Superconducting fluctuations and ^{63}Cu NQR-NMR relaxation in $YBa_2Cu_3O_{7-\delta}$: Effect of magnetic field and a test for the pairing-state symmetry

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(Received 21 June 1996)

Evidence is presented of superconducting fluctuations in the ^{63}Cu NQR-NMR relaxation rate in $YBa_2Cu_3O_{7-\delta}$, as obtained from a careful comparison of measurements carried out in the absence and in the presence of a field parallel to the c axis. It is shown that the field causes a reduction of the relaxation rate W in a range of about 10 K above T_c. This effect is related to the suppression by the magnetic field of the phase-sensitive positive Maki-Thompson contribution while the negative contribution from the DOS fluctuations is almost field independent. Furthermore, it is argued how the fluctuation effects on W can be used to discuss the pairing state symmetry, at variance with the insensitivity of the transport measurements. It is pointed out that the existence of the Maki-Thompson contribution to W evidences an s-wave symmetry component for the pairing in $YBa_2Cu_3O_{7-\delta}$. [S0163-1829(96)52038-2]

One of the most debated issues in solid state physics is presently the problem of the symmetry of the pairing state in the high-temperature superconductors (HTS). The determination of the order parameter symmetry is a crucial step in the attempt to envisage the pairing mechanism, for the subsequent development of a microscopic theory of high-temperature superconductivity. The direct way to analyze the anisotropy of the phase of the order parameter is to look at the phase coherence of Josephson and tunnel junctions. This type of experiment seems to support a superconducting pairing state with $d_{x^2-y^2}$ symmetry in HTS.[1,2] Studies of the amplitude of the order parameter may also be fruitful and in this respect one tool is offered by the superconducting fluctuations (SF) above T_c, since the theory of fluctuation effects is now well established. One of the aims of the present paper is to analyze how the interpretation of experimental results on fluctuation effects in HTS should be changed if one assumes a d- rather than an s-pairing state. Furthermore, we would like to point out that SF above T_c can be evidenced by a comparison of the ^{63}Cu NQR and NMR relaxation rates $W(H=0)$ and $W(H)$, respectively. This comparison offers a test for deriving information on the pairing state. The role of the density of states (DOS) fluctuations in c-axis transport of HTS materials has been widely discussed in a number of theoretical and experimental papers.[3–9] The tunneling character of the interplane electron motion leads to the reduction of the most singular fluctuation contributions (paraconductivity and an anomalous Maki-Thompson one). A less singular negative contribution for $T\rightarrow T_c^+$ related to the fluctuation renormalization of the one-electron DOS is still present.

Recently it was pointed out how the density of states plays an important role in the NMR relaxation rate W.[10] The Aslamazov-Larkin (AL) process does not contribute to W in the case of singlet pairing because of the topological properties of appropriate diagrams for spin susceptibility. The increase, for $T\rightarrow T_c^+$ of another positive contribution, related to the anomalous Maki-Thompson (MT) process, is reduced in the vicinity of the superconducting transition due to the strong pair breaking occurring in HTS. As a result of the competition of MT and DOS contributions with opposite signs a smooth behavior of W on crossing T_c is expected,[10] with a slight maximum above T_c. The occurrence of SF can be evidenced from the comparison of the ^{63}Cu NQR relaxation rate $W(0)$ with the one obtained in an NMR experiment with the external field applied along the c axis. The field causes a further suppression of the positive MT contribution with respect to the one due to intrinsic pair breaking. Then $W(H)$ is decreased with respect to $W(0)$, in a temperature range of about 10 K above T_c.

In the theoretical studies of fluctuation effects in d-wave superconductors the model of tight-binding electrons, with nearest-neighbor transfer and underlying two-dimensional (2D) square lattice, is widely accepted[4,5] with the electron-electron constant

$$V(\mathbf{k},\mathbf{k}')=g_0(\cos k_x a-\cos k_y a)(\cos k_x' a-\cos k_y' a), \quad (1)$$

a being a lattice constant. The main difference between s- and d-wave superconductors lies in the different manifestation of nonmagnetic impurities, which are pair breaking for the last.

In the case of a d-wave superconductor the fluctuation propagator depends upon directions of $\mathbf{k}$ and $\mathbf{k}'$, but using the ansatz

$$L_{\mathbf{kk}'}(\mathbf{q}) = \hat{L}(\mathbf{q})(\cos k_x a - \cos k_y a)(\cos k'_x a - \cos k'_y a) \quad (2)$$

$(\mathbf{q}=\mathbf{k}-\mathbf{k}')$, one can easily solve the Dyson equation for a quantity $\hat{L}(\mathbf{q})$:

$$\hat{L}(\mathbf{q})^{-1} = g_0^{-1} - P(\mathbf{q},\omega_k),$$

$$P(\mathbf{q},\omega_k) = T\sum_{\omega_n} \int \frac{d^2k}{(2\pi)^2}[(\cos k_x a - \cos k_y a)^2 G(\mathbf{k},\omega_n) \times G(\mathbf{q}-\mathbf{k},\omega_k-\omega_n)]. \quad (3)$$

Here

$$G(\mathbf{k},\omega_n)^{-1} = i\omega_n + i\,\mathrm{sgn}\,\omega_n/2\tau - \xi_k,$$
$$\xi_k = -t(\cos k_x a + \cos k_y a) - \mu \quad (4)$$

(t and μ are the transfer integral between the nearest-neighbor sites and the chemical potential, respectively). It is noted that in contrast to an s-wave pairing state, the impurity renormalization of quantity $P(\mathbf{q},\omega_k)$ is absent[3,9] due to the dependence of a bare interaction on the momentum directions.

For temperatures close to T_c Eq. (3) can be easily solved for small $\mathbf{q}$ and ω_k. The divergence of $\hat{L}(\mathbf{q},\omega_k)$ at $\mathbf{q}=\mathbf{0},\omega_k=0$ determines the critical temperature.[4] After straightforward calculations one has

$$\hat{L}(\mathbf{q},\omega_k)^{-1} = \alpha_1\nu\left[\epsilon + \frac{|\omega_k|}{4\pi T}\psi'\left(\frac{1}{2}+\frac{1}{4\pi T\tau}\right) - \frac{\alpha_2(q)}{\alpha_1 4\pi T^2}\psi''\left(\frac{1}{2}+\frac{1}{4\pi T\tau}\right)\right], \quad (5)$$

where $\epsilon=(T-T_c)/T_c$ and T_c is the critical temperature shifted by impurities, in the same manner as paramagnetic impurities shift T_c in the s-wave scenario. In Eq. (5) we have defined $\alpha_1=\langle(\cos k_x a - \cos k_y a)^2\rangle \approx 1$ and $\alpha_2(q)=\langle(\cos k_x a - \cos k_y a)^2\eta^2\rangle \approx a^2t^2q^2$.

Now we turn to the dc conductivity. The contribution of the AL process to in-plane conductivity was calculated by Yip.[3] The current-current response function ignoring factors of order unity is then

$$\sigma_{xx}^{\mathrm{AL}} \approx \psi'\left(\frac{1}{2}+\frac{1}{4\pi T\tau}\right)\frac{e^2}{d\epsilon}.$$

Here the ψ function represents the pair-breaking effect of impurities which in the dirty case reduces the magnitude of the AL conductivity with respect to an s-wave superconductor. As impurity vertex corrections do not contribute, an anomalous MT contribution is absent.[3] Other terms (DOS and regular MT) give

$$Q_{xx}^{\mathrm{DOS}} \approx e^2 T\int \frac{d^2q}{(2\pi)^2}\hat{L}(\mathbf{q},0)T\sum_{\omega_n}\int d\xi_k \nu\left(\frac{\partial \xi_k}{\partial \mathbf{k}}\right)^2 \times G(\mathbf{k},\omega_n)^3 G(-\mathbf{k},-\omega_n),$$

$$\sigma_{xx}^{\mathrm{DOS}} \approx -\frac{e^2}{d}\ln\frac{1}{\epsilon}. \quad (6)$$

In the s-wave case, the DOS contribution does not depend on τ. It is easy to extend the above expressions to layered superconductors. Results are similar to the ones found above: both relevant contributions have the same temperature dependences as for the s-wave case, but different dependences on τ. Namely, the AL contribution is suppressed for dirty superconductors, while the DOS contribution does not depend upon τ.

Let us now consider spin susceptibility and NQR-NMR relaxation rates. From the recovery of the ^{63}Cu signal after RF saturation in both types of experiments one arrives at $1/T_1=2W$ given by

$$2W = \frac{\gamma^2}{2}\int \langle h_+(t)h_-(0)\rangle e^{-i\omega_R t}dt, \quad (7)$$

where γ is the gyromagnetic ratio of the ^{63}Cu nucleus. In Eq. (7) $h_\pm$ are the components of the field at the nuclear site transverse to the c axis both for NQR where the quantization axis is the Z one of the electric field gradient tensor as well as for NMR when the external field is along the c axis itself. ω_R, the resonance frequency, is $\omega_R(0)=31$ MHz in NQR (zero field) and $\omega_R(H)=67$ MHz in NMR for $H=5.9$ T. In the following this difference will be neglected. The ficticious field $\vec{h}$ can be related to the electron spin operators $S_\pm$ through the electron-nucleus Hamiltonian and the relaxation rate can formally be written in terms of a generalized susceptibility. One can write

$$2W = \frac{\gamma^2}{2}k_B T\sum_{\vec{k}} A_k \frac{\chi''(\vec{k},\omega_R)}{\omega_R} \simeq \frac{\gamma^2}{2}k_B T\langle A_k\rangle_{BZ}\sum_{\vec{k}}\frac{\chi''(\vec{k},\omega_R)}{\omega_R}, \quad (8)$$

where A_k is a term involving the square of the Fourier transform of the effective field $\vec{h}$, which can be averaged over the Brillouin zone. In a Fermi gas picture in Eq. (8) one can introduce, in the limit $\omega_R \to 0$, the static spin susceptibility $\chi^o(0,0)$ and the density of states $\rho(E_F)$, namely $W \propto T[\chi^o(0,0)/(1-\alpha)]\hbar\rho(E_F)$ (α is a Stoner-like enhancement factor) and the Korringa law $1/T_1 \propto T$ is thus recovered. Having to discuss only the effect of the external field H on W around T_c^+ in the assumption that the field does not change appreciably the electron-nucleus Hamiltonian [as it is proved by the equality $W(0)=W(H)$ for $T \gg T_c$] we will simply write $W/T \propto \chi_{ab} \equiv \chi$, where χ is then the k-integrated, $\omega_R \to 0$ contribution. The fact that in $YBa_2Cu_3O_{7-\delta}$ the Korringa law is not obeyed above T_c for ^{63}Cu NQR-NMR relaxation rates (most likely because of correlation effects) should not invalidate the comparison of $W(0)$ to $W(H)$ in the relatively narrow temperature range of 10 K above T_c.

For an s-wave the main contribution to spin relaxation originates from the MT process. Instead, the hierarchy of fluctuation contributions changes essentially if one considers the d-wave superconductor. As both the AL and MT processes are absent, the negative DOS term becomes the only one present. Corresponding results for the d-wave superconductor with quasi-two-dimensional spectrum are

$$\frac{\chi_s^{\mathrm{DOS}}}{\chi_s^{(0)}} \approx \frac{(W)_{B=0}^{\mathrm{DOS}}}{(W)^{(0)}} \approx -\frac{T_c}{t}\ln\frac{2}{\epsilon^{1/2}+(\epsilon+r)^{1/2}}, \tag{9}$$

where r is a parameter of effective anisotropy of electron spectrum and $\chi_s^{(0)}$ $(W/T)^{(0)}$ are the normal-state spin susceptibility and the NMR relaxation rate, respectively. By comparing Eq. (9) with the appropriate result for the s-wave case (see Ref. 10) one can see that this type of pairing does not affect the magnitude and temperature dependence of the DOS contribution.

Finally, one can conclude that the only essential difference between s- and d-pairing states in context of the SF theory consists in the absence of an anomalous MT process in the latter. Therefore, studies based on measurements of thermodynamical character do not give the possibility to distinguish the type of pairing on the basis of fluctuation effects experiments. In-plane and out-of-plane conductivity experimental data in zero field do not manifest the signs of the MT term. Nevertheless the measurements of fluctuation conductivity cannot provide reliable tests for possible d or s pairing because the high values of T_c determine strong pair breaking [at least due to the electron-phonon scattering the expected minimal value of $\tau_\phi^{-1} \sim (T/\hbar)(T/\Theta_D)^2$]. Thus the MT process is uneffective even in the case of an s-pairing scenario. Additionally, as the MT contribution to conductivity temperature dependence is similar to an AL one, they can hardly be distinguished. The additional comparison with the s-wave case ψ function gives the numerical factor of order unity, which cannot be tested experimentally. Therefore, the only physical property related to SF which is due to the MT contribution is the NMR relaxation rate, in which the AL process does not contribute at all.[10]

On the basis of the s-wave scenario a positive MT singular contribution was predicted[9] while in Ref. 10 the importance of the negative DOS (independent on phase breaking) fluctuation renormalization was stressed. The concurrence of these two effects should be observable in the relaxation measurements. In the case of d pairing, vice versa, the MT anomalous process in accordance with the consideration presented above does not exist at all and in the NMR relaxation rate above T_c a monotonic decrease with respect to Korringa law has to be observed. Consequently, from the point of view of fluctuation theory, the sign of the correction to the NMR relaxation rate above T_c could be a test for the symmetry of the order parameter. The main results for the fluctuation contributions to the relaxation rate in an external field in the case of an s-wave superconductor are the following: The DOS contribution has the same form as calculated above. The MT contribution is given by

$$\frac{(W)_{B=0}^{MT}}{(W)^{(0)}} \approx \frac{1}{\epsilon_F\tau}\frac{1}{\epsilon-\delta}\ln\frac{\epsilon^{1/2}+(\epsilon+r)^{1/2}}{\delta^{1/2}+(\delta+r)^{1/2}}, \tag{10}$$

where δ is the pair-breaking parameter which is of order $\pi/(8T_c\tau_\phi)$ and $\pi/(8T_c^2\tau\tau_\phi)$ in dirty and clean cases, respectively. While the MT contribution is very sensitive to the presence of pair breaking, the simplest way to discriminate the DOS and MT contributions is applying the external magnetic field, a relatively small value is expected to practically suppress the MT contribution.

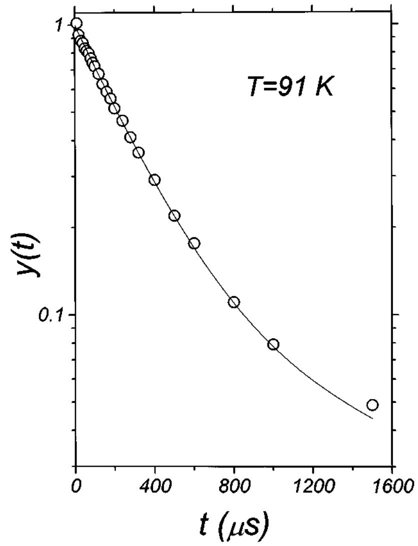

FIG. 1. Example of the recovery law of the ^{63}Cu NMR signal after fast inversion of the $\pm 1/2$ population difference in $YBa_2Cu_3O_{7-\delta}$ and comparison with the theoretical expression reported in the text (solid line).

The ^{63}Cu NQR and NMR relaxation measurements have been carried out in oriented powders of $YBa_2Cu_3O_{6.96}$. From the ^{63}Cu NMR linewidth (FWHI $\simeq 40$ kHz) the spread in the direction of the c axis was estimated within $1-2$ degrees. The superconducting transition was estimated; $T_c = 90.5$ K in zero field and $T_c = 87.5$ K in the field of 5.9 T used for NMR relaxation. In ^{63}Cu NQR measurements the recovery of the amplitude $s(t)$ of the echo signal at the time t after complete saturation of the $\pm 1/2 \rightarrow \pm 3/2$ transition was confirmed of exponential character, thus directly yielding the relaxation rate. The temperature was measured with precision better than 25 mK and the long term stabilization during the measurements was within 100 mK. In the presence of the magnetic field the sample was aligned with $c \| \vec{H}$. The echo signal for the central transition was used to monitor the recovery of the nuclear magnetization after fast inversion of the $\pm 1/2$ populations. From the solution of the master equations one derives for the recovery law $y(t) = 0.9\exp(-12Wt) + 0.1\exp(-2Wt)$. This law was observed to be very well obeyed (Fig. 1) and the relaxation rate was extracted. The experimental error in the evaluation of W was estimated well within 5%. In Fig. 2 the experimental results for $2W(0)$ and $2W(H)$ around T_c are reported. It is noted that $W(0) = W(H)$ for $T \gtrsim T_c + 15$ K while the effect of the field, namely a decrease of the relaxation rate, is present in a temperature range where paraconductivity and anomalies in the c axis transport are observed.

Let us discuss the interpretation of the experimental results in terms of the contributions related to SC fluctuations. The relative decrease of W around $T_c(H)$ and $T_c(0)$ induced by the field is about 20%. Let us evaluate if this decrease is quantitatively consistent with the picture of superconducting fluctuations. First one should estimate the strength of pair breaking. By using the reasonable values $\tau \simeq 10^{-14}$s and $\tau_\phi \simeq 2\times 10^{-13}$s, one finds that the pair-breaking parameter δ is about 0.15. The effective anisotropy parameter r in $YBa_2Cu_3O_{7-\delta}$ can be estimated around 0.1. Finally one can observe that in the zero field the relative MT contribution is

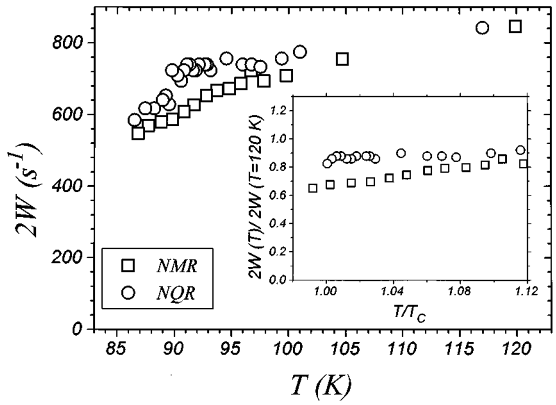

FIG. 2. ^{63}Cu relaxation rates in zero field $2W(0)$ (from NQR relaxation) and $2W(H)$ in a field of 5.9 T (from NMR relaxation of the $-1/2\rightarrow 1/2$ line) in the oriented powders of $YBa_2Cu_3O_{7-\delta}$, with $T_c(0)=90.5$ K and $T_c(H)=87.5$ K. In the inset the relaxation rates, normalized with respect to $W(H)=W(0)$ for $T\gg T_c$, are reported as a function of T/T_c.

larger than the absolute value of the DOS contribution by a factor 1.5, thus providing the positive fluctuation correction to W.

The effect of the field on these two contributions can be expected as follows: In the case of strong pair breaking $\delta_B>\{\epsilon_B,r\}$ $[\epsilon_B=\epsilon+\beta/2, \delta_B=\delta+\beta/2, \beta=2B/H_{c2}(0)]$ there are two different regimes for the fluctuation corrections in the magnetic field.[11] The low-field regime ($\beta\ll\epsilon$) corresponds to a decrease quadratic in β of the fluctuation correction. In the high-field regime ($\epsilon\ll\beta$) one can use the lowest Landau level approximation. In our experiment $\epsilon\approx 0.05$, while β is about 0.2. Since relative corrections to W coincide with relative corrections to conductivity,[11] one easily finds

$$\frac{(W)_B^{\rm DOS}}{(W)^{(0)}}\approx-\frac{\beta}{\epsilon_F\tau}\left(\frac{1}{[\epsilon_B(\epsilon_B+r)]^{1/2}}-\ln\frac{1}{\beta}\right), \qquad (11a)$$

$$\frac{(W)_B^{\rm MT}}{(W)^{(0)}}\approx\frac{\beta}{\epsilon_F\tau}\,\frac{1}{\delta-\epsilon}\left(\frac{1}{[\epsilon_B(\epsilon_B+r)]^{1/2}}-\frac{1}{[\delta_B(\delta_B+r)]^{1/2}}\right). \qquad (11b)$$

Direct calculations according to these equations show that the MT contribution is much more affected by the magnetic field. In fact from Eq. (11a) the modification in $W^{\rm DOS}$ induced by the field is small, of the order of 15%. On the contrary, according to Eq. (11b) the field reduces the MT term to 1/4 of its zero-field value. In the case of d-wave pairing symmetry, as it was already noted above, the MT contribution is absent and the applied magnetic field results only in the slight reducing of the DOS contribution in accordance with the equation similar with Eq. (11a).

If the decrease of W by the magnetic field is due to the reduction of the MT term to SF, then one deduces that the zero-field total fluctuation correction to the NQR relaxation rate is positive and is within 10% of background, due to the partial cancellation of the MT and DOS contribution. In a field of 6 T the total fluctuation correction becomes negative with an absolute value about 15% of the background. The lack of detailed information on the normal-state NMR relaxation rate in HTS does not allow one to achieve more quantitative estimates. However, it should be remarked that the observation of the decrease of W in a magnetic field cannot be accounted for in the case of d-wave pairing. Finally we would like to emphasize the following: It has been recently pointed out by Müller[12] that two type of condensates, with different symmetry but the same transition temperature, can exist in oxide superconductors. It is conceivable that also the spectrum of the fluctuations of the order parameter above T_c could reflect both components, if present. Since the effect of the magnetic field discussed in our paper works only on the component of s symmetry, our conclusion is not in contrast with the experimental evidences indicating d-wave pairing and it could be considered a support to the hypothesis of the SF having simultaneously s and d symmetry.

Summarizing, from the accurate comparison of ^{63}Cu NQR and NMR relaxation rates in zero field and in a field of 5.9 T around T_c^+ in $YBa_2Cu_3O_{7-\delta}$, we have provided evidence of a contribution to W related to the superconducting fluctuations, in a temperature range of about 10 K. The experimental observation of a decrease in W induced by the field is consistent with the hypothesis of a strong reduction of the MT contribution. Since the MT contribution does not exist in the case of a d-wave scenario, the interpretation of the experimental finding is an indication in favor of the presence of an s-symmetry component in the orbital pairing.

Useful discussions with Mohit Randeira and with Andrea Gauzzi are gratefully acknowledged. The work has been carried out with the support of INFN (grant VORS) and of NATO Grant No. CRG 941187. One of us (A.V.) wishes to acknowledge support from the Cariplo Foundation for Scientific Research, in the framework of the Landau Network for a stage at the University of Pavia.

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