Charge Degree of Freedom and the Single-Spin Fluid Model in $YBa_2Cu_4O_8$

A. Suter,* M. Mali, J. Roos, and D. Brinkmann
Physik-Institut, Universität Zürich, CH-8057 Zürich, Switzerland
(Received 28 June 1999)

We present a ^{17}O nuclear magnetic resonance study in the stoichiometric superconductor $YBa_2Cu_4O_8$. A double irradiation method enables us to show that, below around 200 K, the spin-lattice relaxation rate of plane oxygen is not only driven by magnetic fluctuations, but also significantly by quadrupolar fluctuations, i.e., low-frequency charge fluctuations. In the superconducting state, on lowering the temperature, the quadrupolar relaxation diminishes faster than the magnetic one. These findings show that, with the opening of the spin pseudogap, a charge degree of freedom of mainly oxygen character is present in the electronic low-energy excitation spectrum.

PACS numbers: 71.45.–d, 74.25.Nf, 74.72.Bk, 76.60.–k

One of the central issues in understanding cuprate-based high-temperature superconductors (HTSC) has been to determine the minimal number of electronic degrees of freedom which are necessary to describe the physics at the atomic scale of these structures. Zhang and Rice proposed that doped holes, which go into oxygen states, form a spin-resonant singlet state with the quasilocalized holes at copper [1]. Therefore, only *one* spin degree of freedom would be necessary to describe the low-energy dynamics of the electronic system in the normal state of the HTSC. This scenario is often called *single-spin fluid* (SSF) and is described within a t-J model. However, as was discussed by various authors [2], this model might be an oversimplification.

Because of its local character, nuclear magnetic resonance (NMR) is a very attractive method to address these questions. NMR probes the low-energy excitations of the HTSC electronic system, and it provides information about copper and oxygen independently. Studies of the *uniform* spin susceptibility, $\mathrm{Re}\{\chi(q = 0, \omega = 0)\}$ [3], indicate that only one spin degree of freedom is involved, thus supporting the SSF model. On the other hand, oxygen and copper reveal a very different temperature dependence of the spin-lattice relaxation [4] which is related to the *dynamic* spin susceptibility, $\mathrm{Im}\{\chi(q, \omega_L)\}$ [5]. This could suggest independent spin degrees of freedom. However, as pointed out before [6], the hyperfine field, due to antiferromagnetically correlated copper spins, cancels at the oxygen site, and this fact can explain the different temperature dependences within a SSF model.

There is, however, evidence that this view is incomplete. The ^{17}O NMR in Y-Ba-Cu-O HTSC has extensively been studied by various groups. Especially the pronounced temperature dependence of the anisotropy of the experimentally determined effective spin-lattice relaxation rate, $^{17}W_{\mathrm{eff}}$, of the plane oxygen is still puzzling [7–9], while the SSF model predicts an almost temperature independent rate anisotropy. (The meaning of *effective* will be discussed below.) As we pointed out in Ref. [8], it is also very difficult to explain, within a simple SSF model, the ratio of this rate and the yttrium rate, namely $^{17}W_{\mathrm{eff}}/^{89}W$ (with the external magnetic field B_0 parallel to the c axis). Furthermore, in a detailed analysis, Walstedt *et al.* [10] compared their ^{17}O and ^{63}Cu NMR results from $La_{2-x}Sr_xCuO_4$ studies with inelastic neutron scattering data and concluded that a single-band picture is inadequate.

In this Letter, we will show that the plane oxygen spin-lattice relaxation in $YBa_2Cu_4O_8$, below about 200 K, is not only driven by magnetic but also by quadrupolar fluctuations, i.e., low-frequency charge fluctuations. This fact implies that in the temperature region where the spin pseudogap is present, a *charge* degree of freedom has to be taken into account, in addition to the spin degree of freedom; hence the simple SSF model is inadequate.

Our results were obtained by a double irradiation technique which we developed to extract the quadrupolar contribution to the overall NMR relaxation [11]; we sketch this technique as follows. The relaxation of the spin system towards its thermodynamic equilibrium is described by the so-called master equation [12] and, in the interaction representation [13,14], it is given by

$$\frac{d}{dt}\,\mathbf{P}(t) = \mathbf{R}(W, W_1, W_2)[\mathbf{P}(t) - \mathbf{P}(0)] + \mathbf{S}_{\mathrm{rf}}\mathbf{P}(t)\,. \tag{1}$$

Here, $\mathbf{P}(t)$ is the nuclear spin system population vector of the different energy levels with $\mathbf{P}(0)$ being the equilibrium value. The relaxation matrix $\mathbf{R}(W, W_1, W_2)$ is, in general, a function of the magnetic relaxation rate W (causing transitions with $|\Delta m| = 1$) and the two quadrupolar relaxation rates W_1 ($|\Delta m| = 1$) and W_2 ($|\Delta m| = 2$) [13,14]. The transition probabilities for a spin $I = 5/2$ (like ^{17}O) are sketched in Fig. 1. $\mathbf{S}_{\mathrm{rf}}$ denotes transitions due to an additional stimulating radio-frequency (rf) field which is essential for the separation of magnetic from quadrupolar contributions to the relaxation, as will be discussed below. In HTSC, the Zeeman degeneracy is lifted due to the crystal field so that different transitions have distinguishable resonance frequencies [12]. In case the relaxation is purely magnetic, it is easy to show that the saturation of any line does not affect the intensities of others. This is no

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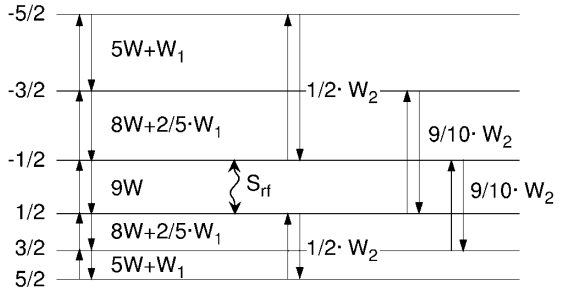

FIG. 1. Probabilities for transitions between the spin energy levels effected by magnetic (W) and quadrupolar (W_1, W_2) spin-lattice relaxation processes for $I = 5/2$. S_{rf} denotes transitions due to a stimulating radio-frequency field.

more true for the general case where W as well as W_1 and W_2 contribute to the relaxation.

In the limit of dynamical saturation [i.e., $d\mathbf{P}(t)/dt = 0$], Eq. (1) can be solved exactly [11]. The essential result is that, mainly due to the $|\Delta m| = 2$ transitions, the intensities of different lines change compared to a standard detection method (e.g., spin-echo sequence) where S_{rf} is zero. In our present experiment, S_{rf} saturates the $(-1/2, 1/2)$ transition, and we observe the other transitions, yielding signals with intensities I_{dyn}. The spin-echo sequence (with $S_{\mathrm{rf}} = 0$) provides signals with intensities I_{se}. For the $(-3/2, -1/2)$ transition the *enhancement* factor, E, is then given by [11]

$$E = \frac{I_{\mathrm{dyn}}}{I_{\mathrm{se}}} = 1 + \frac{\mu}{\zeta}, \qquad (2)$$

with $\mu = 45W_2(10W + 2W_1 + W_2)$ and $\zeta = 4000W^2 + 1000WW_1 + 40W_1^2 + 1100WW_2 + 160W_1W_2 + 45W_2^2$. E is a rather insensitive function with respect to W_1, since W_1 connects the same energy levels as W, except the $(-1/2, 1/2)$ transition [11]. However, E depends significantly on W_2 which makes the separate detection of quadrupole relaxation possible. The enhancement E for various transitions is quite different; for the $(-5/2, -3/2)$ transition, there is almost no enhancement. More information and details concerning the method and its experimental realization as well as different cross-checks of the results are given in Ref. [11].

The measurements were performed on an oriented and ^{17}O enriched $YBa_2Cu_4O_8$ powder sample, used in previous studies [8], in a field of 8.9945 T applied along the c axis; Fig. 2 presents the results for $T = 95$ K. The chain sites O(1) are not of interest in this work and therefore will not be discussed. Also, we are not concerned with the plane oxygen satellites O(2,3) splitting which is due to the orthorhombic symmetry [15] of the crystal. Striking the eye is the negative intensity of the central transition $(-1/2, 1/2)$ in the difference spectrum, which means saturation of this transition. This is in contrast with the central and the satellite transitions of *chain* oxygen which are not

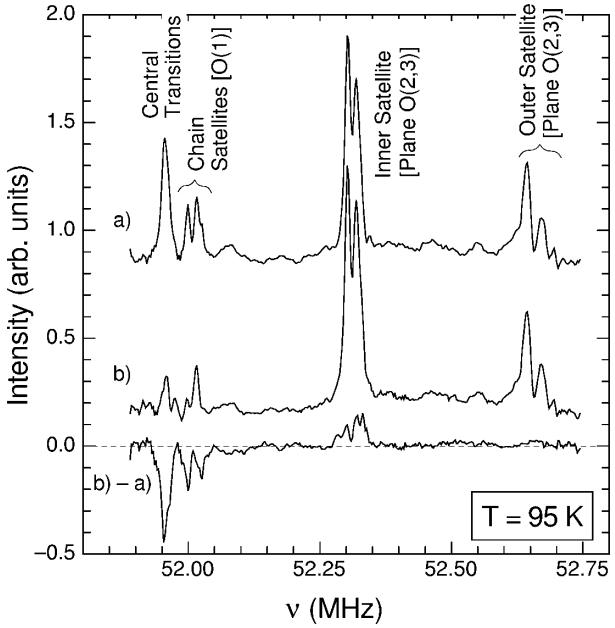

FIG. 2. (a) ^{17}O central transition and high-frequency satellites of chain and plane oxygen in $YBa_2Cu_4O_8$, respectively, obtained by a standard spin-echo experiment. (b) ^{17}O spectrum obtained after dynamic saturation of the $(-1/2, 1/2)$ transition. Bottom: Difference of spectrum (b) and (a).

saturated because O(1) relax considerably faster than plane nuclei for which the pulse sequence was optimized. That this explanation is correct has been proven by the symmetric experiment where we dynamically saturated the outer high-frequency satellite [11].

The most important feature of the difference spectrum is the remaining positive intensity at the position of the $(-3/2, -1/2)$ transition. This intensity enhancement clearly shows that there is a quadrupolar contribution to the relaxation of plane oxygen nuclei. At the position of the $(-5/2, -3/2)$ transition, the intensity is almost zero, as expected from our calculations.

Figure 3 shows, among others, the temperature dependence of the intensity enhancement, E, of the $(-3/2, -1/2)$ transition due to the saturation of the $(-1/2, 1/2)$ transition. With these values, Eq. (2) allows us to calculate $^{17}(W_2/W)$. In doing so, we have set $W_1 = W_2$, which is not only reasonable, if one assumes more or less isotropic quadrupolar fluctuations, but also brings our result in accord with $^{17}W_{\mathrm{eff}}/^{89}W$ data as we will see below. The $^{17}(W_2/W)$ results are plotted in Fig. 3 by using an ordinate axis in such a way that the points coincide with the bullets. In order to estimate $^{17}W_2$ itself, we have remeasured the temperature dependence of the nuclear magnetization recovery (obtained by standard NMR) and then fitted the data by the theoretical expression for combined magnetic and quadrupolar relaxation [14] using $W_1 = W_2$ and W as parameters and our values $W_2/W = W_1/W$. The results of this fit are presented in the inset of Fig. 3.

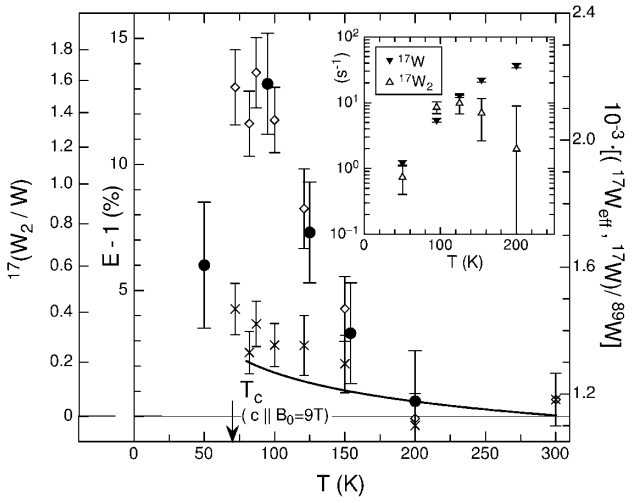

FIG. 3. Temperature dependence of intensity enhancement of the ^{17}O $(-3/2, -1/2)$ transition (•); $^{17}W_{\rm eff}/^{89}W$ (◇); $^{17}W/^{89}W$ (×); theoretical prediction for $^{17}W/^{89}W$ (solid curve) [16]. Inset: ^{17}W and $^{17}W_2$ for plane oxygen.

We stress that ^{17}W is different from the value of $^{17}W_{\rm eff}$ one gets if the fit procedure uses the theoretical expression for *pure magnetic* recovery ($W_1 = W_2 = 0$) [14]. Lacking experimental hints, this fit procedure has been applied in all previous HTSC oxygen relaxation studies, i.e., quadrupolar oxygen relaxation, if any, has been considered to be negligible. Now, having ^{17}W that properly represents the magnetic part of the relaxation, we can evaluate the ratio $^{17}W/^{89}W$ and compare it in Fig. 3 with the ratio $^{17}W_{\rm eff}/^{89}W$ from Ref. [8]. Obviously, the $^{17}W/^{89}W$ temperature dependence becomes much weaker than the $^{17}W_{\rm eff}/^{89}W$ one; it actually approaches the theoretical prediction (solid curve in Fig. 3) of the Millis-Monien-Pines (MMP) model [16]. This agreement is satisfying, and it is based on the assumption $^{17}W_1 \approx {}^{17}W_2$ we made above. The $^{17}W_2$ results have relatively large errors as a consequence of the large $^{17}(W_2/W)$ errors. While the data points suggest, above 100 K, an increase of $^{17}W_2$ with falling temperature, also a temperature independent $^{17}W_2$ is compatible with the errors. Be that as it may, the essential result is the presence of $^{17}W_2$ rather than its temperature dependence in the normal state.

What is the origin of the quadrupolar relaxation? A simple phononic mechanism can be ruled out for two reasons. First, the temperature dependence of the quadrupolar contribution is incompatible with a power law T^α with $\alpha = 2-7$ [12,17] expected for relaxation due to phonons. Second, a dramatic softening of a phonon mode that could in principle lead to the observed temperature dependence is not taking place. Though there is a weak softening of phononic modes in $YBa_2Cu_4O_8$, as observed by Raman scattering experiments [18], the effect, besides occurring at a too low temperature, is much too small to account for the observed strong increase of the quadrupolar contribution in the oxygen relaxation. We can also exclude quadrupolar relaxation due to any defect motion. Such a motion would be clearly observed in the ^{137}Ba relaxation since the ^{137}Ba quadrupole moment is much larger than the ^{17}O one. Yet, we did not detect such an effect [19].

A clue to the origin of the quadrupolar relaxation is provided by the fact that below about 200 K, if the temperature decreases towards T_c, $^{17}(W_2/W)$ grows significantly and then diminishes in the superconducting state. The increase of $^{17}(W_2/W)$ becomes pronounced around a temperature $T^\dagger$ where we recently detected [8] an electronic crossover associated with anomalies in various NMR and NQR (nuclear quadrupole resonance) properties. Whether these two phenomena are related, however, remains an open question. We also suggested [8] that the discrepancy between the experimental temperature dependence of $^{17}W_{\rm eff}/^{89}W$ and the MMP model prediction, which does not include quadrupolar relaxation, could easily be explained by assuming an additional quadrupolar relaxation channel for plane oxygen. The data of Fig. 3 support this idea.

Further information on the nature of $^{17}W_2$ is provided by the pronounced temperature dependence of the anisotropy of the effective relaxation rate $^{17}W_{\rm eff}$ which is not expected within the SSF model [7–9]. Martindale *et al.* [9] tried to explain this dependence by assuming two spin degrees of freedom. In contrast, the uniform spin susceptibility monitored by the different plane nuclei scales perfectly, thus strongly supporting the view of a *single* spin degree of freedom. Therefore, we believe that, below about 200 K, the temperature dependence of the $^{17}W_{\rm eff}$ anisotropy is caused by the additional quadrupolar relaxation channel. If so, this enables us to determine the anisotropy of W_2.

The magnitude of the W_2 rate itself yields an important information on the nature of the quasiparticles. Below 200 K, W_2 is much too large to originate from simple quadrupolar relaxation due to electronlike quasiparticles [20]. Their fluctuation spectral density is smeared out up to frequencies that are extremely high as compared to the nuclear Larmor frequency; therefore, the charge fluctuation amplitude at Larmor frequency, and consequently W_2, is very small. The substantial quadrupolar relaxation we observe indicates that it has to arise either from strongly *correlated* quasiparticles as proposed by different theoretical models [21] or from very strong electron-phonon interactions that could lead to heavy polaroniclike quasiparticles [22]. In both cases, the slowed down quasiparticle dynamics could produce enough low-frequency spectral density necessary to account for the observed quadrupole relaxation.

One nevertheless would expect this relaxation to be equally operative at oxygen and copper sites and, due to the larger copper nuclear quadrupole moment, even more effective at the latter sites. This is not what one observes. Whereas there is a substantial quadrupolar contribution to the oxygen relaxation below 200 K, as shown in this work, no such contribution has been detected in the copper

relaxation. Since the squared ratio of the quadrupole moments of ^{63}Cu and ^{17}O is about 60, one expects that such a contribution would be easily detected. We have measured very accurately (by nuclear quadrupole resonance) the ratio R of the ^{65}Cu and ^{63}Cu relaxation rates at the plane copper site in our sample at 100 K. Our result, $R = 1.1497(35)$, is in the small error limits equal to the squared ratio of the copper gyromagnetic ratios. The high precision of R sets the limit for any possible quadrupolar contribution to the Cu relaxation to less than 1% which is far from what one is expecting.

Finally, let us return to the remark, made at the beginning of this Letter, that antiferromagnetic fluctuations are very well filtered out at the plane oxygen sites. This is true if the fluctuations are commensurate with the crystal structure. However, recent inelastic neutron scattering experiments revealed that there are *incommensurate* antiferromagnetic correlations developing in underdoped $YBa_2Cu_3O_{7-\delta}$ [23]. Most likely such correlations are present also in $YBa_2Cu_4O_8$, so one expects much less efficient filtering of fluctuations at the oxygen site and a more copperlike oxygen magnetic relaxation in contrast to what is observed experimentally. The discrepancy in $YBa_2Cu_4O_8$ is even more pronounced, since, so far, the effective rate $^{17}W_{\rm eff}$ was used to analyze the data and thus the magnetic relaxation rate W got overvalued. The reconciliation of these NMR findings with those gained by neutron scattering experiments poses another challenge to the theory.

In conclusion, we have shown that the spin-lattice relaxation of plane oxygen in $YBa_2Cu_4O_8$ below approximately 200 K is not driven only by magnetic but also by quadrupolar fluctuations (i.e., low-frequency charge fluctuations). In the superconducting state, this newly established quadrupolar relaxation diminishes faster than the magnetic one, indicating that the underlying relaxation process is strongly influenced by the superconducting transition. There are 2 degrees of freedom involved in the low-energy excitations of the electronic system, one of them is the single-spin degree, implying that the single-spin fluid model is partially correct, whereas the other one is the *charge* degree of freedom with predominantly oxygen character, since it is not observed at the copper sites.

The partial support of this work by the Swiss National Science Foundation is gratefully acknowledged.

*Present address: Condensed Matter and Thermal Physics, MST-10 MS K764, Los Alamos National Laboratory, Los Alamos, NM 87545.

[1] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).
[2] V. J. Emery and G. Reiter, Phys. Rev. B **38**, 11 938 (1988); J. P. Lu, Q. Si, J. H. Kim, and K. Levine, Phys. Rev. Lett. **65**, 2466 (1990).
[3] M. Takigawa, A. P. Reyes, P. C. Hammel, J. D. Thompson, R. F. Heffner, Z. Fisk, and K. C. Ott, Phys. Rev. B **43**, 247 (1991); M. Bankay, M. Mali, J. Roos, and D. Brinkmann, *ibid.* **50**, 6416 (1994).
[4] P. C. Hammel, M. Takigawa, R. H. Heffner, Z. Fisk, and K. C. Ott, Phys. Rev. Lett. **63**, 1992 (1989); I. Mangelschots, M. Mali, J. Roos, R. Stern, M. Bankay, A. Lombardi, and D. Brinkmann, *Static and Dynamic Magnetic Properties of Ba, Cu and O in* $YBa_2Cu_4O_8$ *and* $Y_2Ba_4Cu_7O_{15}$ (World Scientific Publ. Co., Singapore, 1993), Vol. 243, p. 262.
[5] T. Moriya, J. Phys. Soc. Jpn. **18**, 516 (1963).
[6] F. Mila and T. M. Rice, Physica (Amsterdam) **157C**, 561 (1989); B. S. Shastry, Phys. Rev. Lett. **63**, 1288 (1989); N. Bulut, D. W. Hone, D. J. Scalapino, and N. E. Bickers, Phys. Rev. B **41**, 1797 (1990).
[7] F. Barriquand, P. Odier, and D. Jérome, Physica (Amsterdam) **177C**, 230 (1991); M. Horvatić, C. Berthier, Y. Berthier, P. Ségransan, P. Butaud, W. G. Clark, J. A. Gillet, and J. Y. Henry, Phys. Rev. B **48**, 13 848 (1993).
[8] A. Suter, M. Mali, J. Roos, and D. Brinkmann, Phys. Rev. B **56**, 5542 (1997).
[9] J. A. Martindale, P. C. Hammel, W. L. Hults, and J. L. Smith, Phys. Rev. B **57**, 11 769 (1998).
[10] R. E. Walstedt, B. S. Shastry, and S-W. Cheong, Phys. Rev. Lett. **72**, 3610 (1994); R. E. Walstedt and S-W. Cheong, Phys. Rev. B **51**, 3163 (1995).
[11] A. Suter, M. Mali, J. Roos, and D. Brinkmann, J. Magn. Reson. **143**, 266 (2000).
[12] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961).
[13] E. Andrew and D. Tunstall, Proc. Phys. Soc. London **78**, 1 (1961).
[14] A. Suter, M. Mali, J. Roos, and D. Brinkmann, J. Phys. Condens. Matter **10**, 5977 (1998).
[15] I. Mangelschots, M. Mali, J. Roos, D. Brinkmann, S. Rusiecki, J. Karpinski, and E. Kaldis, Physica (Amsterdam) **194C**, 277 (1992).
[16] A. J. Millis, H. Monien, and D. Pines, Phys. Rev. B **42**, 167 (1990); H. Monien, D. Pines, and M. Takigawa, *ibid.* **43**, 258 (1991); H. Monien, P. Monthoux, and D. Pines, *ibid.* **43**, 275 (1991); Y. Zha, V. Barzykin, and D. Pines, *ibid.* **54**, 7561 (1996).
[17] J. Van Kranendonk, Physica **20**, 781 (1954).
[18] A. P. Litvinchuck, C. Thomsen, and M. Cardona, Solid State Commun. **83**, 343 (1992).
[19] A. Lombardi, M. Mali, J. Roos, and D. Brinkmann, Physica (Amsterdam) **267C**, 261 (1996).
[20] Y. Obata, J. Phys. Soc. Jpn. **18**, 1020 (1963); **19**, 2348 (1964).
[21] V. J. Emery and S. A. Kivelson, Physica (Amsterdam) **235–240C**, 189 (1994); J. Ranninger and J. M. Robin, Phys. Rev. B **53**, 15 657 (1996).
[22] A. S. Alexandrov and N. F. Mott, Rep. Prog. Phys. **57**, 1197 (1994); *Polarons & Bipolarons* (World Scientific Publishing Co. Pte. Ltd., Singapore, 1995).
[23] H. A. Mook, P. Dai, R. D. Hunt, and F. Doğan, J. Phys. Chem. Solids **59**, 2140 (1998).