Suppression of the Superconducting Condensate in the High-T_c Cuprates by Zn Substitution and Overdoping: Evidence for an Unconventional Pairing State

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By muon spin rotation we studied the depression in condensate density, n_s by Zn substitution in underdoped, optimal-doped, and overdoped $Y_{0.8}Ca_{0.2}Ba_2(Cu_{1-y}Zn_y)_3O_{7-\delta}$. The rapid initial decrease of n_s is inconsistent with s-wave pairing and magnetic scattering but points towards a d-wave pairing state with nonmagnetic scattering in the unitarity limit irrespective of the doping state. A similar conclusion is inferred from the depression of T_c and n_s with overdoping in the pure compounds where pair breaking appears to be associated with increasing three dimensionality. [S0031-9007(96)01076-9]

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The symmetry of the superconducting order parameter (OP) of the cuprate high-T_c superconductors is the subject of ongoing research and debate. Recently, a number of experimental results favor a highly asymmetric OP, possibly $d_{x^2-y^2}$. In spite of this, results from direct studies of the symmetry of the superconducting OP, for example, by angle-resolved photoemission [1] or tunneling experiments [2], are still somewhat controversial. The same ambiguity holds for the attempts to study the integrated excitation spectrum from the T dependence of the superconducting condensate density n_s [3]. It appears that the sample quality may have a significant influence on the experimental results. In fact, the characteristic features of an asymmetric OP are rather sensitive to a small amount of impurities and potential scattering from nonmagnetic impurities causes pair breaking [4]. The averaging over parts of the Fermi surface, where the OP is out of phase, leads to destructive interference and suppresses superconductivity. On the other hand, the structural and electronic asymmetry may be the source of the apparent OP asymmetry. For Y-123, for example, it was shown that the CuO chains become superconducting upon oxygenation [5]. The superconducting state in these one-dimensional CuO chains depends critically on the details of the oxygen content and ordering [5]. Furthermore, the OP's of the CuO_2 sheets and the CuO chains may have opposite sign [6].

Another approach is to study the characteristic response to impurities, which are intentionally incorporated. Depending on the symmetry of the OP, clear differences are predicted for the variation of experimentally accessible parameters such as T_c or n_s [7]. The substitution of Zn for Cu has attracted much attention here because it suppresses T_c exceptionally fast, while not altering the carrier concentration of the CuO_2 sheets, $p_{\rm sh}$ [8–11]. Instead, there are clear signatures of strong pair breaking [8,9]. It is not yet clear if Zn acts purely as a nonmagnetic potential perturbation [12] or if it induces a localized magnetic moment within the antiferromagnetic-correlated matrix of the Cu^{2+} spins [9]. While the rapid depression of T_c may be explained by magnetic pair breaking for any symmetry of the OP, characteristic differences are predicted to occur for the evolution of the superconducting condensate density n_s. These differences should be most pronounced for the low temperature value $n_s(T = 0)$ [7]. The depression of $n_s(T = 0)$ as a function of T_c reduction is expected to be significantly stronger for a system with a d-wave OP, where pair breaking arises from nonmagnetic scattering, than for a system with s-wave OP and pair breaking from magnetic scattering [7]. Even though it should provide a clear answer, this circumstance does not yet appear to have been tested experimentally. In this paper we present the results of such a study which give a clear indication for an unconventional symmetry of the OP.

By transverse-field muon-spin-rotation (TF-μSR) experiments the ratio of the superconducting condensate density to the effective mass n_s/m^*_{ab} [5] was measured for a series of Zn substituted polycrystalline samples $Y_{0.8}Ca_{0.2}Ba_2(Cu_{1-y}Zn_y)_3O_{7-\delta}$ in the underdoped [$\delta = 0.52(1)$], the optimal-doped [$\delta = 0.38(1)$], and the overdoped state [$\delta = 0.16(1)$]. The preparation of Y-123 samples with a high content of Ca on the Y site was described previously [13]. The substitution of 20% of the Y^{3+} by Ca^{2+} introduces additional hole carriers into the CuO_2 sheets, besides the carriers that are transferred from the CuO chains as controlled by the oxygen content δ [5,13]. The evolution of T_c as a function of oxygen content, δ, is shown in Fig. 1 for $y = 0$, 0.02, 0.04, and 0.06. The fully oxygenated sample $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.96(1)}$ is strongly overdoped with $T_c = 46$ K. Upon removing oxygen from the CuO chains T_c first increases towards $T_c = T_{c,\rm max} = 85.5$ K for $\delta = 0.38(1)$ at optimal doping before it decreases towards the underdoped side. Recently, we have shown from μSR experiments that the fully oxygenated CuO chains ($\delta < 0.20$) contribute significantly to the total superconducting condensate [5].

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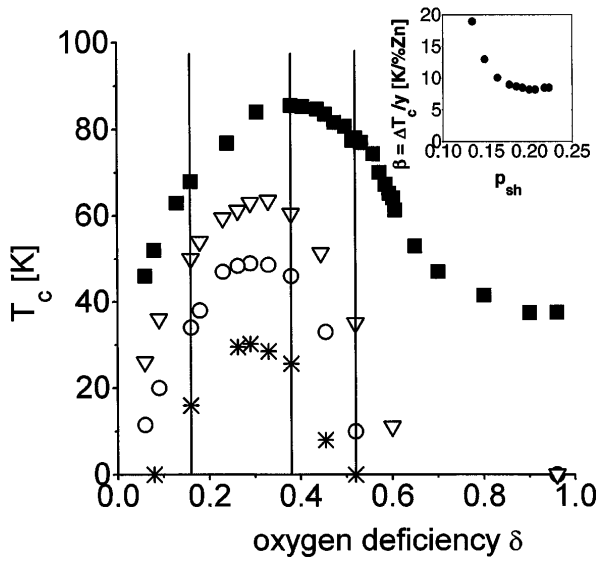

FIG. 1. The evolution of T_c as a function of oxygen deficiency, δ, for $Y_{0.8}Ca_{0.2}Ba_2(Cu_{1-y}Zn_y)_3O_{7-\delta}$ with $y = 0$ (■), $y = 0.02$ (▽), $y = 0.04$ (○), and $y = 0.06$ (∗). Inset: the fractional T_c depression $\beta = \Delta T_c/\Delta y$ as a function of $p_{\rm sh}$.

This "chain condensate" is rather hard to control, as it depends on the details of the oxygen ordering [5]. For the samples used in the present study the CuO_2 sheets are strongly overdoped prior to the formation of this "chain condensate." Any complications with the chain condensate therefore were avoided and most likely even for our overdoped ($\delta = 0.16$) series.

A constant carrier concentration $p_{\rm sh}$ was ensured for each series by annealing under identical conditions. Furthermore, $p_{\rm sh}$ was determined from measurements of the thermoelectric power (TEP) [10,11]. Recently, it was shown that the substitution of Zn affects the TEP only below a temperature T_g that corresponds to the opening of the "pseudogap" in the normal state [11], as probed, for example, by NMR [9] and specific heat [8]. Above T_g the TEP does not depend on the Zn content [11] and, as for Zn-free samples, $p_{\rm sh}$ can be determined from the TEP at room temperature [10,13]. Shown in the inset of Fig. 1 is the evolution of the depression rate $\beta = \Delta T_c/\Delta y$ plotted as a function of $p_{\rm sh}$. For the optimally doped series we find $\beta \sim 10$ K/% Zn in good agreement with the values reported for Ca-free $YBa_2(Cu_{1-y}Zn_y)_3O_7$ [8,9,14]. On progressing from the underdoped to the overdoped side β falls sharply, due primarily to the fact that Zn substitution displaces the maximum in the phase curve $T_c(p_{\rm sh})$ to higher values of $p_{\rm sh}$. We show elsewhere that a similar trend occurs for $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$, in both cases the maximum tracks the pseudogap line $T_g(p_{\rm sh})$ and falls to zero when $T_g = 0$ at about $p_{\rm sh} = 0.19$ [15].

The TF-μSR experiments were performed at the MUSR beam line of the Rutherford Appleton Laboratory (RAL) in Chilton, UK, and at the πM3 beam line at the Paul-Scherrer-Institute (PSI) in Villigen, CH. Disks of sintered or powdered and pressed samples were field cooled in a magnetic field of $B = 40$ mT (RAL) or 0.3 T (PSI) [5]. Only minor differences were observed between the results obtained at 40 mT and 0.3 T. The μSR time spectra were analyzed by performing least squares fits with a Gaussian relaxation function $\exp(-\sigma^2 t^2/2)$. From the Gaussian depolarization rate σ we derived the in-plane penetration depth λ_{ab} and the ratio of the condensate density n_s to the effective mass m^*_{ab} [5,16]:

$$\sigma \propto \lambda_{ab}^{-2} = \frac{4\pi e^2}{c^2}\frac{n_s}{m^*_{ab}}$$

Such a data analysis presupposes that the distribution of μSR precession frequencies $F(\omega_\mu)$ is Gaussian with $\sigma^2 \sim \langle \Delta\omega_\mu^2 \rangle$ [16], a requirement which indeed is satisfactorily fulfilled for our polycrystalline samples. This is evident from the inset of Fig. 2, where $F(\omega_\mu)$, as derived from a fast Fourier transformation (symbols), is presented for three representative samples together with the corresponding Gaussian distributions (solid lines). When $\langle \Delta\omega_\mu^2 \rangle$ is extracted directly from $F(\omega_\mu)$ only minor differences occur (<5%) that do not affect the conclusions drawn in this Letter.

In the following only the low temperature values $\sigma_0 \sim n_s(T = 0)/m^*_{ab}$ are considered. Summarized in Fig. 2 are the results of our TF-μSR experiments, which are shown by the full squares for the optimally doped series of $Y_{0.8}Ca_{0.2}Ba_2(Cu_{1-y}Zn_y)_3O_{6.62(1)}$ for $y = 0$, 0.0025, 0.0035, 0.005, 0.01, 0.02, 0.04, and 0.06; by the full circles for the underdoped series for $\delta = 0.52(1)$ and $y = 0$, 0.0025, 0.005, 0.01, and 0.02; by the full triangles for the overdoped series for $\delta = 0.16(1)$ and $y = 0$, 0.005, 0.01, 0.02, 0.04, and 0.06; and by the open circles for the overdoped series of $La_{1.79}Sr_{0.21}Cu_{1-y}Zn_yO_4$ for $y = 0$, 0.01, and 0.02. Finally, as shown by the crosses, we have included previous data on almost fully oxygenated $YBa_2(Cu_{1-y}Zn_y)_3O_{7-\delta}$ [17]. The ratio of the condensate density relative to that of the Zn-free sample, $\sigma_0(y)/\sigma_0(y = 0) = n_s^0(y)/n_s^0(y = 0)$, is plotted as a function of the depression of the critical temperature, $[T_c(y) - T_c(y = 0)]/T_c(y = 0)$. In the following, we assume that the changes in the effective mass of the carriers due to the Zn substitution are negligible compared to those in n_s. This assumption is supported by measurements of the specific heat [8] and the ^{89}Y-NMR Knight shift [9], which indicate that $N(\varepsilon_F)$ is not affected by the Zn substitution. The most striking feature of our data is the very rapid initial decrease (for low Zn content) of he condensate density, which is even more pronounced than the corresponding suppression of T_c. In fact, such a rapid depression of n_s is the characteristic feature which is expected for a system with a $d_{x^2-y^2}$-wave OP when nonmagnetic impurities lead to isotropic scattering in the unitarity limit [7] as is shown in Fig. 2 by the solid line. The dashed line represents the Born limit for weak nonmagnetic scattering and a $d_{x^2-y^2}$-wave OP[7]. The corresponding behavior for an s-wave OP (where T_c is substantially reduced only by magnetic scattering)

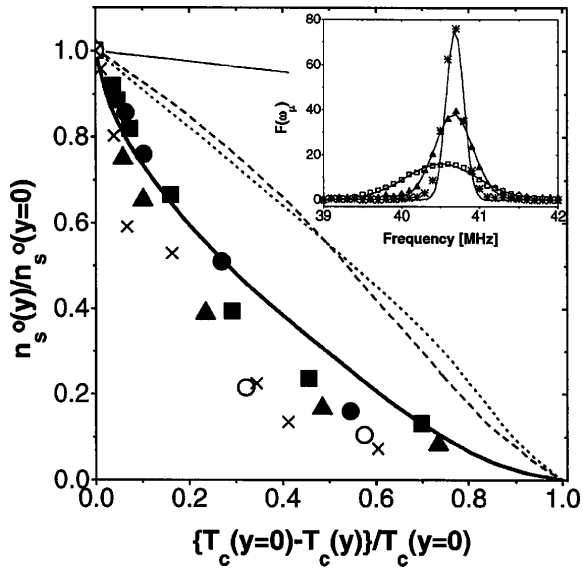

FIG. 2. The depression of the normalized superconducting condensate density $n_s^0(y)/n_s^0(y=0)$ plotted as a function of the relative decrease in T_c. Data are shown for the underdoped (●), optimally doped (■), and overdoped series (▲) of $Y_{0.8}Ca_{0.2}Ba_2(Cu_{1-y}Zn_y)_3O_{7-\delta}$ and for overdoped $La_{1.79}Sr_{0.21}Cu_{1-y}Zn_yO_4$ (○). The crosses represent previous results for almost fully oxygenated $YBa_2(Cu_{1-y}Zn_y)_3O_{7-\delta}$ [17]. The expected behavior for a $d_{x^2-y^2}$ symmetry of the OP and nonmagnetic elastic scattering in the unitarity limit (Born limit) is shown by the solid (dashed) line. The corresponding case of an isotropic s-wave OP with magnetic scattering is shown by the dotted (thin solid) line for the dirty (clean) limit. Inset: Shown are the spectra of $F(\omega_\mu)$ as derived by fast Fourier transformation for three representative samples of the optimally doped series with $y = 0.0035$ (□), 0.02(▲), and 0.06 (*). The solid lines represent the Gaussian distributions where σ was derived by fitting the μSR time spectra.

is shown for the so-called "clean limit" ($\ell \gg \xi_0$, thin solid line [18]) and the "dirty limit" ($\ell \ll \xi_0$, dotted line [19]), where ξ_0 is the superconducting coherence length and ℓ is the transport mean free path. Estimates for ℓ may be derived from the residual resistivity of Zn substituted Y-123 single crystals [14]. With $\Delta\rho^{2D}(T \to 0) = 227\ \Omega/\Box$ per CuO_2 sheet and 1% Zn,

$$\ell^{2D} = \frac{m_e v_F^{2D}}{e^2 n^{2D} \Delta\rho^{2D}} = \frac{\hbar\sqrt{2\pi}}{\sqrt{n^{2D} e^2 \Delta\rho^{2D}}},$$

$n^{2D} = p_{sh}/ab$, and $p_{sh} \sim 0.18$ we derive $\ell^{2D} \sim 4.1/y$ [Å]. This implies that our samples are in the clean limit and for any model based on an isotropic s-wave OP, therefore, the dotted line should be relevant. A very similar result can be expected for an anisotropic s-wave OP where the rapid depression of T_c again can be explained only in terms of magnetic pair breaking [20]. Clearly, an adequate description of our experimental data can be achieved only by a model that is based on a $d_{x^2-y^2}$- wave OP (or a similarly unconventional OP which changes sign in k space so its average over the Fermi surface is almost zero), where Zn causes strong potential scattering in the unitarity limit [7]. Our results contradict a scenario where strong pair breaking is thought to arise from inelastic scattering on magnetic moments that are induced by the Zn [9]. This conclusion is supported by recent Al-NMR studies on Al-substituted $La_{1.85}Sr_{0.15}CuO_4$ [21].

Given an unconventional symmetry of the superconducting OP, the question arises why other potential perturbations, like the Ca substituents on the Y site, do not have such a deleterious effect. While superconductivity is almost completely destroyed by 6% of Zn on the Cu site, the substitution of 20% Ca on the nearby Y site has hardly any effect on the superconducting state, but for the changes in p_{sh}. The only possible answer is that the dynamics of the superconducting charge carriers of the cuprate high temperature superconductors must be confined to the two-dimensional (2D) CuO_2 sheets. In a three-dimensional (3D) system, instead, superconductivity would be strongly suppressed by electron-electron scattering [22] and/or potential scattering from structural perturbations which are always present within the M-O interlayers that separate the CuO_2 sheets. Based on these considerations one may come to a natural understanding of the suppression of both T_c and the condensate density n_s in the overdoped regime [23]. There is conclusive experimental evidence that the dynamics of the carriers becomes more three-dimensional once p_{sh} increases beyond optimal doping. With increasing p_{sh} a systematic reduction of the electronic anisotropy was reported for all systems investigated to date [24]. Studies of the optical reflectivity indicate that coherent c-axis charge transport sets in beyond optimum doping [25], while on the underdoped side a pseudo gap exists in the c-axis excitation spectrum [26]. At the same time photoabsorption measurements indicate a strong increase in the carrier occupation of the "off-plane" $O(p_z)$ orbitals [27]. The reduction of T_c and n_s in the overdoped regime [23] can thus be explained by the increasing 3D electron dynamics which brings into play additional strong pair breaking mechanisms. Shown in Fig. 3 by the asterisks are our data on optimally- doped to overdoped $Tl_2Ba_2CuO_{6+\delta}$ [23] reanalyzed in terms of the above scenario. In analogy to the case of the Zn substituted samples the suppression of n_s is displayed as a function of the relative T_c suppression. In this case, however, the undisturbed values of n_s^0 and T_c^0 cannot be measured by experiment. It is still possible, however, to find reasonable estimates. We assumed that $T_c^0 = T_{c,max}$ throughout the overdoped regime. In fact, given a d-wave OP whose pairing mechanism most likely is based on the antiferromagnetic fluctuations, it is more likely that T_c^0 decreases on the overdoped side. To estimate the condensate density in the absence of pair breaking we assumed that n_s^0 continues to grow linearly with p_{sh} on the overdoped side. For the relationship between T_c and p_{sh} we adopted the empirical formula $p_{sh} = 0.16 \pm \{(1 - T_c/T_{c,max})/82.6\}^{1/2}$ [13]. For the overdoped side we then derive that $n_s^0(p_{sh}) = n_s^0(p^*)\{1 + [(1 - T_c(p_{sh})/T_{c,max})/82.6]^{1/2}/0.11\}$, where $n_s^0(p^*)$ is the

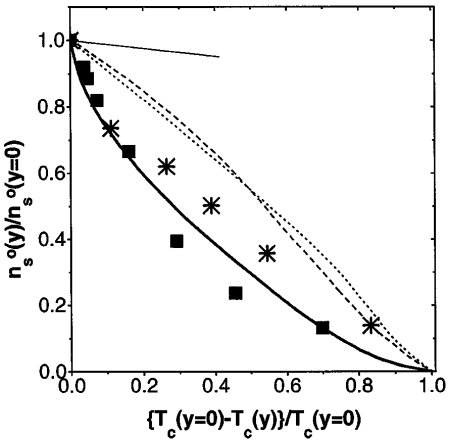

FIG. 3. The depression of the normalized superconducting condensate density $n_s^0(y)/n_s^0(y=0)$ as a function of the relative decrease in T_c. Asterisks show the data for optimally doped to overdoped $Tl_2Ba_2CuO_{6+\delta}$ [23]. For comparison, the theoretically expected behavior as well as the data for the optimally doped $Y_{0.8}Ca_{0.2}Ba_2(Cu_{1-y}Zn_y)_3O_{6.62(1)}$ are shown by the same symbols as in Fig. 2.

condensate density measured at optimum doping. With $T_c^0 = T_{c,\max} = 90$ K and $n_s^0(p^*) \sim \sigma(T=0,p^*) = 2.7\ \mu s^{-1}$ [23] we then derive the values shown in Fig. 3. Clearly, the result of these estimates is consistent with a d-wave model in which pair breaking is caused by nonmagnetic scattering when the electron dynamics becomes more 3D on the overdoped side. We point out that the estimates for the relative suppression of the condensate density were chosen conservatively. Given the uncertainty in our estimates, we cannot address the question if the nonmagnetic scattering introduced in the overdoped regime is in the unitarity limit or in the Born limit. A further question is whether the 3D electron-electron scattering or rather the scattering from structural defectors in the M-O interlayers is the primary source of the suppression of n_s and T_c. The universal nature of the phase diagram would suggest the former.

In summary, from TF-μSR measurements we determined the depression in condensate density due to Zn substitution in underdoped, optimal-doped, and overdoped $Y_{0.8}Ca_{0.2}Ba_2(Cu_{1-y}Zn_y)_3O_{7-\delta}$ and $La_{1.79}Sr_{0.21}Cu_{1-y}Zn_yO_4$. The combined depression in T_c and n_s is inconsistent with an isotropic or anisotropic s-wave pairing state but points to a d-wave scenario where Zn causes nonmagnetic (elastic) scattering. We come to a similar conclusion concerning the intrinsic depression in T_c and n_s with overdoping in the pure compounds. Here the pair-breaking elastic scattering is associated most likely with the increasingly 3D electron dynamics in the overdoped state, which is attributable to the closing of the normal state pseudogap.

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Note added.—We see no evidence for a d-wave to s-wave crossover with overdoping as has been suggested by recent angle-resolved photoemission studies [R. J. Kelley *et al.*, Science **211**, 1255 (1996)].

[1] H. Ding *et al.*, Phys. Rev. Lett. **74**, 2784 (1995); Z.-X. Shen *et al.*, Phys. Rev. Lett. **70**, 1553 (1993).
[2] P. Chaudhari and S.-Y. Lin, Phys. Rev. Lett. **72**, 1084 (1994); D. A. Wollman *et al.*, Phys. Rev. Lett. **71**, 2134 (1993); I. I. Mazin *et al.*, Phys. Rev. Lett. **75**, 2574 (1995).
[3] See, for example, W. N. Hardy *et al.*, Phys. Rev. Lett. **70**, 3999 (1993); J. E. Sonier *et al.*, Phys. Rev. Lett. **72**, 744 (1994); N. Klein *et al.*, Phys. Rev. Lett. **71**, 3355 (1993).
[4] P. A. Lee, Phys. Rev. Lett. **71**, 1887 (1993); A. A. Abrikosov, Physica (Amsterdam) **214C**, 107 (1993).
[5] J. L. Tallon *et al.*, Phys. Rev. Lett. **74**, 1008 (1995); C. Bernhard *et al.*, Phys. Rev. B **52**, 10 488 (1995).
[6] R. Combescot and X. Leyronas, Phys. Rev. Lett. **75**, 3732 (1995).
[7] H. Kim *et al.*, Phys. Rev. B **49**, 3544 (1994); Y. Sun and K. Maki, Phys. Rev. B **50**, 6059 (1995); P. J. Hirschfeld and N. Goldenfeld, Phys. Rev. B **48**, 4219 (1993); T. Hotta, J. Jpn. Phys. Soc. **62**, 274 (1993).
[8] J. W. Loram *et al.*, Physica (Amsterdam) **171C**, 243 (1990).
[9] H. Alloul *et al.*, Phys. Rev. Lett. **67**, 3140 (1991).
[10] S. D. Obertelli *et al.*, Phys. Rev. B **46**, 14 928 (1992).
[11] J. L. Tallon *et al.*, Phys. Rev. Lett. **75**, 4114 (1995).
[12] R. E. Walstedt *et al.*, Phys. Rev. B **48**, 10 646 (1993); A. Janossy *et al.*, Phys. Rev. B **50**, 3442 (1994).
[13] J. L. Tallon *et al.*, Phys. Rev. B **51**, 12 911 (1995).
[14] T. P. Chien *et al.*, Phys. Rev. Lett. **67**, 2088 (1991).
[15] J. L. Tallon *et al.*,(unpublished).
[16] B. Pümpin *et al.*, Phys. Rev. B **42**, 8019 (1990).
[17] C. Bucci *et al.*, Physica (Amsterdam) **235–240C**, 1849 (1994).
[18] K. Maki (private communication).
[19] K. Maki, in *Superconductivity*, edited by R. D. Parks, (Marcel Dekker, New York, 1969), Vol. II, p. 1035.
[20] L. S. Borkowski and P. J. Hirschfeld, Phys. Rev. B **49**, 15 404 (1994).
[21] K. Ishida *et al.*, Phys. Rev. Lett. **76**, 531 (1996).
[22] A. J. Leggett, Physica (Amsterdam) **199–200B**, 291 (1994).
[23] Ch. Niedermayer *et al.*, Phys. Rev. Lett. **71**, 1764 (1993).
[24] K. Kishio, in *Coherence in Superconductors*, edited by G. Deutscher and A. Revcolevischi (World Scientific, Singapore, 1995).
[25] K. Tamasaku *et al.*, Phys. Rev. Lett. **72**, 3088 (1994).
[26] D. N. Basov *et al.*, Phys. Rev. B **50**, 3511 (1994).
[27] C. T. Chen *et al.*, Phys. Rev. Lett. **68**, 2543 (1992).