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Responses of the pseudogap and *d*-wave superconductivity to high magnetic fields in the underdoped high-T_c superconductor $YBa_2Cu_4O_8$: An NMR study

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The responses to the magnetic field (H) of the pseudogap and the superconductivity in the underdoped high-T_c cuprate $YBa_2Cu_4O_8$ ($T_c=74$ K) are reported up to 23.2 T based on NMR measurements. Even though 23.2 T reduces T_c by 26%, no effect is seen on the normal-state pseudogap, which persists in the temperature range where the superconductivity is destroyed by the field. For temperatures $T \leq 15$ K, the spin Knight shift increases with increasing H and also the H and T variation of the ^{63}Cu nuclear spin-lattice relaxation rate ($1/T_1$) is $1/T_1 \propto TH$. A possible explanation for this finding is offered as due to the H-induced quasiparticle states that extend from the d-wave vortex centers with ungapped spectrum. [S0163-1829(99)50438-4]

The high-temperature superconducting (SC) Cu-oxides (high-T_c cuprates) exhibit many unconventional aspects. First, there is the puzzling appearance of the so-called pseudogap in the normal state above T_c. This is a phenomenon of suppression of the spectral weight of the quasiparticles, which was first suggested as a spin gap by nuclear magnetic resonance (NMR)[1] and neutron-scattering experiments,[2] but shown to be a quasiparticle gap.[3] In the NMR measurement, the pseudogap is characterized by the decrease of $1/T_1T$ above T_c which probes the low-energy dynamical susceptibility. The pseudogap was also found subsequently in resistivity,[4] optical reflectivity,[5] and others.[6] Perhaps the most direct evidence is from the angle-resolved photoemission spectroscopy (ARPES).[7] The ARPES finding of the $d_{x^2-y^2}$-like symmetry of the pseudogap has led many people to propose that it is a precursor of $d_{x^2-y^2}$ superconductivity caused by Cooper pairs formed above T_c.[8,9]

Another aspect of the cuprates which has attracted great attention is the SC state. There is strong evidence that the pairing symmetry is d-wave, which differs from s-wave symmetry in that it has nodes at the Fermi surface. The low-energy excitations are gapless, which leads to new phenomena such as a power-law temperature (T) dependence for the thermodynamic quantities at low T. Because of this anisotropy of the SC energy gap, the response of d-wave superconductors to a magnetic field is also of great interest. Substantial works have been devoted to the study of the vortex state.[10–18] The gap for d-wave superconductivity vanishes in the nodes leading to a divergent ξ along the nodal directions. The corresponding quasiparticle state associated with vortices is, therefore, expected to have very different properties from those of s-wave superconductors.[19]

In this paper, we report the responses to the magnetic field (H) of the pseudogap and the superconductivity in the underdoped high-T_c cuprate $YBa_2Cu_4O_8$ based on ^{63}Cu NMR measurements in the CuO_2 plane at fields up to 23.2 T. The T_c of this sample is 74 K (Ref. 20) which is slightly lower than the typical value of 80 K. However, no difference in $1/T_1$ arising from this difference of T_c was detected by measuring a later sample of $T_c=80$ K. We used aligned powder as described previously.[21] The T_c under the field $H=23.2$ T parallel to the c axis was found to be 55 K by measuring the frequency shift of the NMR resonance circuit. Figure 1 shows some typical spectra at various H and T for the central transition at which measurements of $1/T_1$ and the Knight shift K were made. The alignment is satisfactorily good. For the field alignment $H \| c$ axis, the planar site Cu(2) is well separated from the CuO chain site Cu(1) at all H and T. For $H \perp c$ axis, the separation between the two spectra is good at low fields, but they overlap at $H=23.2$ T. The full width at half maximum of Cu(2) is ~ 90 Oe at $T=77$ K for both field alignments. At $T=4.2$ K, it increases to ~ 220 Oe ($H \| c$) and ~ 250 Oe ($H \perp c$) at $H=23.2$ T.

$1/T_1$ for $H \| c$ axis were extracted from fitting the nuclear magnetization to $[M(\infty)-M(t)]/M(\infty)=0.9\exp(-6t/T_1)+0.1\exp(-t/T_1)$ under magnetic field and $[M(\infty)-M(t)]/M(\infty)=\exp(-3t/T_1)$ at $H=0$, respectively. The strength of the RF field H_1 was ~ 100 Oe. No H_1 dependence of $1/T_1$ was observed down to half the value of H_1

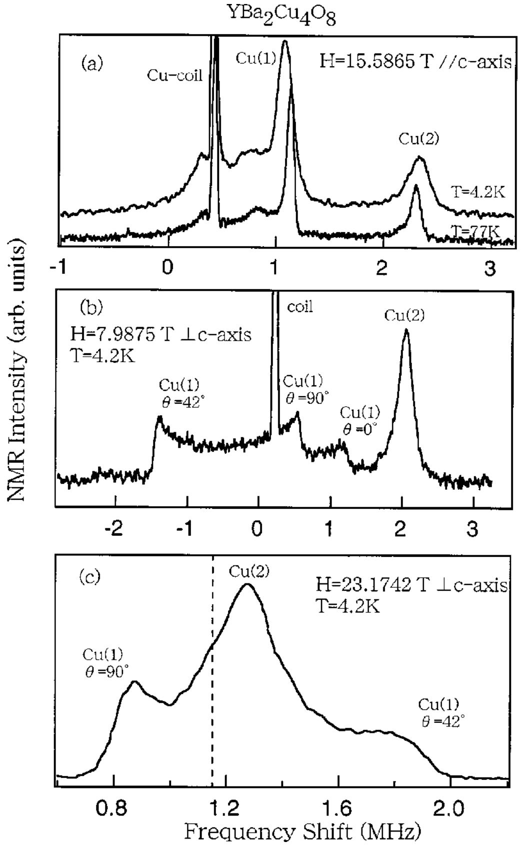

FIG. 1. Typical ^{63}Cu NMR spectra at various H and T. The bottom axis is the frequency (f) shift from γH ($\gamma = 11.285$ MHz/T). (a) The unlabeled two broad peaks are from Cu(1) $\pm\frac{1}{2},\pm\frac{3}{2}$ transitions. (b) θ is the angle between H and the ab axis. (c) The dashed line shows the Cu(2) position if K_{ab} were the same as that at $H=8$ T (see text); the peak for Cu(1), $\theta=0°$ is beyond the measured f range. The spectra in (a) and (b) were obtained by sweeping H at fixed f and then converted to the f spectra.

that we used. K for $H\perp c$ axis was measured by sweeping frequency at fixed field H_0 and determined from the relation[22] $\Delta\omega/\omega = K + 3\nu_Q^2/[16(\gamma_n H_0)^2(1+K)] + \delta$, where $\Delta\omega/\omega$ is the measured frequency shift of the resonance peak, ν_Q is the quadrupolar frequency, and δ is the shift due to the fourth-order perturbation of the nuclear quadrupolar interaction. We have used the T-dependent value of ν_Q reported in Ref. 23. We estimate δ to be 0.01% at 8 T and negligibly small (10^{-6}) at 23.2 T.

First, we discuss the results above $T_c(H=0)=74$ K. Figure 2 shows the T dependence of $1/T_1T$ for ^{63}Cu at $H=0$ T,[20] 11 T, 15.6 T, and 23.2 T for $H\|c$ axis. $1/T_1T$ is related to the dynamical susceptibility $\chi(q,\omega)$ by $1/T_1T = 3k_B/4(1/\mu_B^2\hbar^2)\Sigma_q A_q A_{-q}[\mathrm{Im}\chi(q,\omega)/\omega]$,[24] where A_q is the hyperfine coupling constant and *Im* means the imaginary part. In optimal or overdoped materials, $1/T_1T$ increases down to T_c as T is lowered.[25] This behavior is understood as due to the development of antiferromagnetic spin correlations as T decreases. In underdoped materials, however, $1/T_1T$ increases with decreasing T down to a certain temperature T^* which is above T_c but starts to decrease upon further cooling, forming a broad peak around T^*. As seen in Fig. 2, in $YBa_2Cu_4O_8$, $T^*\simeq 160$ K. We refer this T^*, around which anomalies are also observed in resistivity[4] and

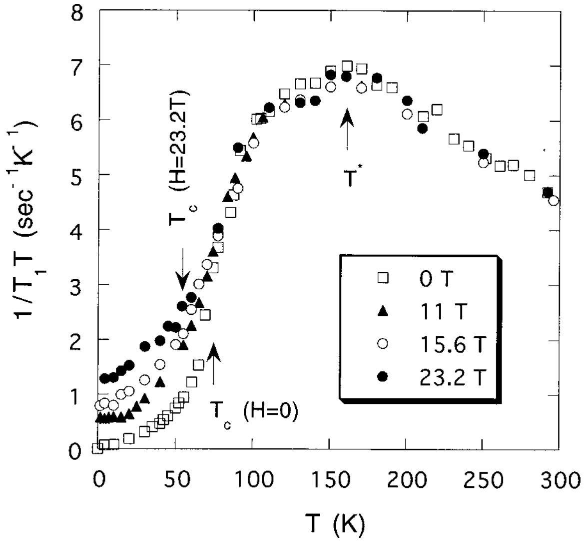

FIG. 2. $1/T_1T$ vs T and $H\|c$ axis for planar ^{63}Cu. The pseudogap temperature T^* is not affected by the field.

optical reflectivity,[5] to the pseudogap temperature. There are many theoretical proposals for the pseudogap, including the resonating-valence-bond spin-singlet formation,[26] spin-density-wave instability[27] and the SC precursor that the incoherent Cooper pairs are formed above T_c.[8,9] The recent ARPES measurements have revealed that the pseudogap has a $d_{x^2-y^2}$ symmetry which evolves smoothly into the SC state.[7] This result has been widely considered to favor the superconductivity precursor scenarios.

As seen in Fig. 2, we found that the magnetic field of 23.2 T, which reduces T_c from 74 K to 55 K, i.e., by 26% of its original value, has no effect on the pseudogap. This result appears to argue against superconductivity precursor scenarios since one expects that the strong magnetic field would have a strong effect on the superconducting fluctuations due to quantization of orbital motions. It is therefore suggested that the pseudogap is a consequence of strong electron-electron correlation effects.

Next we discuss the results well below $T_c(H=0) = 74$ K. Figure 3 shows the shift K_{ab} of ^{63}Cu at $H=8$ T and 23.2 T perpendicular to the c axis. The spin part of K_c for $H\|c$ axis is small. Our data at $H=8$ T in the normal state are in good agreement with those of Zimmerman *et al.*, who measured K_{ab} from 80 to 500 K.[28] No appreciable field effect on K_{ab} was found in the normal state. However, K_{ab} is substantially increased by H at low T [also see Fig. 1(c)]. The measured shift is decomposed as $K_{ab}=K_s+K_{dia}+K_{orb}$ where K_s is the shift due to spin susceptibility, and K_{orb} and K_{dia} are, respectively, the contributions of the orbital susceptibility and SC diamagnetism. Furthermore, K_s is related to the density of states (DOS) at the Fermi level by $K_s = -4\mu_B^2 A_s \int_0^\infty N_s(E)[\partial f(E)/\partial E]dE$, where A_s is the hyperfine coupling constant. At low T, $K_s \propto N_s(0)$. In general, K_{orb} is considered to be T and H independent in the range where our experiment is carried out. We estimate the diamagnetic shift to be $-0.02\%, -0.009\%$, and -0.005% at $H=8$ T, 15.6 T, and 23.2 T, respectively, by using $H_{dia} = (\phi_0/4\pi\lambda_{ab}\lambda_c)\ln(\beta e^{-1/2}d/\sqrt{\xi_{ab}\xi_c})$, where ϕ_0 is the flux quantum, λ is the penetration depth, d is the vortex distance, and $\beta=0.381$.[29] We have used $\xi_{ab}=22$ Å extracted from

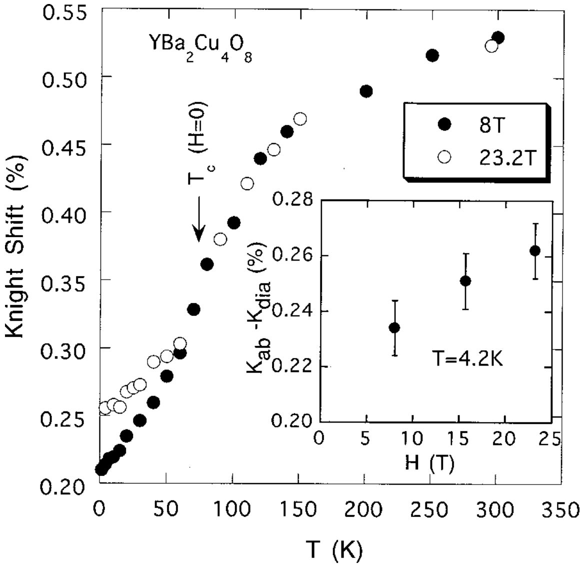

FIG. 3. Knight shift of planar ^{63}Cu at 8 and 23.2 T with field perpendicular to the c axis. The reduction of T_c by $H=23.2$ T for this field alignment is estimated to be 2.5 K. The inset shows the field dependence of $K_{ab}-K_{dia}$ at $T=4.2$ K.

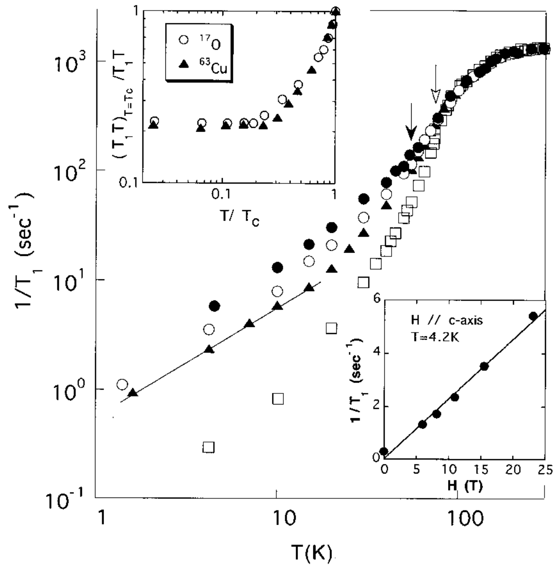

FIG. 4. $1/T_1$ of ^{63}Cu vs T at various $H\|c$ axis. The symbols are the same as those in Fig. 2. The open and filled arrows indicate T_c at 0 and 23.2 T, respectively. The solid line indicates the $1/T_1 \propto T$ relation. The upper inset shows $1/T_1T$ normalized by its value at $T_c(H)$ vs reduced temperature $T/T_c(H)$ for ^{63}Cu and ^{17}O at $H=11$ T. The lower inset shows $1/T_1$ vs H at $T=4.2$ K. The line is a linear fit that omits the zero-field datum, which might be affected by extrinsic relaxations due to, e.g., magnetic impurities.

$H_{c2}(H\|c \text{ axis})=70$ T which was determined from the initial slope of T_c suppression by the field,[30] $\lambda_{ab}=\sqrt{\lambda_a\lambda_b}=1300$ Å, $\lambda_c=9000$ Å (Ref. 31), and the relation $\lambda_c/\lambda_{ab}=\xi_{ab}/\xi_c$. Actually, Barrett *et al.* observed for $YBa_2Cu_3O_7$ ($T_c=90$ K) a diamagnetic shift of -0.02% at $H(\perp c)=8$ T using an NMR measurement of ^{89}Y.[32] Although we could measure the shift at lower H, the diamagnetic shift then becomes significant which prevents a reliable evaluation of K_s. After accounting for the diamagnetic contribution, $K_s=K_{ab}-K_{dia}$ is plotted against H in the inset of Fig. 3. We find that K_s increases by $0.03\%\pm0.01\%$ on going from 8 to 23.2 T.

It is hard to explain in the framework of theories for conventional superconductors the present experimental finding which appears to be compatible with the specific-heat measurements.[17] Since the vortex core volume fraction $\sim H/H_{c2}(H\perp c)\leq 0.05$ is very small, where $H_{c2}(H\perp c)$ is estimated to be 490 T from ξ, quasiparticles in the cores only cannot generate a detectable shift in the full NMR spectrum. Also, the NMR line broadening due to field inhomogeneity in the presence of vortices is given by $1/\sqrt{2}[\phi_0/(2\pi)^{3/2}\lambda^2]$ for BCS superconductors.[29] The line broadening due to such field inhomogeneity is estimated to be 53 Oe for $H\|c$ axis and 8 Oe for $H\perp c$ axis, which is not sufficient to account for the much larger linewidth observed here.

Alternatively, an H-induced gapless state due to d-wave vortex, which has been proposed theoetically,[10–15] may explain the experimental finding. In d-wave superconductors, there are gapless regions (nodes) in particular directions in momentum space. For $d_{x^2-y^2}$ gap symmetry, the nodes are along lines tilted 45° from the Cu-O bonds in the CuO_2 plane. This condition leads to a divergent ξ along the nodes which implies that the quasiparticles are not localized in the core,[11,13] in contrast to s-wave superconductors.[19] In fact, recent theories have indicated that the quasiparticle states are extended outside the core and that they have a continuous excitation spectrum without a gap.[10–15] Volovik[10] found that the DOS associated with an isolated vortex is proportional to $\sqrt{H}$. At high fields, these gapless regions extend along the four nodal directions from a vortex core and overlap each other, forming spatially-connected stripes of gapless regions.[13,15] Ichioka *et al.*,[15] found that in high density of vortices the DOS still increases with increasing field up to H_{c2}, but varies as $N_s(0)/N_0=(H/H_{c2})^{0.41}$, where N_0 is the normal-state DOS. In this situation, the NMR spectrum is a superposition of parts from the regions which are less or little affected by the presence of vortices and those from the regions around vortex cores where the local DOS is larger. The measured shift is a weighted average of various shifts. That the H-induced increase of K_s at low T is quite small is because $H_{c2}(H\perp c)$ is large. In fact, preliminary measurements on an overdoped material which has a smaller H_{c2}, revealed a more significant change of K_s. The spatially inhomogeneous Knight shift may also explain the larger broadening of the NMR line below T_c.

If this is the case, the appearance of H-induced residual DOS in the SC state should also be probed by the T_1 measurements. We plot $1/T_1$ as a function of T in Fig. 4 in logarithmic scales. We remark that there was a short component of T_1 at low T whose fraction was only a few percent of the total; its origin is unclear. The values of $1/T_1$ in Figs. 2 and 4 are those obtained from the fitting of the theoretical equation to the predominant magnetization. There, it is seen that $1/T_1T$ is substantially enhanced by H below $T_c(H=0)=74$ K. The most prominent feature is that when H is large, $1/T_1T$ becomes independent of T below 15 K. It should be emphasized that this conclusion does not depend on the origin of the all short-T_1 component, since if one plots the magnetization as a function of $T\times t$ one finds that the data for all $T \leqslant 15$ K fall on a single curve. The magnetization vs $T \times t$ plot for $H = 11$ T can be found in Fig. 4 of Ref. 30 and qualitatively the same plot was obtained at higher fields. This $1/T_1T = const$ behavior was also observed for the ^{17}O nuclei.[30] In the upper inset of Fig. 4, we plot $1/T_1T$ normalized by its value at $T_c(H = 11\ \mathrm{T})$ against the reduced temperature, $T/T_c(H = 11\ \mathrm{T})$. We see that the data for both ^{63}Cu and ^{17}O fall on the same curve below T_c. Since $1/T_1$ in the d-wave SC state can be described in terms of the DOS as $1/T_1T \propto \int N_s^2(E) f(E)[1 - f(E)] dE$, where $f(E)$ is the Fermi function, this result is strong evidence that $1/T_1$ of both the ^{63}Cu and ^{17}O nuclei probes the same DOS. Note that $1/T_1T \propto N_s(0)^2$ at low T. Moreover, the magnitude of $1/T_1$ below 15 K increases linearly with increasing H. The lower inset of Fig. 4 shows the H dependence of $1/T_1$ at 4.2 K. A spin diffusion to the quasiparticle state with continuous excited spectrum within the core which we suggested previously[30,33] might be able to explain the T_1 result, but cannot explain the Knight-shift result. The identical T dependence of T_1 for both ^{63}Cu and ^{17}O below T_c also appears to argue against the scenario of spin diffusion to the core, since the nuclear spin-spin relaxation time T_2 for these two nuclei is largely different (by a factor of ~ 10).

Thus, the experimental findings appear to be consistent with field-induced gapless regions due to d-wave symmetry of the superconductivity. Since ξ saturates at temperatures far below T_c, the $1/T_1T$ and K_s become T independent at $T \leqslant 15$ K. It is, however, difficult to extract an accurate amount of the intrinsic H-induced DOS at present. More work needs to be done to quantitatively account for the experimental results.

In summary, we have investigated the responses to high magnetic field of the normal-state pseudogap and the superconductivity in the underdoped high-T_c superconductor $YBa_2Cu_4O_8$ ($T_c = 74$ K) based on the NMR measurements. We have found that a field of 23.2 T, which reduces T_c by 26% has no effect on the pseudogap, suggesting that it has a distinct origin from that of the superconductivity. At low temperatures we found that the Knight shift increases with increasing H, being consistent with a field-induced DOS at the Fermi surface. The H and T variations of $1/T_1$ as $1/T_1 \propto TH$ are also consistent with the emergence of H-induced DOS.

Note added in proof. After submitting this manuscript, two papers [K. Gorny *et al.*, Phys. Rev. Lett. **82**, 177 (1999) and V. F. Mitrovic *et al.*, *ibid.* **82**, 2784 (1999)] on the spin-lattice relaxation under magnetic fields in the normal state of the optimally doped $YBa_2Cu_3O_7$, inconsistent with each other though, have appeared.

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[1] Y. Yasuoka *et al.*, in *Strong Correlation and Superconductivity*, edited by H. Fukuyama *et al.* (Springer-Verlag, Berlin, 1989), p. 254; W.W. Warren *et al.*, Phys. Rev. Lett. **62**, 1193 (1989).
[2] J. Rossat-Mignod *et al.*, Physica C **185-189**, 86 (1991).
[3] J.W. Loram *et al.*, Physica C **235-240**, 134 (1994); J. Supercond. **7**, 243 (1994).
[4] B. Bucher *et al.*, Phys. Rev. Lett. **70**, 2012 (1993).
[5] D.N. Basov *et al.*, Phys. Rev. Lett. **77**, 4090 (1996).
[6] G.V.M. Williams *et al.*, Phys. Rev. Lett. **78**, 721 (1997); J. Babroff *et al.*, *ibid.* **78**, 3757 (1997); M. Oda *et al.*, Physica C **281**, 135 (1997).
[7] H. Ding *et al.*, Nature (London) **382**, 51 (1996); A.G. Loeser *et al.*, Science **273**, 325 (1996).
[8] V.J. Emery and S.A. Kivelson, Nature (London) **374**, 434 (1995).
[9] J. Ranninger and J.M. Robin, Phys. Rev. B **53**, R11 961 (1996); B. Janko *et al.*, *ibid.* **56**, R11 407 (1997).
[10] G.E. Volovik, Pis'ma Zh. Éksp. Teor. Fiz. **58**, 457 (1993) [JETP Lett. **58**, 469 (1993)].
[11] Y. Wang and A.H. MacDonald, Phys. Rev. B **52**, R3876 (1995).
[12] H. Won and K. Maki, Phys. Rev. B **53**, 5927 (1996).
[13] M. Ichioka *et al.*, Phys. Rev. B **53**, 15 316 (1996).
[14] M. Franz and Z. Tesanovic, Phys. Rev. Lett. **80**, 4763 (1998).
[15] M. Ichioka, A. Hasegawa, and K. Machida, Phys. Rev. B **59**, 184 (1999).
[16] K. Karrai *et al.*, Phys. Rev. Lett. **69**, 152 (1992).
[17] K.A. Moler *et al.*, Phys. Rev. Lett. **73**, 2744 (1994); B. Revaz *et al.*, *ibid.* **80**, 3364 (1998).
[18] I. Maggio-Aprile *et al.*, Phys. Rev. Lett. **75**, 2754 (1995); Ch. Renner *et al.*, *ibid.* **80**, 3606 (1998).
[19] C. Caroli, P.G. de Gennes, and J. Matricon, Phys. Lett. **9**, 307 (1964).
[20] Y. Kodama *et al.*, Physica C **185-189**, 1033 (1991).
[21] G.-q. Zheng *et al.*, Physica C **193**, 154 (1992); J. Phys. Soc. Jpn. **62**, 2591 (1993).
[22] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).
[23] H. Zimmermann *et al.*, Physica C **159**, 681 (1989).
[24] T. Moriya, J. Phys. Soc. Jpn. **18**, 516 (1963).
[25] See, e.g., K. Asayama *et al.*, Prog. Nucl. Magn. Reson. Spectrosc. **28**, 28 (1996).
[26] T. Tanamoto, H. Kohno, and H. Fukuyama, J. Phys. Soc. Jpn. **63**, 2739 (1994).
[27] A.P. Kampf and J.R. Schrieffer, Phys. Rev. B **41**, 6399 (1990); K. Miyake and O. Narikiyo, J. Phys. Soc. Jpn. **63**, 3821 (1994); J. Schmalian, D. Pines, and B. Stojkovic, Phys. Rev. Lett. **80**, 3839 (1998).
[28] H. Zimmermann *et al.*, Physica C **185-189**, 1145 (1991).
[29] P.G. de Gennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966).
[30] G.-q. Zheng *et al.*, Physica C **227**, 169 (1994).
[31] D.N. Basov *et al.*, Phys. Rev. B **50**, 3511 (1994).
[32] S.E. Barret *et al.*, Phys. Rev. B **41**, 6283 (1990).
[33] K. Ishida *et al.*, Solid State Commun. **90**, 563 (1994); J.A. Martindale *et al.*, Phys. Rev. B **50**, 13 645 (1994).