^{89}Y nuclear magnetic resonance study of Ca-doped $Y_{1-x}Ca_xBa_2Cu_3O_y$ from the underdoped to the overdoped superconducting regime

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^{89}Y NMR linewidth, Knight shift, spin-echo dephasing, and spin-lattice relaxation measurements have been carried out in $Y_{1-x}Ca_xBa_2Cu_3O_y$. Underdoped and overdoped samples have been obtained by means of Y^{3+} for Ca^{2+} substitutions in the parent chain-empty antiferromagnetic (AF) $YBa_2Cu_3O_{6.1}$ and in the chain-full $YBa_2Cu_3O_7$, respectively. Unexpected effects, as the divergence of relaxation rate with the concurrent broadening of the NMR line in the underdoped superconducting phase and the inadequacy of the Korringa relation between the relaxation rate $1/T_1$ and Knight shift, even in the overdoped regime, suggest that a revision of the commonly accepted view of $YBa_2Cu_3O_{6+y}$ compounds is required. In particular the linear temperature dependence of T_1^{-1} and the temperature behavior of Knight shift cannot be accounted for over all the temperature range. In the underdoped superconducting phase the divergence of $1/T_1$ on cooling is associated with the slowing down of excitations possibly related to sliding motions of orbital currents, or with the concurrent freezing of AF correlated spins. Echo-dephasing measurements evidence an extreme slowing down of longitudinal spin fluctuations which appear to be driven by a different dynamic, related either to flux line motions or to ^{63,65}Cu spin-lattice relaxation.

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I. INTRODUCTION

In spite of an intense research activity along the last 15 years, relevant microscopic aspects of high-temperature superconductors (SC) are still under debate. Besides the pairing mechanism, those issues involve Cu^{2+} spin dynamics and its interplay with carriers charge and spin fluctuations and, in underdoped compounds, the spin gap and/or the charge gap opening at a temperature T^* above the transition temperature T_C as well as the coexistence of superconductivity and magnetism. The normal-state phase diagram in the underdoped regime seems to be more complex than expected. The overdoped regime has been less studied and it also exhibits some unexplained features. In short, it is the evolution with the hole concentration that presents the major challenge in regards to the microscopic mechanism underlying high-T_C superconductivity.

Nuclear magnetic resonance–nuclear quadrupole resonance (NMR-NQR), muon spin relaxation (μSR), and, in part, electron paramagnetic resonance (EPR) have recently provided relevant information on the doping dependence of the internal fields, of the low-energy spin excitations, of the antiferromagnetic (AF) correlation, of the density of states around the Fermi level and of other quantities.[1] ^{89}Y nucleus, lacking of quadrupole moment and filtering out the AF correlations, has already been used in several NMR studies[2–9] and allowed to investigate the evolution with doping of the phase diagram and, in particular,[4] of the density of states $\rho(E)$, in which charge and spin excitations for conventional Fermions can be imbedded.[10]

In this paper we present and discuss the results of systematic ^{89}Y NMR measurements of the linewidth, of the Knight shift, of the echo-dephasing time, and of nuclear spin-lattice relaxation time T_1, in $Y_{1-x}Ca_xBa_2Cu_3O_y$ (YBCO) superconductors, spanning from the underdoped to the overdoped regime, in the temperature range 1.5–300 K. Preliminary ^{89}Y NMR T_1 and linewidth data in $Y_{0.85}Ca_{0.15}Ba_2Cu_3O_{6.1}$ have been published[11] and two unexpected results were found. The NMR line was observed to broaden on cooling below about 80 K and the ^{89}Y relaxation rate to display a peak around 8 K, with recovery law of stretched exponential character. Later on Singer and Imai[12] confirmed the aforementioned observations in underdoped YBCO, also reporting ^{63}Cu T_1 and ^{89}Y Knight shift and T_1 in other three samples with different Ca and/or oxygen content.

II. EXPERIMENTAL DETAILS AND RESULTS

The hole concentration n_h in YBCO depends from the transfer of carriers from CuO chains to CuO_2 planes. The properties of underdoped YBCO are related not only to the oxygen content but also to the chain ordering.[13,14] The best way to change n_h without affecting the chain ordering and at the same time to attain the overdoped regime is by means of Ca^{2+} for Y^{3+} substitution. In chain-empty $Y_{1-x}Ca_xBa_2Cu_3O_6$ the substitution for x up to 0.25 (and $n_h = x/2 \leqslant 0.12$) leads to the underdoped regime without affecting[15] the coordination of Cu(1) ions, which remain in the $3d^{10}$ electronic configuration. By starting from optimally doped $YBa_2Cu_3O_7$ through Ca substitution one can attain the overdoped regime, with oxygen-full CuO chains.

The samples of chemical composition $Y_{1-x}Ca_xBa_2Cu_3O_y$ were prepared by solid-state reaction of oxides and carbonates in flowing oxygen at 1000 K for about 100 h. X-ray

TABLE I. Superconducting transition temperature T_C in overdoped and underdoped $Y_{1-x}Ca_xBa_2Cu_3O_y$ and estimated number of holes per CuO_2 unit.

x	y	T_c (K)	n_h
0	6.65	62.5	0.12
0.05	6.97	82.0	0.18
0.1	6.96	73.0	0.20
0.1	6.96	70.0	0.21
0.2	6.98	49.5	0.23
0.25	6.1	35±1	0.07
0.15	6.10	34±1	0.07
≈0.15	6.05	20±2	0.06
0.1	6.10	14±2	0.06

powder diffraction was used to check the presence of a single phase. The oxygen stoichiometry was first estimated by thermogravimetry and energy dispersive spectrometry. Then the samples were either oxygenated close to $y=7$ by annealing in oxygen atmosphere (25 atm) at 450 K for about 100 h or reduced as much as possible by leaving them under vacuum for about 100 h. The final oxygen content turned out to be $y=6.97\pm0.02$ for overdoped YBCO and $y=6.10\pm0.05$ for the underdoped samples. The zero-field transition temperatures $T_C(0)$ were estimated from magnetization curves in $H=20$ G. Sharp transitions were detected in overdoped as well as in underdoped samples having $T_C\gtrsim50$ K (see Table I). In strongly underdoped compounds the transition was observed to broaden. It can be remarked that the local disorder evidenced[12] in ^{63}Cu NQR spectra and related to electric-field gradient distribution is not manifested in the ^{89}Y NMR spectra. In Table I the transition temperature $T_C(0)$ and the hole concentration n_h, estimated according to the empirical expression[8] $T_C/T_C^{max}=1-82.6(n_h-0.16)^2$, are reported.

In Fig. 1 the Knight shift K_S of the ^{89}Y resonance line with respect to the one in a reference solution of YCl_3 (after the substraction of temperature independent 150 ppm chemical shift contribution) is reported. The ^{89}Y NMR linewidth [full width at half intensity (FWHI)] is practically temperature independent down to T_C in optimally doped and in overdoped compounds, showing only a little increase on cooling. In the superconducting phase of the overdoped samples only the broadening due to the vortex lattice[1] occurs. On the contrary, in underdoped compounds the linewidth (Fig. 2) increases sizeably well above T_C.[11] Below T_C the line broadening superimposes to the one due to vortex lattice[11] $\delta\nu_{FL}\propto\lambda_L(T)^{-2}$ (λ_L is the London penetration length).

The ^{89}Y spin-lattice relaxation rates $1/T_1$ are reported as a function of temperature in the normal state (Fig. 3) and in the superconducting phases (Fig. 4) for typical overdoped and underdoped samples. The recovery laws in the normal phase are described by a single exponential, as expected for $I=1/2$, with a site-independent fluctuation dynamics. In overdoped compounds an exponential recovery law is detected also below T_C. In underdoped compounds a fast relaxing component, of stretched exponential character, is found to arise progressively on cooling below about 60 K, increasing

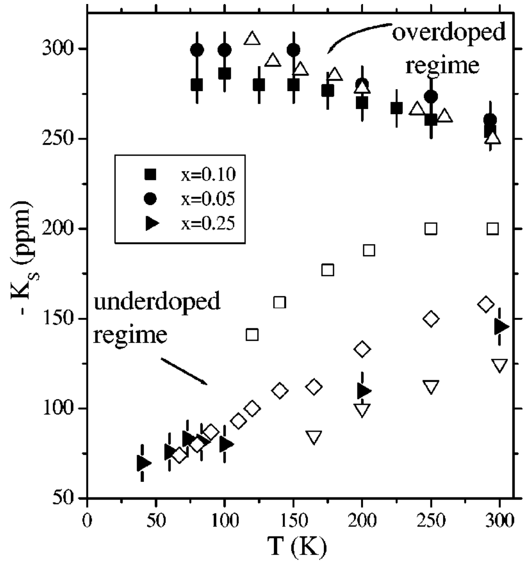

FIG. 1. ^{89}Y NMR Knight shift as a function of temperature in underdoped and overdoped regimes of $Y_{1-x}Ca_xBa_2Cu_3O_y$. The data represented by down triangles and by open diamonds are from Ref. 12 for $x=0.22$, while the ones represented by open squares and up triangles are from Ref. 5 for $x=0.20$.

at the expenses of the slow relaxing, single-exponential recovery (inset in Fig. 4). The long T_1 component follows approximately the temperature dependence expected in the superconducting phases, while the fast relaxing component shows a divergent behavior on cooling, with a maximum of the relaxation rate occurring at a temperature T_g around 8 K. The relaxation rate in the superconducting phase of overdoped samples is roughly the one expected below T_C, once the contribution from vortex motions around the irreversibility temperature is taken into account.

Finally in Fig. 5 the temperature behavior of the effective

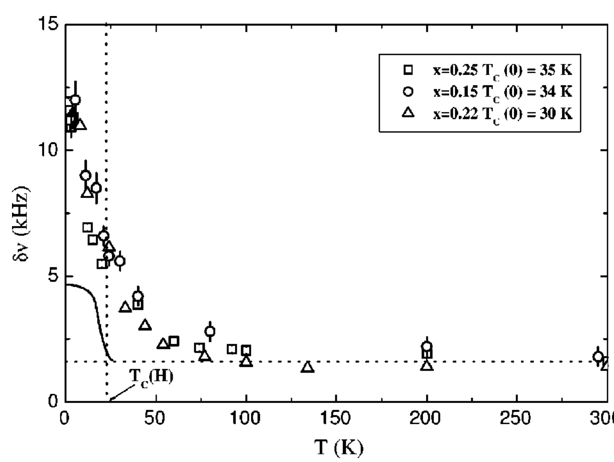

FIG. 2. ^{89}Y NMR linewidth $\delta\nu$ (FWHI), in $H_0=9$ T, as a function of temperature in the underdoped regime of $Y_{1-x}Ca_xBa_2Cu_3O_{6.1}$. The data reported as triangles are from Ref. 12. The solid line below $T_C(H)$ tracks the behavior of the linewidth $\delta\nu_{FL}$ expected from the vortex lattice, for $T_C(H)\approx25$ K (see Ref. 1 and references therein for details).

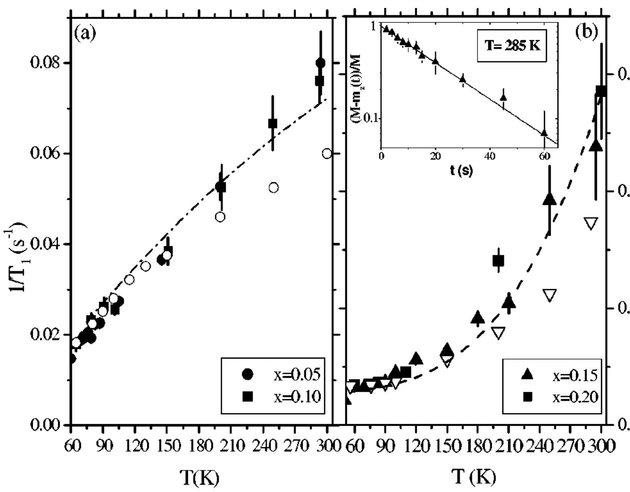

FIG. 3. ^{89}Y NMR relaxation rate in the normal state, in overdoped $Y_{1-x}Ca_xBa_2Cu_3O_{6.95}$ (a) and in underdoped $Y_{1-x}Ca_xBa_2Cu_3O_{6.1}$ compounds (b). The data for $x=0.22$ [T_C (0)≈75 K (open circles) and $T_C(0)=30$ K (open triangles)] are from Ref. 12. The dashed-dotted line, in (a), is the best-fit behavior in overdoped compounds, by using the generalized susceptibility as given in Ref. 20. The dashed line, in (b), tracks the effect of the spin-gap opening occurring below about 350 K. In the inset a typical recovery plot observed in the normal state is reported.

decay rate $1/T_2$, namely, the inverse of the echo decay time to e^{-1} from the initial (extrapolated) amplitude, is reported, as detected in the standard $\pi/2$-τ-π sequence (Hahn echo) or in Carr-Purcell-Meiboom-Gill (CPMG) sequence.

III. ANALYSIS OF THE DATA AND DISCUSSION

The NMR line shape results, in principle, from several contributions. One source is related to the dipolar interaction with like (^{89}Y) and unlike (^{63,65}Cu) nuclei, and yields a Gaussian line shape.[16] Due to other sources of broadening, such as field inhomogeneity, distribution of demagnetization factors, etc., the FWHI $\delta\nu$ of the ^{89}Y NMR line is found around 1 KHz. $\delta\nu$ depends only little on doping and should be practically temperature independent, down to T_C. In the superconducting state extra broadening is due to the bulk distribution of the local field induced by the flux-lines lattice and ^{89}Y linewidth tracks the local-field modulation.[17] It is evident from Fig. 2 that another line broadening mechanism is present at low temperature in the underdoped compounds, arising well above $T_C(H)$.

As regards the shift of ^{89}Y NMR line, K_S originates from the field-induced polarization of delocalized Fermi-like carriers or from the field at the Y site due to the localized magnetic moments at the Cu^{2+} spin, depending on the interpretative model. Since the field is mostly due to the scalar transferred hyperfine interaction, one can consider the shift K_S as isotropic. K_S is related to the spin susceptibility,

$$K_S=\frac{H_D}{g\mu_B}\chi_{\rm spin}=H_D g\mu_B\chi', \tag{1}$$

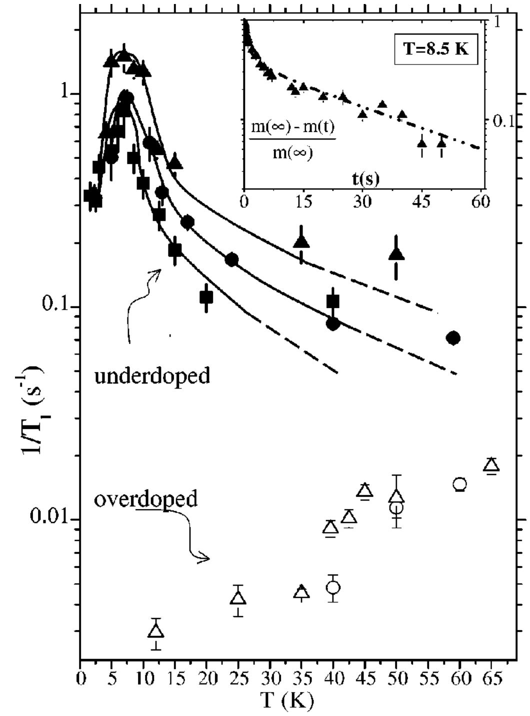

FIG. 4. ^{89}Y relaxation rate, in the low-temperature range for overdoped $Y_{1-x}Ca_xBa_2Cu_3O_{6.95}$ [open symbols: $x=0.05$ (squares); $x=0.10$ (triangles)] and for underdoped $Y_{1-x}Ca_xBa_2Cu_3O_{6.1}$ [closed symbols: $x=0.25$ (squares); $x=0.15$, $T_C(0)=20$ K (triangles), $x=0.15$, $T_C(0)=34$ K (circles)]. The lines are guides for the eye. The inset evidences that in underdoped regime the recovery law is the sum of two components. The fast relaxing component has a stretched exponential character and T_1 has been taken as the value at which it reduces to e^{-1}.

where H_D is the z-component of the magnetic field at the Y site and where the static uniform spin susceptibility χ' (in eV^{-1} units) has been introduced, while $\chi_{spin}\equiv g^2\mu_B^2\chi'$.

In cuprates the $3d$ electron band is rather narrow and in tight-binding models the magnetic properties are usually well described within a localized spin approximation, with maximum spin density at Cu(2) site. Then χ' in Eq. (1) can be thought of as the $q=0,\omega=0$ limit of the generalized spin susceptibility $\chi(\vec{q},\omega)$ pertaining to the Cu^{2+} magnetic moments.

In the somewhat opposite interpretative model the doping induces a Fermi liquid of itinerant holes. In this case H_D can be written as $(8\pi/3)\langle u_k\rangle^2 g\mu_B$ ($\langle u_k\rangle$ being the average of the Bloch function for carriers at the Fermi surface), namely, the hyperfine contact term, and the static susceptibility is usually written as

$$\chi'(0,0)=\frac{\rho(E_F)}{1-\mathcal{I}\rho(E_F)} \tag{2}$$

with $\rho(E_F)$ being the density of states at the Fermi level and $\mathcal{I}\equiv\mathcal{I}_{q=0}$ a doping-dependent coupling constant which accounts for the AF correlation. Within the scenario of delocalized carriers a phenomenological way to account for the evo-

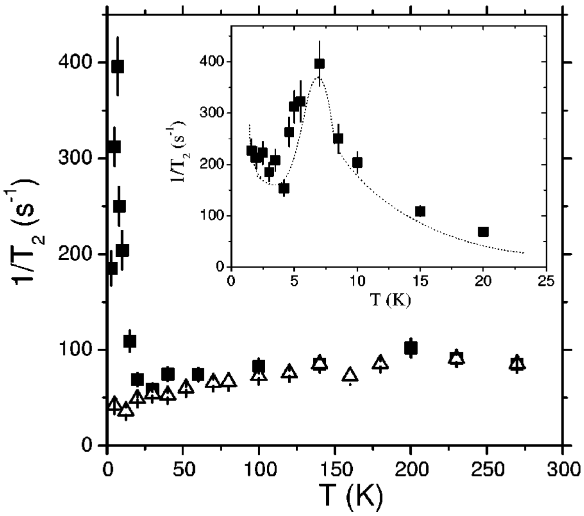

FIG. 5. Inverse of the dephasing time of the spin echo in $Y_{0.75}Ca_{0.25}Ba_2Cu_3O_{6.1}$ for the Hahn (squares) and for CPMG (triangles) sequences, as a function of temperature. In the inset the blow up of data for the Hahn echo in the low-temperature range is shown (the dotted line is a guide to the eye).

lution of K_S with doping in the overdoped regime is to add an energy independent $\rho(E)$ with a density of states showing a singularity at the Fermi level.[4] A form of $\chi(0,\omega)$, somewhat including the features of both models will be recalled later on.

The ^{89}Y relaxation rate can be conveniently written in terms of the dynamical spin susceptibility,[1,18,19]

$$T_1^{-1} = \frac{^{89}\gamma^2}{2N} k_B T \sum_{\tilde{q}} A_{\tilde{q}}^2 \frac{\chi''_{\pm}(\tilde{q},\omega_m)}{\omega_m} \tag{3}$$

and the form factor A_q^2 can be assumed independent of the orientation of the external magnetic field. For localized moments one has[1] $A_{\tilde{q}}^2 = H_D^2\{\cos^2(q_x a/2)\cos^2(q_y b/2)\cos^2(q_z d/2)\}$ (d is the distance between adjacent CuO_2 planes) with $H_D \simeq 36$ KOe. For ferromagnetic correlation among planes $q_z = 0$.

For delocalized carriers (DC) A_q^2 is practically q independent. A recent attempt to derive a form of $\chi(\vec{q},\omega)$ suitable to fit the temperature dependence of ^{63,65}Cu, ^{17}O, and ^{89}Y T_1 in optimally doped is due to Zavidonov and Brinkmann,[20] by using a two-times Green function method, within a t-J model framework. We recall that because of the q dependence of A_q^2 filtering out the AF fluctuations, to a good approximation, the relaxation rate becomes

$$\frac{1}{T_1} = \frac{^{89}\gamma^2}{2} H_D^2 \frac{k_B T}{N} \sum_{\vec{q}} \frac{\chi_S(0,0)}{\Gamma_{\vec{q}}(0)}, \tag{4}$$

where the form factor has been taken q independent, as for delocalized carriers. In optimally doped YBCO, in the temperature range 100–300 K the experimental behavior of $1/T_1$ has been rather well reproduced.

The linear temperature dependence of the relaxation rate in the normal state is a characteristic mark of optimally doped and overdoped $Y_{1-x}Ca_xBa_2Cu_3O_y$. It should be remarked that this behavior is not in agreement with the Korringa relation $T_1 T \propto K_S^{-2}$, since K_S in overdoped compounds is temperature dependent, decreasing by about 20–25% on increasing T from 80 K to 300 K (Fig. 1). This anomaly was already pointed out by Nandor *et al.*[9] in optimally doped YBCO, by extending the measurements up to about 800 K.

The data for K_S and T_1 in the overdoped sample with $x \simeq 0.10$ can be compared with the theoretical calculation by using the generalized susceptibility given in Ref. 20, in correspondence to the value $n_h = 0.21$ for the hole concentration. A partial agreement for the T dependence of K_S is found. However, the linear T dependence of $1/T_1$ could be reproduced only over a limited temperature range, similarly to what was already found in optimally doped YBCO.

In underdoped compounds, in agreement to previous observations,[2–6] the linear temperature dependence of $1/T_1$ breaks down due to the pseudogap opening. For a Fermi-like spectrum of excitations, since $1/T_1 \propto \rho^2(E_F)$, the pseudo-gap is manifested not only in the spin but also on charge excitations, as observed by means of various techniques.[10] ^{89}Y NMR results indicate that a DC model can hardly be applied in the underdoped regime. One may speculate that the spin-gap opening has to involve a phenomenon of magnetic character, such as antiferromagnetic fluctuations leading to a local situation similar to the one occurring in the parent AF, with a gap between two Hubbard bands.

In the SC state the temperature dependence of $1/T_1$ in overdoped (and in optimally doped) YBCO is substantially the one expected for spin-singlet and d wave pairings, with a slight shoulder around $T \cong 50$ K possibly due to the flux-lines motions. The behavior in underdoped compounds (Fig. 4) is dramatically different. A sharp peak in $1/T_1$, around $T_g \simeq 8$ K, is detected and for $T \lesssim 50$ K the recovery law takes a stretched exponential character. The peak in $1/T_1$ is a neat indication of the occurrence of slowing down of the spin fluctuations in the 20 MHz range. It points out that a further source of relaxation, not present in overdoped samples, has to be taken into account. On general physical grounds, in view of the frequency and temperature dependence of T_1's and of the nonexponential recovery law, one can write the relaxation rate due to the extra contribution in underdoped SC phase as $1/T_1 \approx {}^{89}\gamma^2 \langle h_{eff}^2\rangle J(\omega_L,\tau_e)$, $J(\omega_L,\tau_e)$ is the spectral density at $\omega_L = {}^{89}\gamma H_0$ and τ_e effective correlation time for the transverse fluctuations of $\vec{h}_e(t)$ at nuclear site with mean square amplitude $\langle h_{eff}^2\rangle$. The stretched exponential recovery corresponds to

$$e^{-(t/T_1^e)^{1/2}} = \int_0^\infty p\left(\frac{1}{T_1}\right) e^{(-t/T_1)} d\left(\frac{1}{T_1}\right) \tag{5}$$

where

$$p\left(\frac{1}{T_1}\right) = \frac{T_1}{2\sqrt{\pi}\left(\frac{T_1}{T_1^e}\right)^{1/2}} e^{-T_1/4T_1^e}$$

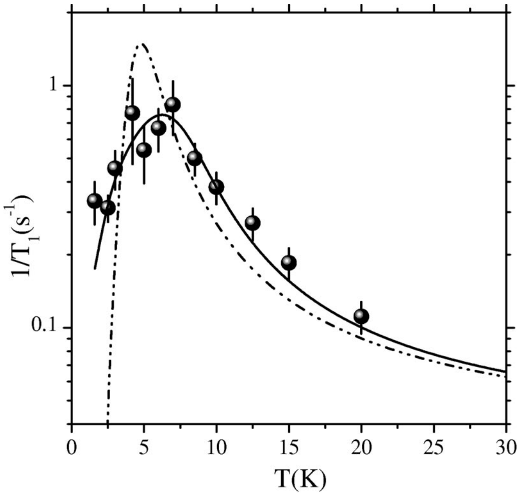

FIG. 6. Fit of ^{89}Y relaxation rate in $Y_{0.75}Ca_{0.25}Ba_2Cu_3O_{6.1}$ for a single energy E (dashed-dotted line) and for a rectangular distribution (solid line). The best-fit values derived from the solid line turn out $E = 22$ K, $\Delta = 16$ K, and $\tau_0 = 8\times10^{-10}$ s.

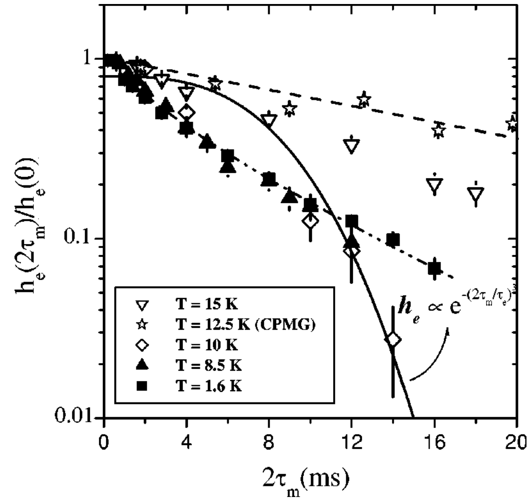

FIG. 7. Normalized echo amplitude for representative temperatures. The stars indicate the decay of the echo amplitude after a CPMG pulse sequence. The lines are guide for the eye.

is a distribution function that can be related to the distribution of the energy barriers E, yielding an average correlation time $\langle \tau_e \rangle = \tau_0 e^{[\langle E \rangle / k_B T]}$.

From the condition that for $T \simeq T_g$ the maximum in the relaxation rates implies $J(\omega_L, \langle \tau_e(T_g) \rangle) \simeq 1/\omega_L$ one can extract $\sqrt{\langle h_{eff}^2 \rangle}$ from the experimental $T_1(T = T_g)$ data. One obtains $\sqrt{\langle h_{eff}^2 \rangle} \simeq 15$ Oe, a value about a factor 10 smaller than the one in underdoped $La_{2-x}Sr_xCuo_4$.[21] The reduced effective field indicates that in bilayer compounds the correlation between adjacent CuO_2 planes partially cancels the effective fluctuating field at Y site and that the extra contribution to $1/T_1$ in the low-temperature range of underdoped compounds could possibly arise from the sliding motions of orbital currents.[22] In Fig. 6 the data for $Y_{0.75}Ca_{0.25}Ba_2Cu_3O_{6.1}$ in the low-temperature range are fitted by assuming a rectangular distribution for E, of width Δ, leading to[23] $J(\omega_L, \tau_e) = [1/2\omega_L(\Delta/T)][\mathrm{arctg}(\tau_0 \omega_L e^{(E+\Delta)/T}) - \mathrm{arctg}(\tau_0 \omega_L e^{(E-\Delta)/T})]$ (with E and Δ in Kelvins) and one obtains $\tau_0 \simeq 8\times10^{-10}$ s, $E = 22$ K, and $\Delta = 16$ K.

Now we discuss the data for the echo dephasing. For $T \geqslant 30$ K the data obtained from the Hahn or CPMG sequence practically coincide. In the low-temperature region an enhancement of the decay rate of the Hahn echo around 7 K is observed. Below about 3 K, an increase in T_2^{-1} begins to appear. Accordingly, the function $h_e(2\tau_m)$ shows a significant changeover (Fig. 7). For $T \geqslant 10$ K $h_e(2\tau_m)$ is practically exponential. Around $T \simeq 10$ K the decay function appears roughly of the form $h_e(2\tau_m) \propto e^{-\tau_{m^3}/\tau_e}$. In the low-temperature range, $T < 7$ K, the function $h_e(2\tau_m)$ changes again to a form resembling the stretched exponential. Having obtained from the T_1 data the temperature behavior of τ_e (correlation time for the transverse fluctuation) one can derive an estimate of the order of magnitude and of the temperature behavior of the dynamical contribution to $T_2^{-1} \sim \gamma^2 \langle h^2 \rangle 2\tau \approx (\delta\omega_z)^2 \tau$ by assuming for $(\delta\omega_z)^2$ a value corresponding to a fraction of the linewidth, say $\delta\nu \sim 1$ KHz. Thus the dynamical contribution to T_2^{-1} would become of the order of $100 s^{-1}$ only around 2.5 K, then rapidly increasing on cooling and flattening at $T \sim 1.2$ K. The conclusion is that the slowing down of the spin dynamics causing the maximum in T_1^{-1} could be responsible only of the slight increase in T_2^{-1} detected below about 2 K (see Fig. 5). Therefore the peak in T_2^{-1} observed around 7 K is due to a dynamic different from the one yielding the peak in T_1^{-1} at about the same temperature.

Extra peaks in the spin-echo dephasing rate have already been detected in optimally doped YBCO, around $T \simeq 30$ K (see Ref. 24 and references therein), including for NQR ^{63}Cu T_2, which would at first sight rule out the hypothesis of a contribution due to vortex dynamics. In view of the complex phase diagram that has been argued to characterize the low-temperature phases of underdoped cuprates, with a variety of low-energy excitations[25] one cannot disregard the hypothesis of the "extra peak" in $1/T_2$ indicative of a novel type of dynamics driving the transverse fluctuations of the local field at the Yttrium site. Nevertheless, a conventional source for the peak observed in $1/T_2$ can still be envisaged in the vortex dynamics. In strongly underdoped $YBa_2Cu_4O_8$, the effective correlation time describing vortex motions has been proved[26] to diverge on cooling below T_C, reaching the millisecond range at about 10 K, with an (extrapolated) irreversibility temperature around (0.2–0.3) T_C. For an order of magnitude estimate of the contribution to the echo decay from the vortex lattice motion one can write

$$1/T_{2\mathrm{FL}} \sim \gamma^2 \langle \Delta H^2 \rangle \frac{2\tau_{\mathrm{FL}}}{1 + (\tau_{\mathrm{m}}/\tau_{\mathrm{FL}})^2}$$

while the echo decay function can be expected of the form $h(\tau_m) \propto \exp[-\tau_m/\tau_{FL}]^3$. The maximum in $(T_2^{-1})_{FL}$ should occur at the temperature where τ_{FL} is of the order of the characteristic measuring time τ_m in the Hahn echo. Then a very small amplitude $\sqrt{\Delta H^2} \sim 0.2$ Oe of the dynamical ripple in the local-field distribution accounts for the experimental results $(T_2^{-1})_{max} \sim 400\ s^{-1}$, at $T \simeq 7$ K.

Another possible source for the extra peak in $1/T_2$ is the fluctuations in the local field induced by ^{63}Cu nuclear spin-lattice relaxation, with a characteristic time $T_1^{Cu} \simeq \tau_m$. This value of ^{63}Cu T_1 would be feasible if ^{63}Cu spin-lattice relaxation has a T dependence similar to the one of ^{89}Y. We remark that ^{63}Cu T_1 measurements in the low-T range are prevented by the very short transverse relaxation time (wipe-out effect, see Refs. 12 and 21 for a thorough discussion). If ^{63}Cu $1/T_1$ has a maximum on decreasing temperature similar to the one evidenced in ^{89}Y spin-lattice relaxation, then at low temperature the condition $\tau_m \simeq T_1^{Cu}$ can be matched again to yield a peak in ^{89}Y $1/T_2$.

Finally we observe that spin-glass dynamics are extremely complex, involving motions on many different time scales at the same temperature. The aforementioned picture is strictly based on an activated model. Spin glasses are far more complex, and may well exhibit a peaking of fluctuations over a wide range of time scales within a narrow range of temperatures, possibly accounting for the simultaneous peaks in T_1 and T_2. However, it appears difficult to quantitatively justify these simultaneous peaks even considering a very broad frequency distribution and, therefore, a different relaxation mechanism has to be invoked.

The broadening of the NMR line starts in a temperature range where no effects of the vortices nor ''static'' contribution from the slowing down of the spin dynamics discussed above are active. It is feasible that the broadening results from a stripelike modulation in a quasistatic local field,[12] the site-dependent field in the neighborhood of ''stripes'' preventing the occurrence of a common spin temperature.

IV. SUMMARIZING REMARKS

By means of ^{89}Y NMR spectra and relaxation measurements the evolution with doping of the microscopic magnetic properties in YBCO's superconductors compounds has been investigated. In order to change the number of holes per CuO_2 unit and to span from the underdoped to the overdoped regime, without affecting the CuO chains, the Ca^{2+} for Y^{3+} substitution was performed. ^{89}Y NMR linewidth $\delta\nu$, Knight shift K_S, T_1, T_2 in a temperature range 1.6–300 K at 9 T have been measured.

In the normal phase $T > T_C(H)$ an analysis of the data is attempted on the basis of a generalized spin susceptibility which includes charge and spin excitations. However this form seems to reproduce the experimental relation between K_S and T_1 in the overdoped regime only in a limited temperature range, while it cannot justify the breakdown of the conventional Korringa relation. Only a heuristic depletion of hole density of states, corresponding to the pseudogap opening, can justify the departure from the linear dependence of T_1^{-1} in the underdoped compounds.

As regards the superconducting phase, in the overdoped regime the behavior of T_1 is the one expected for spin-singlet and d-wave pairings, with a slight shoulder at $T \cong 50$ K, due to flux line motions. In underdoped compounds, instead, T_1^{-1} and the echo decay rate show a peak at $\simeq 8$ K, while $\delta\nu$ increases on decreasing temperature for $T \leqslant 80$ K. The behavior of T_1 can be tentatively attributed to sliding motion of orbital currents often described as glass-spin freezing of magnetic moments. A wide distribution of effective correlation time for transverse fluctuations is indicated. This source of relaxation could be present also in the dynamical contribution to the echo decay rate T_2^{-1}, but only below about 2 K. Instead an extra peak in T_2^{-1} is detected at about 7–8 K. It has been argued how this effect could be due to a very small fluctuation amplitude in the local-field distribution due to the vortex lattice or to ^{63}Cu T_1 processes, with a characteristic correlation time of the motion reaching the millisecond range typical of the Hahn echo measure. Finally an indirect evidence of a contribution to the linewidth broadening possibly due to stripelike charge inhomogeneities has been indicated as the possible source of the lack of a common spin temperature responsible for the stretched exponential character in the spin-lattice relaxation recovery.

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