results fitted by the theoretical relaxation function of $m(t)=0.9\exp(-6t/T_1)+0.1\exp(-t/T_1)$. The inset of (b) indicates that $m(t)$ plotted against the time multiplied by the temperature, tT, is on a single curve, showing that all $^{63}T_1$ components follow the T_1T = const law below 7 K.

tude of the uncertainty of the data is comparable to the size of the symbol. For both sites, $^{63}(1/T_{1\perp})$ reveals a similar relaxation behavior as seen in most of the high-T_c cuprates, i.e., a power-law-like behavior without any coherence peak followed by $T_1T=$ const behavior well below T_c.

The relaxation behavior in the superconducting mixed state is affected by normal fluxoid cores. An array of fluxoids gives rise to two different relaxation processes: (a) the thermal fluctuation of fluxoids which generate the transverse fluctuating field[11] and (b) the spin diffusion to vortex cores.[12] In the former, $1/T_1$ should be suppressed with increasing field, whereas in the latter, $1/T_1$ is enhanced with increasing the number of fluxoids. The nuclear relaxation measurements in the superconducting mixed state were reported in YBCO (Refs. 13,14) and $YBa_2Cu_4O_8$ (Y124) (Ref. 15), thus far. From the result that $1/T_1$ is linearly enhanced by the magnetic field, the nuclear relaxation for these compounds was shown to be dominated by the spin diffusion process to vortex cores. By contrast, $^{63}(1/T_1)$ for $Bi_2Sr_2CaCu_2O_8$ (Bi2212) (Ref. 16) and Tl2223,[17] which followed the T_1T=const law, did not reveal any appreciable field dependence down to low temperatures. As a result, the relaxation behavior in these compounds was concluded to be dominated by the presence of residual DOS at the Fermi level. As discussed extensively in the literatures,[16–20] the gapless superconductivity caused by some imperfections presenting in the crystals provided an important clue to address the pairing state for high-T_c cuprates to be of a d-wave type in which the nonmagnetic potential scattering acts as pair breaker.

The magnetic-field dependences of $^{63}(1/T_{1\perp})$ at low-T in Hg1223 for both Cu sites were measured in a field range of 6–11 T. Below 7 K where all the T_1 components follow the $T_1T=$ const law, $^{63}(1/T_{1\perp}T)$ is well fitted by

$$^{63}(1/T_{1\perp}T)=a+bH \qquad (3)$$

for both Cu sites as displayed in the insets of Figs. 3(a) and 3(b). The relaxation process in the mixed state is affected by

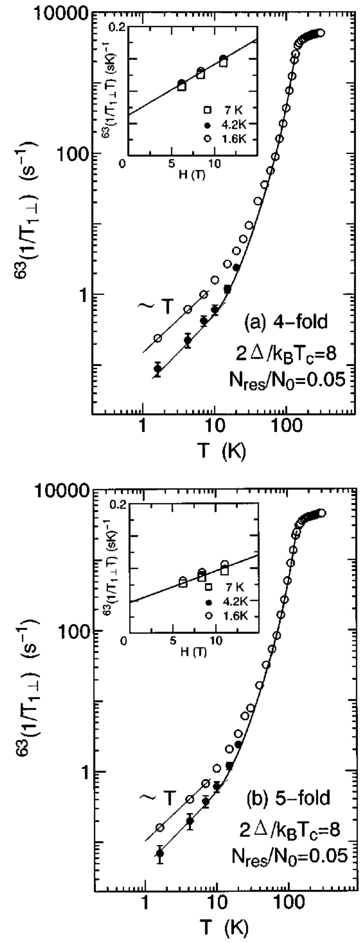

FIG. 3. T dependence of $^{63}(1/T_{1\perp})$ below T_c for the (a) fourfold and (b) fivefold site under the magnetic field perpendicular to the c axis. ○ and ● indicate the values at 11 T and the extrapolated value to the zero magnetic field, respectively. Insets indicate the magnetic-field dependence of $^{63}(1/T_{1\perp}T)$ at several temperatures below 7 K.

the normal electrons in the *cores* of the fluxoids, accompanied by the exchange of the energy among the nuclei via mutual spin flips (T_2 process) between those nuclei close to the core to more distant nuclei, i.e., spin diffusion process. In the high-T_c cuprate, since the indirect nuclei spin-spin relaxation rate $1/T_{2G}$ is much larger than $1/T_1$ and the superconducting coherence length $\xi(\sim 20$ Å) is quite shorter than the London penetration depth, $\lambda\sim 6000-9000$ Å, which means that the magnetic field penetrates the sample uniformly, a rapid spin diffusion process dominates the nuclear relaxation process of the planar Cu site as argued extensively in the literature.[13–15] $1/T_{1\perp}$ can be hence expressed as follows:[21]

$$(1/T_1)_{obs,i}=(1/T_{1n,i})\frac{S_n}{S_s+S_n}+(1/T_{1s,i})\frac{S_s}{S_s+S_n}.$$

Since $S_n \ll S_s$ and $(1/T_{1n,i}) \gg (1/T_{1s,i})$,

$$(1/T_1)_{obs,i}=(1/T_{1n}-1/T_{1s})_i(H/\Phi)\xi_j\xi_k+(1/T_{1s})_i$$
$$(i,j,k=a,b,c), \qquad (4)$$

where $1/T_{1n}$, $1/T_{1s}$, S_s, and S_n are the relaxation rates in and out of vortex cores, the area in the superconducting and the normal state induced by the magnetic field. Φ is the flux quantum and ξ_i is the coherence length along the i direction. When the above formula is divided by the temperature, T, a good correspondence between the experiment and the theory is obtained with such relations as

$$a=(1/T_{1s}T), \tag{5}$$

$$b=[(1/T_{1n}T)-(1/T_{1s}T)]\xi_{\parallel}\xi_{\perp}/\Phi. \tag{6}$$

Below 7 K, it is remarkable that $^{63}(1/T_{1s})$ inherent to the superconducting state follows the $T_{1s}T$=const law which is indicative of the gapless nature of superconductivity. Furthermore, $^{63}(1/T_1)_{obs}$ above 7 K was also confirmed to follow Eq. (4). The T dependence of $^{63}(1/T_{1s})$ is plotted by closed circles (●) in Figs. 3(a) and 3(b) together with the results below 7 K. It is important to note that $^{63}(1/T_{1s})$ decreases over four orders of magnitude below T_c and behaves as T_1T = const below 7 K. In contrast to the case for Bi2212 (Ref. 16) and Tl2223,[17] the relaxation behavior in the mixed state at low-T for Hg1223 is significantly affected by the spin diffusion process to vortex cores. On the other hand, the superconductivity has been found to be in the gapless state as well. In order to compare the fraction of the residual DOS present in Hg1223 with that in Tl2223, $(1/T_{1s}T)$ normalized by the value at T_c is related to a residual fraction of the DOS as seen in the formula

$$(1/T_{1s}T)/(1/T_1T)_{T=T_c}=(N_{\rm res}/N_{T_c})^2, \tag{7}$$

where N_{T_c} is defined as an effective DOS at T_c. $N_{\rm res}/N_{T_c}$ for Hg1223 is estimated to be ~0.05, which is much smaller than $N_{\rm res}/N_{T_c}$~0.3 for Tl2223.[17]

Now, we analyze the T dependence of $^{63}(1/T_{1s})$ below T_c for both sites in terms of the two-dimensional (2D) gapless d-wave model with line nodes at the cylindrical Fermi surface as $\Delta(\phi)=\Delta(T)\cos 2\phi$ with $d_{x^2-y^2}$ symmetry where the residual DOS, $N_{\rm res}$, at the Fermi level is taken into account. The gapless d-wave model consistently explained the NMR results in Bi2212,[16] $Tl_2Ba_2CuO_{6+\delta}$,[18] Tl2223,[17] $TlSr_2CaCu_2O_{7-\delta}$,[22] $La_{2-x}Sr_xCuO_4$ ($x\geqslant 0.20$),[19] and Zn-doped YBCO.[20] As extensively argued in the literature,[23–25] such residual DOS is produced at the Fermi level by treating the impurity scattering in terms of the unitarity limit in the d-wave model. It is crucial that not only the magnetic impurity scattering, but also the potential scattering by some imperfections lead to the pair breaking. As indicated by the solid lines in Figs. 3(a) and 3(b), $^{63}(1/T_{1s})$ is well reproduced with parameters of $2\Delta/k_BT_c=8$ and $N_{\rm res}/N_{T_c}=0.05$. Furthermore, a reduction rate of T_c by impurity scattering, $\Delta T_c/T_{c0}$ is estimated to be as small as 0.02 for $N_{\rm res}/N_{T_c}=0.05$, which is smaller than $\Delta T_c/T_{c0}$ = 0.13 for $N_{\rm res}/N_{T_c}=0.30$ in Tl2223. From this result, the quality of Hg1223 is demonstrated to be better than Tl2223 as supported also from the narrower NMR linewidth.

In summary, the ^{63}Cu nuclear relaxation rate, $^{63}(1/T_1)$, in the superconducting mixed state in Hg1223 has revealed the T_1T=const law at low temperatures with a linear magnetic field dependence below 7 K, regardless of its distribution. The latter experimental signature is consistent with the relaxation process characteristic for the rapid spin diffusion to the normal electrons in the vortex cores via mutual spin flips as observed for YBCO and Y124. By eliminating the contribution to T_1 associated with fluxoids, the value of T_1T=const inherent to the superconducting state has been deduced. As a result, the superconducting state of Hg1223 is concluded to be of the gapless type with a finite DOS at the Fermi level, which amounts to 5% of the value at T_c, $N_{\rm res}/N_{T_c}\sim$ 0.05. Based on the 2D d-wave model, it has been shown that this gapless state, which is possibly produced by some imperfections, does not suppress the T_c at all with a small T_c-reduction rate of $\Delta T_c/T_{c0}=0.02$ for $N_{\rm res}/N_{T_c}\sim$ 0.05, which is smaller than $\Delta T_c/T_{c0}=0.13$ for $N_{\rm res}/N_{T_c}\sim$ 0.3 in Tl2223. A cause for the higher value of T_c in Hg1223 than that in Tl2223 is hence ascribed to the better quality of Hg1223.

The author 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 "Science of High Temperature Superconductivity" from the Ministry of Education, Science and Culture.

[1] A. Schilling *et al.*, Nature (London) **363**, 56 (1993).
[2] C. W. Chu *et al.*, Nature (London) **365**, 323 (1993).
[3] H. Ihara *et al.*, Jpn. J. Appl. Phys. **32**, L1732 (1993).
[4] G.-q. Zheng *et al.*, J. Phys. Soc. Jpn. **64**, 3184 (1995).
[5] K. Magishi *et al.*, J. Phys. Soc. Jpn. **64**, 4561 (1995).
[6] T. Moriya *et al.*, J. Phys. Soc. Jpn. **59**, 2095 (1990); T. Moriya and K. Ueda, *ibid.* **63**, 1871 (1994).
[7] P. Monthoux *et al.*, Phys. Rev. Lett. **67**, 3448 (1991); P. Monthoux and D. Pines, Phys. Rev. B **49**, 4261 (1994).
[8] For a review, see for example: *Proceedings of the International Conference on Materials and Mechanism of Superconductivity IV, Grenoble, 1994*, edited by P. Wyder [Physica **C235-240** (1994)].
[9] M. Hirabayashi *et al.*, J. Phys. Soc. Jpn. **32**, L1206 (1993).
[10] A. Narath, Phys. Rev. B **13**, 3724 (1976).
[11] E. Ehrenfreund *et al.*, Solid State Commun. **7**, 1333 (1969).
[12] C. Caroli and J. Matricon, Phys. Kondens. Mater. **3**, 380 (1965).
[13] J. A. Martindale *et al.*, Phys. Rev. B **50**, 13 645 (1994).
[14] K. Ishida *et al.*, Solid State Commun. **90**, 563 (1994).
[15] G.-q. Zheng *et al.*, Physica C **227**, 169 (1994).
[16] K. Ishida *et al.*, J. Phys. Soc. Jpn. **63**, 1104 (1994).
[17] G. -q. Zheng *et al.*, Physica C (to be published).
[18] K. Fujiwara *et al.*, Physica C **184**, 207 (1991).
[19] S. Ohsugi *et al.*, J. Phys. Soc. Jpn. **63**, 700 (1994).
[20] K. Ishida *et al.*, J. Phys. Soc. Jpn. **62**, 2803 (1993).
[21] I. B. Goldberg and M. Weger, J. Phys. Soc. Jpn. **24**, 1279 (1968).
[22] K. Magishi *et al.* (unpublished).
[23] S. Schmitt-Rink *et al.*, Phys. Rev. Lett. **57**, 2575 (1986).
[24] T. Hotta, J. Phys. Soc. Jpn. **62**, 7895 (1993).
[25] P. J. Hirschfeld and N. Goldenfeld, Phys. Rev. B **48**, 4219 (1993).