Evidence for Charge Instability in the CuO_3 Chains of $PrBa_2Cu_3O_7$ from $^{63,65}Cu$ NMR

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(Received 17 October 1997)

NMR and NQR measurements have been performed on Cu(1) chain sites in $PrBa_2Cu_3O_7$ between 300 and 4.2 K. The spin-lattice relaxation rate $1/T_1$ has been measured in the whole temperature range 4.2–300 K. Static and dynamic NMR and NQR parameters undergo a crossover at 180 K and an energy gap opens at $T^\dagger \approx 120$ K, as revealed by the temperature dependence of $1/T_1$. These results are consistent with a charge density wave occurring in the quasi-one-dimensional CuO_3 chains and reveal the *internal* electronic properties of the chains in the "123" compounds. [S0031-9007(98)05545-8]

PACS numbers: 71.45.Lr, 74.72.Jt, 76.60.Gv

There is an increasing interest in the physics of hole-doped CuO_3 chains, as they may play a subsequent role in the normal and superconducting states of $(R)Ba_2Cu_3O_7$ (R = rare earth) and $YBa_2Cu_4O_8$ high temperature superconductors. These chains are believed to act as a charge carrier (holes) reservoir for the CuO_2 planes in the latter systems. Nevertheless, there is no well-established consensus on the nature of the low-energy excitations in the chains [1,2]. The spin phase diagram has been extensively studied in the insulating chains of Sr_2CuO_3 [3]. Unfortunately, recent experimental investigations have shown the difficulty of hole doping in such systems. In "123" compounds the possibility that these chains carry some part of the supercurrent is still controversial. In-plane anisotropy of the magnetic penetration depth [4] and specific-heat measurements [5] seem to suggest the presence of part of a superconducting condensate on the chains. Some authors have shown a fall at $T_c = 90$ K both in the T dependence of $1/T_1$ [6] measured in $YBa_2Cu_3O_7$ on Cu(1) (chain) sites and in the local spin susceptibility measured on Cu(1) by the NMR line shift [7]. These effects were sometimes attributed to proximity-induced superconductivity, from the CuO_2 planes to the CuO_3 chains. Edwards *et al.* [8,9] observed a spatially varying energy gap, detected by scanning tunneling microscopy at 20 K in $YBa_2Cu_3O_7$ CuO_3 chains. They claimed that their results are consistent either with a short-range charge density wave (CDW) or a proximity-coupled supercurrent in the chains. Finally, incommensurate one-dimensional fluctuations have been detected in $YBa_2Cu_3O_{6.93}$ CuO_3 chains by neutron scattering [10].

These results strongly suggest that the CuO_3 chains of 123 compounds display an intricate electronic structure, as has also been observed in the "124" family. For the latter system, Suter *et al.* [11] performed NQR and NMR measurements in the double-chain compound $YBa_2Cu_4O_8$ and observed an electronic crossover both on the Cu(1) and on the Cu(2) sites. They analyzed their results in the framework of a CDW driven by the CuO_2 planes. Pulsed-neutron-scattering data [12] also revealed collective displacements of chain oxygen atoms in $YBa_2Cu_4O_8$, which raises the question of the origin of this CDW.

All of these experiments face a common difficulty: How can one separate the internal physics of CuO_3 chains from possible proximity effects induced by the CuO_2 planes? Among the fully doped $(R)Ba_2Cu_3O_7$ cuprates, $PrBa_2Cu_3O_7$ appears as an exception as it exhibits insulating CuO_2 planes with antiferromagnetic (AF) order below $T_N \approx 280$ K [13,14]. In order to explain the absence of superconductivity, Fehrenbacher and Rice [15] proposed a model that is still a matter of debate, in which the absence of in-plane conductivity is explained by in-plane hole localization through Pr-O hybridization. Nevertheless, several studies suggest that the CuO_3 chains remain metallic on a local scale in this compound [16–19]. $PrBa_2Cu_3O_7$ thus offers a unique opportunity for studying the internal physics of quasi-one-dimensional CuO_3 chains, isolated from the contributions of CuO_2 metallic and superconducting planes.

In this Letter, we present NMR and NQR measurements between 300 and 4.2 K on the Cu(1) chain site in $PrBa_2Cu_3O_7$. New NQR line-shape measurements at 300 K show that the effective charge in the CuO_3 chains of $PrBa_2Cu_3O_7$ deduced from the electric field gradient (EFG) value should be approximately the same as in $YBa_2Cu_3O_7$, which supports the Pr-O localization model of Fehrenbacher and Rice [15]. The value of $1/T_1$, measured by means of NMR, NQR, and the NQR line shape, undergoes a dramatic change below 120 K. NMR measurements of the temperature dependence of $1/T_1$ reveal the *opening of a gap* in the electronic excitations at $T^\dagger \approx 120$ K. We show how these results are consistent with *a charge density wave transition in the quasi-one-dimensional CuO_3 chains.*

Our experiments were performed on a highly homogeneous powder of $PrBa_2Cu_3O_7$. The conditions of single

crystal synthesis favor Ba/Pr substitution, leading to the progressive occupancy of the O(5) antichain site [20] and therefore to structural disorder in the CuO_3 chains. Our procedure was therefore as follows. A mixture of carefully dried rare earth oxides Pr_6O_{11} (freshly calcined), $BaCO_3$ and CuO in stoichiometric amounts (Pr:Ba:Cu = 1-2-3), was reacted in air for a week at 955 °C. This promotes the growth of single crystal grains and prevents Pr substitution on the Ba sites. The sample was likely ground to disperse the mixture without destroying the crystals and then annealed at the same temperature for four days. This procedure was repeated several times. Finally, the crucible was quenched in atmospheric air and the optimum composition was obtained by annealing the powder under a flow of oxygen while slowly cooling from 450 to 200 °C at 1 °C per hour and subsequently maintaining it for 100 h at 100 °C. The sample was characterized by x-ray diffraction, and the lattice parameters $a = 3.8617(1)$, $b = 3.9280(1)$, and $c = 11.7035(4)$ Å confirm the low substitution rate of Ba by Pr, as this substitution would induce a transition to a tetragonal phase ($\frac{c}{3} \approx a = b$) [21].

Our measurements were made on a powder oriented along the c axis in an epoxy resin under an applied field of 6 T. NMR and NQR ^{63,65}Cu spectra were obtained by varying the frequency and integrating the spin-echo intensity after a $\pi/2$-τ-π pulse sequence. The NMR experiments were done with the static magnetic field H_0 parallel to the c axis and in some cases to the ab-plane direction. The spin-lattice relaxation rate T_1^{-1} of Cu(1) was measured using a differential antiringing recovery pulse sequence [22].

^{63,65}Cu(1) NQR spectra between 300 and 4.2 K are shown in Fig. 1. The ^{63,65}Cu(1) NQR spectrum is remarkably well resolved at high temperatures. To our knowledge, no data have been published for $T > 25$ K. In the low temperature range ($4.2 < T < 20$ K), the anomalously broadened line observed agrees quite well with previous studies by Nehrke *et al.* [23]. The line shape at 300 K is very similar to that measured in other $(R)Ba_2Cu_3O_7$ systems, and we obtained $^{63}\nu_{\mathrm{NQR}} = 21.36$ MHz for Cu(1). Our spectrum shows clearly that the CuO_3 chains are quite well ordered in our sample and that the low-temperature linewidth cannot be attributed to structural disorder as claimed by Nehrke *et al.* [23]. Moreover, the NQR frequency is very sensitive to the local electronic charge distribution. Comparison of the value $^{63}\nu_{\mathrm{NQR}}$ Cu(1) with that obtained in other $(R)Ba_2Cu_3O_7$ compounds [24] leads us to conclude that the CuO_3 chains carry approximately the same number of holes per copper site in $PrBa_2Cu_3O_7$ as in $YBa_2Cu_3O_7$. This result supports the theoretical models that assume localization of in-plane holes in $4f$-Pr-$2p_\pi$-O orbitals [15]. Indeed, in-plane hole localization is not expected to induce a major change in the local charge of CuO_3 chains. Other models have suggested that in-plane holes are filled when trivalent Y is replaced by Pr, assumed to be tetravalent; this situation, however, should result in a hole antitransfer from planes to chains, which would most probably strongly affect the local EFG of Cu(1).

We now turn to the temperature dependence of the NQR results for the line shape, the ^{63}Cu(1) spin-lattice relaxation rate $^{63}T_{1\mathrm{NQR}}^{-1}$ and the spin-spin relaxation rate $^{63}T_2^{-1}$. The full width at half-maximum (FWHM) of the ^{63}Cu(1) NQR line starts to increase below 170 K (see Fig. 1), whereas below this temperature $^{63}T_2^{-1}$ (Fig. 2) sharply increases. Since the NQR linewidth is broadened between 4.2 and 25 K (for temperatures higher than the Pr AF ordering temperature, 17 K), Nehrke *et al.* [23] claimed that this effect was independent of the magnetic phase of the Pr sublattice as they detected no transferred hyperfine field at the Cu chain site. Another effect must therefore be responsible for the broadening of the NQR line. For a pure magnetic relaxation mechanism, one expects a single-exponential law behavior of the longitudinal magnetization decay, $\exp(-t/T_{1\mathrm{NQR}})$. This,

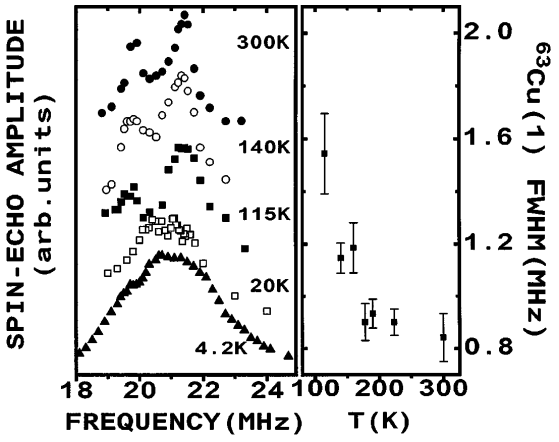

FIG. 1. ^{63,65}Cu(1) NQR spectra of $PrBa_2Cu_3O_7$ measured between 300 and 4.2 K. The right side displays the full width at half-maximum of the ^{63}Cu(1) NQR line, fitted to a Gaussian.

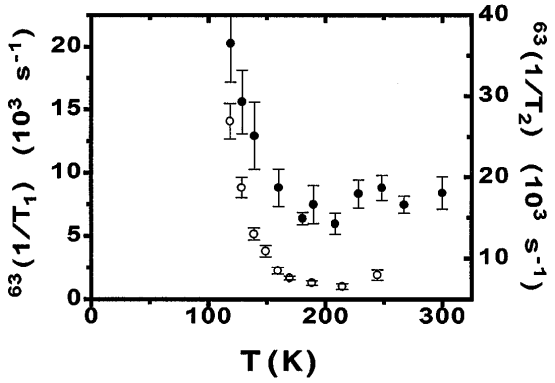

FIG. 2. Temperature dependence of ^{63}Cu(1) $1/T_1$ (solid circles) and $1/T_2$ (open circles) obtained by NQR at 21.35 MHz.

however, fails to fit our data. Instead, we used a stretched-exponential form [25]:

$$\exp[-(t/T_{1\mathrm{NQR}})^{\lambda}], \tag{1}$$

to account for the $1/T_1$ distribution ($\lambda = 0.55 \pm 0.05$ for $120 < T < 270$ K). Below 180 K, $^{63}T_{1\mathrm{NQR}}^{-1}$ increases as shown in Fig. 2. The distribution of $^{63}T_1^{-1}$ raises the question of a charge-fluctuation relaxation mechanism. Nevertheless, the accuracy of the measurements is limited by the jump in $^{63}T_2^{-1}$, which is such that the signal falls below the sensitivity of our experiment in the temperature range between 100 and 30 K. No reliable comparison can therefore be made between the two copper isotopes. For this reason, in this temperature range we checked the low-energy excitations on the Cu(1) site through the NMR spin-lattice relaxation rate.

In $PrBa_2Cu_3O_7$, the local field induced by the antiferromagnetic order in the CuO_2 planes below 280 K shifts the Cu(2) NMR line to frequencies above the Cu(1) line and prevents any overlap between these lines when $H_0 \parallel c$ [13]. This makes it possible to study the behavior of T_1^{-1} on Cu(1). Figure 3(a) displays the values of $^{63,65}T_{1\mathrm{NMR}}^{-1}$ measured in 8.497 T at 97.24 MHz, obtained assuming

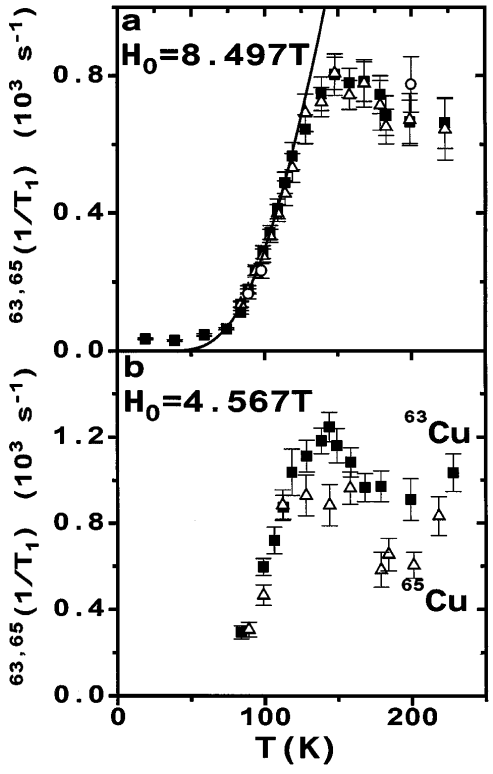

FIG. 3. (a)Temperature dependence of $1/T_1$ at $H_0 = 8.497$ T with the field parallel to the c axis on the Cu(1) site for the ^{63}Cu (solid squares) and the ^{65}Cu (open triangles) isotopes. The solid line is a fit to an exponential. Open circles: $^{63}1/T_1$ measured with $H_0 \parallel ab$. (b) Temperature dependence of $1/T_1$ at $H_0 = 4.567$ T with the field parallel to the c axis on the Cu(1) site for the ^{63}Cu (solid squares) and the ^{65}Cu (open triangles) isotopes.

the following decay behavior:

$$1/10 \exp(-t/T_1) + 9/10 \exp(-6t/T_1) \tag{2}$$

which is expected for a relaxation of magnetic origin. The relaxation rate shows a marked maximum at about 150 K, and a gaplike state opens in the low-energy excitations below $T^{\dagger} \approx 120$ K. We define this temperature as the onset below which $\ln(T_1)$ is linear with respect to $1/T$. Using the relation $1/T_1 \equiv \exp(-\Delta/k_B T^{\dagger})$, we deduce a gap energy $2\Delta/k_B T^{\dagger} = 7 \pm 0.2$ ($2\Delta = 72$ meV). This value is remarkably close to that obtained by Edwards *et al.* [8,9] for the $YBa_2Cu_3O_7$ chains. Under this magnetic field, the relaxation rates of the two copper isotopes are roughly equal in the whole range of temperature. Moreover, for a smaller field ($H_0 = 4.567$ T $\parallel c$ axis at 53.87 MHz) the ratio $^{63}T_1^{-1}/^{65}T_1^{-1}$ is, within experimental error, equal to the square of the nuclear quadrupole moment ratio, $^{63}Q^2/^{65}Q^2 = 1.16$ in the temperature range $120 < T < 220$ K [see Fig. 3(b)]. *This implies EFG fluctuations associated with a dynamic charge process* in this temperature range, and confirms the deviation from single-exponential behavior in NQR experiments. $^{63}T_1^{-1}/^{65}T_1^{-1}$ is never equal to $^{63}\gamma^2/^{65}\gamma^2$ in our measurements, which rules out the hypothesis of a purely magnetic relaxation mechanism. We therefore fitted our data at 8.497 and 4.567 T to a quadrupolar relaxation form [26],

$$1/2 \exp(-2W_1 t) + 1/2 \exp(-2W_2 t), \tag{3}$$

where W_1 and W_2 represent the contributions from EFG fluctuations to the $\Delta m = 1$ and $\Delta m = 2$ transitions between the nuclear energy levels E_m. The relaxation rates $^{63,65}W_1$ obtained at 8.497 and 4.567 T reveal the same behavior as with the fit to the magnetic relaxation rate: Critical fluctuations arise below 180 K, and a gap opens below 120 K. We still obtain $^{63}T_1^{-1} \approx {}^{65}T_1^{-1}$ at 8.497 T, whereas $^{63}T_1^{-1}/^{65}T_1^{-1} \approx {}^{63}Q^2/^{65}Q^2$ at 4.567 T. Finally, measurement of $^{63}T_1^{-1}$ at 200, 99, and 89 K with the field $H_0 = 8.497$ T parallel to the ab-plane direction yielded the same values within the error bars as those with $H_0 \parallel c$, both with Eqs. (2) and (3). This suggests that the relaxation at Cu(1) is quite isotropic in $PrBa_2Cu_3O_7$, as is found in $YBa_2Cu_3O_7$ [7,27]. Moreover, the frequency dependence of $^{63}T_1^{-1}$ (observed from the 8.497 T to the 4.567 T data) is consistent with charge fluctuations of a 1D diffusive mode in the chain segments [28]. On the other hand, the similar values of T_1^{-1} found at 8.497 T for the two isotopes even in the case of the quadrupolar decay, indicate that there are probably two channels for the relaxation: the charge-fluctuation mechanism ($1/T_{1Q}$) and magnetic fluctuations ($1/T_{1M}$). In this case, there is no obvious expression for the relaxation.

We now discuss why the hypothesis of a spin density wave (SDW) mechanism seems to be ruled out by our results. A transition to a SDW phase should involve magnetic fluctuations, and one would expect

that ${}^{63}T_1^{-1}/{}^{65}T_1^{-1} \equiv ({}^{63}\gamma/{}^{65}\gamma)^2$. One would also expect some kind of antiferromagnetic zero-field NMR spectrum on Cu(1) at low temperatures due to a local field that is proportional to the very large gap $2\Delta = 72$ meV. Our results disagree with these predictions: (i) The $1/T_1$ measurements reveal quadrupole fluctuations, (ii) the NQR line is broadened at the beginning of the transition, (iii) the excellent correlation between $1/T_2$ and the increase in FWHM of the NQR line below 180 K strongly supports a charge mechanism, whereas $1/T_2$ measured on the $(\frac{1}{2}, -\frac{1}{2})$ NMR line is nearly constant in this range of temperature, and (iv) there is no clear evidence of AF order at low temperatures on Cu(1).

Finally, we studied the behavior of the local spin susceptibility on the Cu(1) sites by measuring the position of the NMR line as a function of the temperature with $H_0 \| c$. An accurate determination of the shift tensor is possible only with a reliable estimate of the asymmetry parameter η of the electric field gradient tensor, which is not known accurately on the Cu(1) site in $PrBa_2Cu_3O_7$. Another difficulty comes from the strong paramagnetic contribution from the Pr sublattice and the AF ordering at 17 K, which prevents a direct estimate being made of the orbital part of the shift $K_{\alpha,\mathrm{orb}}$ at low temperatures. Only the relative T variation of the $(\frac{1}{2}, -\frac{1}{2})$ central line frequency $\Delta f_{(1/2,-1/2)}$ with $H_0 \| c$ can be given. This parameter measured at $H_0 = 8.497$ T is roughly constant from 200 to 170 K and decreases monotonically below 170 K, revealing a loss in the local static spin susceptibility as expected for a CDW transition. The absence of any discontinuity in the slope of $\Delta f_{(1/2,-1/2)}$ at 120 K excludes a magnetic phase transition at this temperature.

In conclusion, our data reveal unambiguously the existence of a collective charge instability (i.e., a charge density wave) occurring in the CuO_3 chains. Up to now, NMR and NQR have been used extensively to study charge and spin density waves in quasi-one-dimensional materials such as organic conductors, $NbSe_3$, and the blue bronzes [28–31], and the highly correlated hole-doped CuO_3 chain opens a new field of investigation. Since CuO_3 segments are expected to remain metallic at low temperature [16–19], this charge instability should be different from a true Peierls transition. The commensurate or incommensurate character of this transition and the physical origin (phonon modes or electronic correlations) remain to be investigated. Our findings are to be compared with the charge instability reported in under-doped $YBa_2Cu_4O_8$ by Suter *et al.* [11], who speculate on the possible relation with the spin-gap phenomenon. Finally, these results call for other experiments in $YBa_2Cu_3O_7$, in order to confirm the existence of such instabilities in the chains of superconducting compounds and give new insight into the interplay between chains and planes.

We thank C. Berthier, J. P. Boucher and M. Horvatić for helpful discussions, and P. Ségransan for the use of his NMR data acquisition software. This work was partially supported by the DRET, France, Grant No. 94-099.

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