Spin Gap in $HgBa_2Ca_2Cu_3O_{8+\delta}$ Single Crystals from ^{63}Cu NMR

M.-H. Julien,[1] P. Carretta,[1,*] M. Horvatić,[1] C. Berthier,[1,2] Y. Berthier,[2] P. Ségransan,[2] A. Carrington,[3] and D. Colson[4]
[1]*Grenoble High Magnetic Field Laboratory, Centre National de la Recherche Scientifique and Max-Planck-Institut für Festkörperforschung, Boîte Postale 166, 38042 Grenoble Cedex 9, France*
[2]*Laboratoire de Spectrométrie Physique, Université Joseph Fourier Grenoble 1 (URA 08 CNRS), Boîte Postale 87, 38402 Saint-Martin d'Hères Cedex, France*
[3]*Commissariat à l'Energie Atomique, Département de Recherche Fondamentale sur la Matière Condensée, Laboratoire de Cryophysique, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France*
[4]*Commissariat à l'Energie Atomique, Service de Physique de l'Etat Condensé, Saclay, 91191 Gif sur Yvette Cedex, France*
(Received 17 October 1995)

We report on ^{63}Cu NMR spectra, T_1 and T_{2G} measurements in single crystals of underdoped, three-layered, $HgBa_2Ca_2Cu_3O_{8+\delta}$, with $T_c \simeq 115$ K. We show clear evidence for the opening of a spin gap below $T^* \simeq 230$ K, the highest temperature reported so far. Also, the characteristic energy of the spin fluctuations is found to be higher than in $YBa_2Cu_3O_{6+x}$; both features are presumably related to the very high T_c in this compound. Below T^*, $^{63}T_1$ has the same temperature dependence in the three CuO_2 planes, which is difficult to explain within a pure interlayer spin pairing. [S0031-9007(96)00319-5]

PACS numbers: 74.25.Nf, 74.72.Jt, 76.60.–k

A comprehensive description of the magnetic properties of high-T_c superconductors, particularly the different behaviors observed in underdoped and overdoped compounds [1], is considered a stringent test for any microscopic theoretical description of these materials. One of the key features of the underdoped regime is the opening of a gap in the spin excitations (hereafter spin gap) at a temperature T^* well above T_c. First unambiguously seen in $YBa_2Cu_3O_{7-\delta}$ (YBCO) by inelastic neutron scattering (INS) [2], this gap corresponds to a progressive transfer of low frequency excitations at $\mathbf{Q}_{\mathrm{AF}} = (\pi/a, \pi/a)$ towards higher energies. The NMR fingerprint of the spin gap is a decrease of the ^{63}Cu nuclear spin-lattice relaxation rate $^{63}(T_1)^{-1}$ [3] without any reduction of the spin-spin relaxation rate $(^{63}T_{2G})^{-1}$ [4]. In underdoped YBCO and $La_{2-x}Sr_xCuO_{4+\delta}$, the uniform spin susceptibility χ_0 [5,6], the resistivity [6,7], the Hall coefficient [6,7], and the electronic specific heat [6,8] show systematic anomalies below a characteristic temperature T_0, which is greater than both T^* and T_c. However, it is unclear if this originates from a loss of spin excitations at $\mathbf{q} = \mathbf{0}$, or from features in the density of states [9,10]. We note that T_0 varies strongly with hole doping n_h [5–8] and is insensitive to Zn doping [11,12], whereas T^* depends more weakly on n_h, but is depressed by Zn [12]. Clearly, a careful distinction has to be made between the behaviors of the dynamic spin susceptibility at $\mathbf{q} = \mathbf{0}$ and $\mathbf{q} = \mathbf{Q}_{\mathrm{AF}}$.

Despite considerable theoretical and experimental work, a thorough understanding of the influence of n_h and the number of CuO_2 planes per unit cell on the spin gap is still lacking. Early attempts to describe the phase diagram as a function of n_h were based on the formation of a resonating valence bond state in the 2D t-J (or t-t'-J) model [13]. A quite different approach, based on a scaling analysis of the 2D quantum Heisenberg antiferromagnet (2DQHAF) phase diagram [14], has been proposed by Pines and collaborators [15]. Following Millis and Monien [16], several authors have also suggested that the transverse magnetic coupling within a CuO_2 bilayer plays a central role in the opening of the spin gap [17].

In this Letter, we present an investigation of ^{63}Cu NMR in underdoped $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) single crystals, having a $T_c \simeq 115$ K. We show that a spin gap opens below T^* as high as 230 K, and that the characteristic energy of the spin fluctuations is higher than in underdoped YBCO. This is argued to be related to the higher T_c. The T dependence of T_1 is the same for inner and outer planes, which questions the pure interlayer spin-pairing picture.

Small single crystals of Hg-1223 were grown using a single-step synthesis as described in Ref. [18]. A mosaic of 23 of them (total weight $\sim$1 mg), with common c axis, was made in order to increase the NMR signal. ac susceptibility measurements ($H_{\mathrm{ac}} \simeq 1$ Oe, applied $\|ab$) on this mosaic revealed a broad superconducting transition between 134 and 110 K. However, specific heat measurements on selected crystals showed that the bulk T_c was within the range 113–116 K (see inset in Fig. 1), and so the transition observed in the susceptibility or in the resistivity is presumably due only to surface inhomogeneity. We emphasize that no sign of oxygen distribution could be detected from the NMR measurements since well-defined lines and no distribution of the relaxation rates were observed. All experiments were carried out by standard spin-echo pulse sequences in a field of 15 T. For $H_0\|ab$, we identified the lines corresponding to the two copper sites (Fig. 1): Cu(2) in the outer planes and Cu(1) in the inner plane. For $H_0\|c$, the lines could not be separated. We found that the Cu(1) lines were much narrower than the Cu(2) ones, probably because the inner plane is more distant from the Hg-O layer which is the source of

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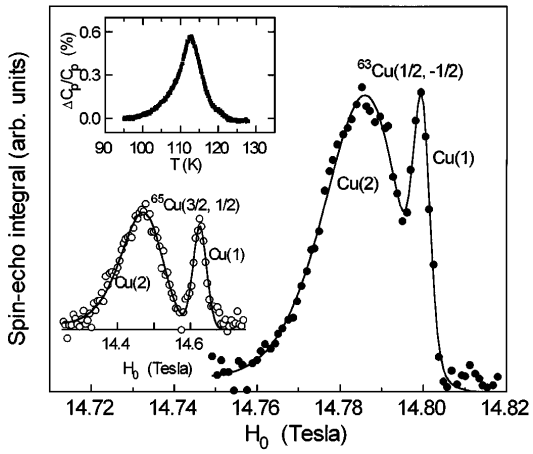

FIG. 1. Field sweeps of the ^{63}Cu(1) and ^{63}Cu(2) lines: (1/2, –1/2) (filled circles) and (3/2, 1/2) transitions (open circles). Inset: Anomaly at $T_{\rm peak} = 113$ K in the electronic part of the specific heat, for one crystal from the mosaic (an approximate phonon background has been subtracted).

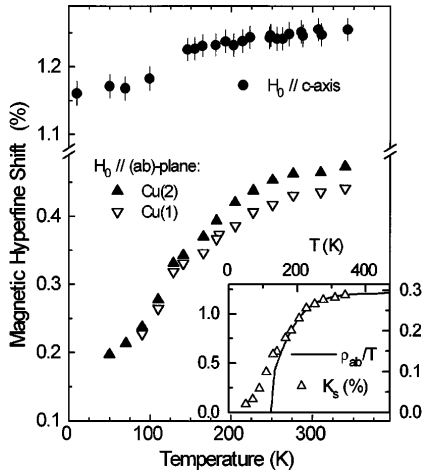

FIG. 2. ^{63}Cu magnetic hyperfine shift data. Inset: Spin part of the MHS (triangles, right scale in %), and in-plane resistivity divided by T (solid line, left scale in $\mu\Omega\,{\rm cm\,K^{-1}}$) from Ref. [25].

most of the disorder in the structure. From the position of the NMR lines we estimated the ^{63}Cu quadrupolar coupling frequencies: $^{63}\nu_Q^{\rm Cu(1)} = 9.7 \pm 0.1$ MHz, $^{63}\nu_Q^{\rm Cu(2)} = 13.7 \pm 0.1$ MHz.

Figure 2 presents the MHS (i.e., the line position corrected for the quadrupolar shift) arising from a T-dependent spin contribution $K_s = (A + 4B)\chi(\mathbf{q} = \mathbf{0}, \omega = 0)/g\mu_B$ and from a T-independent orbital term $K_{\rm orb}$; A and B are the on-site and transferred hyperfine coupling constants, respectively. The decrease of K_s below $T_0 \simeq 370$ K is characteristic of underdoped samples [1]. Note that the T dependence of $^{63}K_s$ is nearly the same for the two nonequivalent sites, as found in $Tl_2Ba_2Ca_2Cu_3O_{10-\delta}$ [19]. The shifts get slightly closer as T decreases (Fig. 2), and we can tentatively conclude that the inner plane is slightly less doped than the outer ones. There rests some uncertainty, however, as the hyperfine coupling constants are not accurately known.

To proceed with a more quantitative analysis, we assume that the hyperfine on-site tensor A does not change significantly among the cuprates, so that the values for YBCO [20], $A_{ab} = 70$ kOe and $A_c = -332$ kOe, are applicable to Hg-1223. This assumption is supported by the fact that the orbital shifts measured here, $K_{ab}^{\rm orb} = 0.19\%$, $K_c^{\rm orb} = 1.16\%$, are similar to those for YBCO [20]. From the anisotropy of K_s, we can then estimate that $B^{\rm Cu(2)} = 136$ kOe and $B^{\rm Cu(1)} = 146$ kOe (absolute values $\pm 15\%$). These values are much higher than for YBCO ($B = 83$ kOe), revealing a stronger hybridization between Cu and O orbitals. This might imply that the in-plane superexchange J between copper spins should be higher in Hg-1223. A possible reason for this is that Hg-based materials have the flattest CuO_2 planes of all cuprates; i.e., the Cu-O-Cu bond angles are the closest to 180° [21]. The absolute values of χ_0 deduced from K_s at $T = 350$ K, $\chi_0 = 5.3 \times 10^{-5}$ and 4.4×10^{-5} emu/mole for the outer and inner planes, respectively, are close to that measured for $YBa_2Cu_3O_{6.63}$ (6.0×10^{-5} emu/mole at 300 K [22]), and the T dependence is quite similar.

A test for the A and B values is the anisotropy of T_1:

$$\left(\frac{1}{^{63}T_1}\right)_{c,ab} = k_B T \frac{^{63}\gamma^2}{2\mu_B^2 N} \sum_{\mathbf{q}} \frac{1}{2}\left\{F_{ab}^2 + F_{ab,c}^2\right\} \frac{\chi''(\mathbf{q}, \omega_L)}{\omega_L},$$

where $F_{c,ab} = A_{c,ab} + 2B(\cos q_x + \cos q_y)$ and ω_L is the NMR frequency. Using a phenomenological form of the susceptibility $\chi''(q, \omega) \simeq \chi''_{\rm AF}(q, \omega)$ [23,24], with the AF part approximated by a Gaussian (with a width equal to the correlation length ξ/a), we find (for $\xi/a > 2$) that $(^{63}T_1)_{ab}^{-1}/(^{63}T_1)_c^{-1} = 2.2 \pm 0.1$, in remarkable agreement with experiment (2.17 ± 0.10).

The inset to Fig. 2 shows previously reported data for the in-plane resistivity ρ_{ab} for single crystals with the same bulk T_c as those reported here [25]. ρ_{ab} deviates from linearity below $T_0 \simeq 370$ K, the same temperature at which we estimate that χ_0 starts to decrease. Furthermore, it is striking to observe the almost perfect scaling of K_{ab} and ρ_{ab}/T, from T_0 down to a few tens of a kelvin above T_c.

In Fig. 3 we show the T dependence of $(^{63}T_1T)^{-1}$, for both sites and $H_0 \| ab$ along with preliminary data for the nuclear spin-spin relaxation rate $(^{63}T_{2G})^{-1}$. For the latter measurements H_0 was $\| c$ as the spectrum was too broad for $H_0 \| ab$, and so each $(^{63}T_{2G})^{-1}$ value is an average of the Cu(1) and Cu(2) sites. However, in light of the $^{63}K_s$ and $(^{63}T_1)^{-1}$ data, we do not expect a large difference in the magnitude and the T dependence of $(^{63}T_{2G})^{-1}$ for the two Cu sites. This assumption has indeed been confirmed in optimally doped Hg-1223, therefore justifying our analysis [26]. While $(^{63}T_1T)^{-1}$ increases with decreasing T and starts to drop at $T^* \simeq 230$ K, $(^{63}T_{2G})^{-1}$ continues increasing and eventually saturates below

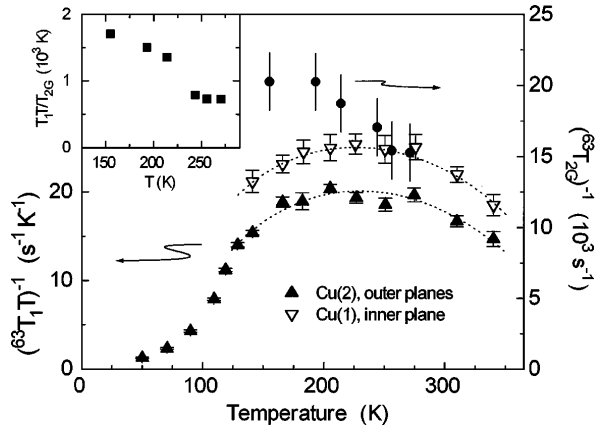

FIG. 3. Nuclear spin-lattice relaxation rate divided by temperature $(^{63}T_1T)^{-1}$ measured with $H_0\|ab$ for the Cu(1) and Cu(2) sites, and the nuclear spin-spin relaxation rate $(^{63}T_{2G})^{-1}$, measured with $H_0\|c$. The dotted lines are guides to the eye. Inset: The quantity $^{63}(T_1T/T_{2G})$ vs temperature.

$\sim$200 K. The combination of these two behaviors demonstrates unambiguously the opening of a spin gap [27].

The first remarkable point is that the decrease of $(T_1T)^{-1}$ occurs at a temperature much higher than in all other systems studied so far (typically $120 \leq T^* \leq 165$ K), suggesting that the higher T_c at optimal doping in Hg-1223 ($T_c^{\max} \sim 160$ K under pressure [28]) is related to the higher T^*. Indeed, the ratio $T^*/T_c^{\max}$ is approximately the same as in YBCO, which clearly favors superconductivity mediated by spin fluctuations. Until now, the only compounds in which T_0, T^*, and T_c were so well separated belonged to the low doping regime of YBCO. Thus our findings provide a new element in the spin gap phenomenology, which puts constraints on theoretical descriptions of the cuprates. A relationship between T^* and $T_c^{\max}$ finds natural basis in the resonating valence bond [13] and quantum disorder [15] models. However, data in more strongly underdoped samples are needed to discriminate between these two spin-liquid pictures.

Secondly, this first clear observation of a spin gap in a three-layered compound does not seem to be in favor of a *pure* interlayer spin pairing, since in that case one expects a faster decrease of $(T_1T)^{-1}$ for the inner plane. Indeed, extending to three layers the simple RPA calculation of CuO_2 planes coupled by a weak $J_\perp$ [29], we found that the dynamic susceptibility should be different in the inner and outer layers, in contradiction with our experimental result. However, we cannot rule out that $J_\perp$ is strong enough to ensure a common spin temperature in the three planes, thus more detailed calculations for a three-layered system are desirable. Note that our results do not exclude the possibility that $J_\perp$ is primarily important to stabilize the spin-gap state.

There are several possible approaches in the description of the relaxation rate data. Several authors [23,30] have used mean-field dynamic spin susceptibilities for a nearly antiferromagnetic Fermi liquid (NAFL) in which the correlation length ξ varies as $T^{-1/2}$ and the dynamic critical exponent $z = 2$ (z relates the characteristic frequency of the spin fluctuations $\omega_{\rm SF}$ to ξ; $\omega_{\rm SF} \propto \xi^{-z}$). This leads, for large values of ξ, to a constant ratio for the quantity $T_1T/(T_{2G})^2$. These models contain no parameters which can describe the spin gap state. Sokol and Pines [15] have proposed that the transition between the underdoped and the overdoped regime corresponds to the crossover from the quantum critical regime (QC) of the 2DQHAF, with $z = 1$, to a NAFL. In the QC regime, the ratio T_1T/T_{2G} should be constant.

All the above descriptions share the same problem in that they postulate a T dependence of the correlation length and require rather large values of ξ, in contradiction with the inelastic neutron scattering results for YBCO [2]. We therefore use a numerical analysis where we can fully investigate the effect of different ξ/a values [31]. Neglecting the quasiparticle contribution:

$$(T_1T)_c^{-1} = \frac{k_B\,{}^{63}\gamma^2}{2\mu_B^2 N}\,\frac{\chi'_{\mathbf{Q}_{\rm AF}}}{\omega_{\rm SF}}\sum_{\mathbf{q}}|F_{ab}(\mathbf{q})|^2\,\frac{g(\xi\Delta\mathbf{q})}{h(\xi\Delta\mathbf{q})}\,,$$

$$(T_{2G})_c^{-2} = \frac{0.69\gamma_n^4}{8\hbar^2\gamma_e^4 N}\chi'^2_{\mathbf{Q}_{\rm AF}} \times\left\{\sum_{\mathbf{q}} g^2(\xi\Delta\mathbf{q})|F_c(\mathbf{q})|^4 - \left[\sum_{\mathbf{q}} g(\xi\Delta\mathbf{q})|F_c(\mathbf{q})|^2\right]^2\right\},$$

where $\Delta\mathbf{q} = \mathbf{Q}_{\rm AF} - \mathbf{q}$, the functions g and h contain the $\mathbf{q}$ dependence of χ' and $\omega_{\rm SF}$, and $g(\mathbf{0}) = h(\mathbf{0}) = 1$. For simplicity, we take $g = 1/h$ to be Gaussians. For a given pair of experimental values of $(T_1T)^{-1}$ and $(T_{2G})^{-1}$, we can then compute $\omega_{\rm SF}$ and $\chi'_{\mathbf{Q}_{\rm AF}}$ as a function of ξ/a. We find that $\omega_{\rm SF} = f(\xi)T_1T/T_{2G}$, with $\xi f(\xi)$ slowly increasing with ξ in the range $1 \leq \xi/a \leq 2$, and reaching a constant value for $\xi/a \geq 2$. We conclude therefore that if T_1T/T_{2G} is T independent while ξ varies with T, then $\omega_{\rm SF} \propto \xi^{-1}$ (i.e., the $z = 1$ regime) even for ξ/a as low as 2. Experimentally we see that the ratio T_1T/T_{2G} (inset Fig. 3), seems to become constant above 250 K, as expected in the QC regime of a doped 2DQHAF [15].

Within a model of spin fluctuation induced pairing, Monthoux and Pines [32] found that, for the NAFL case, T_c is determined by an expression analogous to the usual BCS one with the Debye energy replaced by the product $\xi^2\omega_{\rm SF}$ (i.e., the range of energy in which the pairing interaction is effective). By analogy, in the QC regime, the relevant energy scale is likely to be $\Omega_{\rm SF} = \xi\omega_{\rm SF}$. As discussed above, this quantity is experimentally well defined even if ξ is not known; we calculate that for Hg-1223 $\Omega_{\rm SF} = 95$ meV and for $YBa_2Cu_3O_{6.63}$ [33] $\Omega_{\rm SF} = 75$ meV. It is clearly seen that the magnetic energy scale $\Omega_{\rm SF}$ is higher for the Hg compound, although the

magnitude and the T dependence of the uniform spin susceptibility are quite comparable. Note that the analysis of our data within the framework of Ref. [15] leads to the same conclusions ($\Omega_{SF} = 77$ meV for Hg-1223, and 64 meV for $YBa_2Cu_3O_{6.63}$), and to a value of $\xi/a = 3.5$ at 370 K.

In conclusion, we have demonstrated by NMR relaxation rate measurements the opening of a spin gap at $\mathbf{q} = \mathbf{Q}_{AF}$ at a temperature $T^* \simeq 230$ K in underdoped single crystals of $HgBa_2Ca_2Cu_3O_{8+\delta}$. The Cu sites in inner and outer planes present the same T dependence of T_1, which seems incompatible with the interlayer spin-pairing scenario. Quantitative analysis of the ratio T_1T/T_{2G} shows that the magnetic energy scale in this compound is higher than in the underdoped YBCO system. This is consistent with a higher value of the transferred hyperfine field B, possibly leading to a higher value of J [34]. These features and the fact that Hg-1223 exhibits the highest value of T_c (when optimally doped), as well as the highest value of T^* (when underdoped), seem to be a strong indication of the role of antiferromagnetic spin fluctuations in the pairing mechanism of the cuprates.

We thank H. Monien, D. Pines, A. Sokol, and J. Cooper for helpful discussions. M. H. J. acknowledges P. A. Lee and A. J. Millis for useful comments on this work.

*Present address: Department of Physics "Alessandro Volta," University of Pavia, Via Bassi, 6-27100 Pavia, Italy.

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