In-Plane Charge Modulation below T_c and Charge-Density-Wave Correlations in the Chain Layer in $YBa_2Cu_3O_7$

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Nuclear quadrupole resonance (NQR) measurements have been performed on Cu(2) plane sites and Cu(1) chain sites in fully doped $YBa_2Cu_3O_7$ between 300 and 4.2 K. The sharp increase of the Cu(1) NQR linewidth across the superconducting transition and the T dependence of the Cu(1) spin lattice relaxation rate confirm the existence of a charge-density-wave state (CDW) in the chains. The simultaneous broadening of the Cu(2) linewidth below T_c and the anomalous T dependence of Cu(1) and Cu(2) NQR parameters indicate that these in-chain CDW correlations are strongly involved in the appearance of an in-plane charge modulated structure below T_c.

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$YBa_2Cu_3O_y$ (Y-123), which is probably one of the most widely studied high T_c superconductors, presents a unique feature as regard to the one dimensional Cu-O chains which play the role of charge reservoir. While the CuO_2 planes, which are known to be the source of the superconductivity, have mainly held the attention of physicists, the physics of chains and their interaction with CuO_2 planes remains poorly understood. The highly ($y > 6.9$) or fully doped ($y \cong 7$) Y-123 offers the best opportunities to go deeper in the study of such interactions as the chains are almost full of oxygen. Among the various experimental studies devoted to the chains, two main approaches have been followed. The first one is based on the possibility of *a charge-density-wave (CDW) ground state in the Cu-O chains,* which was discussed in the context of positron annihilation [1], scanning tunneling microscopy [2,3], and neutron scattering [4] experiments. However, an unambiguous experimental evidence for a CDW transition was only so far obtained in the particular case of the $PrBa_2Cu_3O_7$ system [5]. A second trend supposes a *superconducting state induced in the chains* below T_c by the *proximity with* CuO_2 *planes,* frequently discussed in connection with macroscopic measurements such as magnetic penetration depth [6] or specific heat [7] studies. The decrease of the local Cu(1) spin susceptibility χ_o below T_c, probed by the copper NMR line shift, has also been presented as a clue in favor of the induced superconductivity scenarios in Y-123 [8], and more recently in Y-124 [9]. Here, one should emphasize that in contradiction with the last argument, the Cu(1) spin-lattice relaxation rate (SLRR) $1/T_1$ [10] is smoothly T dependent across the superconducting transition. Last, thermal conductivity [11] and microwave absorption [12] experiments have been interpreted as evidences for a growth of superfluid density in the chains direction below the temperature range 65–55 K, raising the question of a possible chain-induced superconductivity far below T_c ($T_c = 93.8$ K for an oxygen stoichiometry $y = 6.9$ [11], and $T_c = 93.4$ K for $y = 6.9$ [12]).

Recently, Krämer and Mehring have presented Cu(2) nuclear quadrupole resonance (NQR) experiments in highly doped Y-123 [13] revealing an in-plane charge ordering in the superconducting state below 35 K. The existence of such a transition is a crucial point, as it was theoretically predicted [14] that a *CDW state in the chains* may trigger such an in-plane charge ordering, and that it may account for the anomalies detected in the superconducting state by macroscopic measurements.

In this Letter, we demonstrate the existence of CDW correlations in the chains of fully doped Y-123. We show experimentally that this chain CDW state is closely related to the in-plane charge ordering below T_c. These conclusions are obtained by analyzing the T dependence of the static and dynamic NQR parameters of both Cu(1) and Cu(2) sites in the whole temperature range 300–4.2 K. The copper NQR frequency ν_Q is directly proportional to the electric field gradient surrounding the copper nuclei, which is itself very sensitive to the charge environment. As a consequence, the NQR linewidth $\Delta\nu_Q$ reflects the local charge distribution around the copper sites. Thus, NQR is an extremely sensitive tool for the detection of CDW states in Y-123 chains and planes. Moreover, as NQR is a local probe, its field of investigation extends even to the case of short-range CDW correlations.

The sample used was a highly homogeneous powder of fully doped Y-123 ($T_c^{\mathrm{midpoint}} = 89.5$ K; $y \cong 7$). The Cu NQR spectra were obtained by varying the frequency and integrating the spin echo intensity after a $\pi/2 - \tau - \pi$ pulses sequence. The Cu(1) and Cu(2) $1/T_1$ were measured using a differential antiringing recovery pulse sequence. Much attention was paid to ensure that an optimal thermal equilibrium of the sample was obtained, especially for temperatures near T_c.

The high doping level was confirmed by the almost symmetric shape of the Cu(2) and Cu(1) NQR lines and by the

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absence of any significant signal at the frequencies corresponding to Cu(1) surrounded by one or two oxygen vacancies [15]. For each copper site, a unique doublet was found, with frequencies corresponding, respectively, to the ratio of the nuclear quadrupole moments of the two copper isotopes ($^{63}Q/^{65}Q = 1.08$) and with intensities proportional to the ratio of their natural isotopic abundance ($^{65}A/^{63}A = 0.45$). The sharpness of the lines (without any overlap between the two isotopes contribution) allowed us to realize very accurate fits for Cu(1) and Cu(2) line shapes using Lorentzian functions. In the following, $^{63}\nu_Q(1)$ and $^{63}\nu_Q(2)$ refer to the copper chain and copper plane ^{63}Cu isotope NQR frequencies, respectively, and $\Delta^{63}\nu_Q(1)$ and $\Delta^{63}\nu_Q(2)$ refer to the corresponding linewidths, defined as full width at half maximum (FWHM).

The temperature dependence of the static NQR parameters of Cu(1) and Cu(2) sites is shown in Fig. 1. We mainly focus on data nearly above and below T_c. The evolution of $\Delta^{63}\nu_Q(1)$ versus T, which so far had never been investigated so precisely, shows a sharp step across the superconducting transition. Comparing the additional broadening of the Cu(1) line below T_c for the two copper isotopes suggests a quadrupolar line broadening. This strongly indicates that the local Cu(1) charge environment becomes suddenly distributed below T_c. We also observe a well marked dip at $T \cong T_c$ in the T dependence of the NQR frequency $^{63}\nu_Q(1)$ as previously observed by Riesemeier *et al.* [16]. This dip has been discussed in connection with the lattice anomalies detected by various experimental probes at T_c [17], but the effect of a charge instability transition arising in the chains might also be considered. Besides the rapid growth of $\Delta^{63}\nu_Q(1)$, the Cu(1) SLRR shown in Fig. 2 surprisingly decreases smoothly across T_c and falls down only below 70 K. This crossover is apparent both on the $1/^{63}T_1(T)$ and $1/^{63}T_1\,T(T)$ Cu(1) SLRR representations. Furthermore, a plateau is observed between 130 K and T_c in the T dependence of $1/^{63}T_1\,T(T)$ (see inset in Fig. 2). Because of the lower accuracy of the ^{65}Cu isotope SLRR measurements, the respective contributions from magnetic and quadrupolar fluctuations to the Cu(1) relaxation were difficult to estimate. Nevertheless, our comparison for $1/T_1$ of the two copper isotopes reveals the presence of these two types of fluctuations. In this context, the plateau mentioned above can be a consequence of the slowing down of the quadrupolar fluctuations at a temperature higher than that at which the Cu(1) line broadens. An important feature which emerges from our data is the strongly different behavior of the Cu(1) T-dependence SLRR as compared to that of Cu(2) which presents a well known sudden decrease below T_c associated to the opening of the superconducting energy gap in overdoped Y-123 [18]. This rules out a proximity induced superconducting state in the chains just below T_c. Moreover, the alternative possibility of a plane induced superconductivity with a freezing temperature lower than T_c has been discussed in Ref. [19] and has been ruled out by penetration-depth anisotropy measurements [20]. Considering the tendency of 1D CuO_3 chains surrounded by insulating CuO_2 planes, to undergo a CDW state below 120 K as observed in $PrBa_2Cu_3O_7$ [5] and taking into account the more complicated situation in Y-123, due to the presence of metallic/superconducting CuO_2 planes which can interact with the chains, we think that our data are consistent with the onset of CDW correlations in the chains of this cuprate

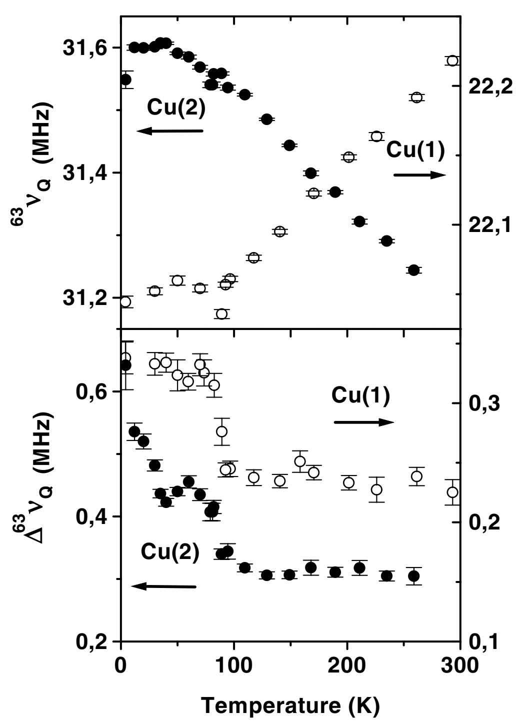

FIG. 1. T dependence of the frequency $^{63}\nu_Q$ (upper panel) and of the full width at half maximum $\Delta^{63}\nu_Q$ (lower panel) of the ^{63}Cu NQR lines on the Cu(1) (open circles) and Cu(2) (solid circles) sites in $YBa_2Cu_3O_7$

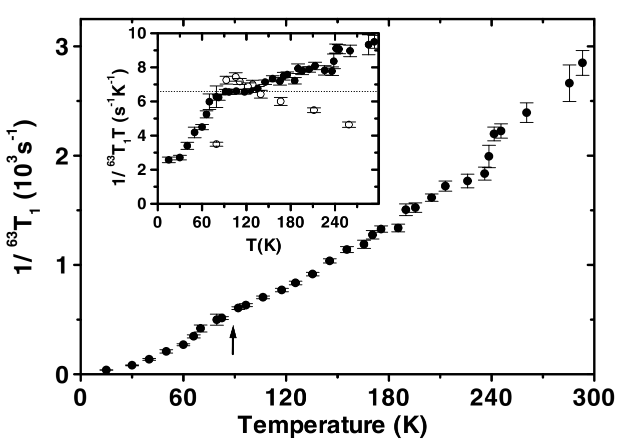

FIG. 2. T dependence of the spin lattice relaxation rate ($1/^{63}T_{1NQR}$) on Cu(1) chain sites in $YBa_2Cu_3O_7$. The inset shows ($1/^{63}T_1T$) vs T for Cu(1) (solid circles) and Cu(2) (open circles) sites. The arrow indicates the value of T_c.

below T_c. At this stage, we cannot make a distinction between a short- or long-range CDW state.

The copper plane NQR linewidth $\Delta^{63}\nu_Q(2)$ displays nearly the same T dependence as $\Delta^{63}\nu_Q(1)$ for $T > 60$ K. Once again, a strong increase of the linewidth below T_c is present. In addition, a similarity in the T dependence below T_c of the Cu(2) and Cu(1) sites NQR frequencies is observed with local maxima, respectively, near 40 K and 50 K. All these features strongly suggest a complex interaction between the chains CDW state and the in-plane charge dynamics. More surprising is the nonmonotonic variation of $\Delta^{63}\nu_Q(2)$ below T_c, which displays a local maximum at 60 K and a minimum at 40 K. As previously discussed in Ref. [21] , this puzzling behavior of $\Delta^{63}\nu_Q(2)$ implies that the in-plane charge ordering evolution below T_c is probably more subtle that a simple transition to a CDW state in the plane below 35 K, as initially proposed in Ref. [13].

In order to understand these intricate features, it is necessary to discuss in more detail how the CDW state sets in the chains of $YBa_2Cu_3O_7$. It has been demonstrated [22] that in Y-123, the electron-electron Coulomb scattering between the planes and chains charge carriers may cause a temperature dependent effect which breaks the CDW order parameter in the chains, until the CuO_2 planes become superconducting. Thus, in the normal state, only very short-range CDW correlations are allowed. Such local CDW correlations are consistent with the plateau observed in the T dependence of $1/^{63}T_1\ T(T)$ below 130 K. Next, across the superconducting transition, the Coulomb scattering vanishes and the setting of a 1D CDW state correlated on larger distances along the chain axis direction (Fig. 3, upper left panel) is allowed. The resulting charge modulation on Cu(1) sites induces the rapid growth of $\Delta^{63}\nu_Q(1)$. Nevertheless, a true 2D long-range CDW order in the chain layer, correlated from one chain to its neighbors (Fig. 3, upper right panel), appears only well below T_c, as the Coulomb scattering is not absolutely suppressed just below T_c, but progressively diminishes following an exponential T dependence [19]. The Cu(1) $1/^{63}T_1$ diminution versus T, which becomes more pronounced below 70 K, is likely consistent with the opening of an energy gap associated with a long-range CDW order. This feature would be the signature of a transition between 1D short-range order (SRO) and 2D long-range order (LRO) CDW states. On the other hand, there is no important change in the $\Delta^{63}\nu_Q(1)$ T dependence below 70 K, as the charge modulation in each chain (considered independently of its neighbors) is roughly the same in the case of short-range or long-range CDW states (see Fig. 3). As a result, the local charge distribution on the copper chain sites is nearly the same in both regimes as probed by the NQR linewidth.

Now, we must consider how this crossover between SRO and LRO CDW states in the chains can be associated to an in-plane charge modulation, and why $\Delta^{63}\nu_Q(2)$ (and $\Delta^{63}\nu_Q(1)$ to a lesser extent) displays an anomalous T-dependence below T_c. Kamimura *et al.* have recently proposed a model [14], in which each Cu(2) site should have its charge modulated in connection with a CDW charge modulation in the chains, as shown in Fig. 3. They suppose that the hole doping per unit cell ξ in CuO_2 planes is closely related to the hole doping η in Cu-O chains by the condition of charge neutrality $\eta + 2\xi = 2$. If one considers that in the unit cell of $YBa_2Cu_3O_7$ there is 0.25 hole per CuO_2 plane [average charge $+2.25e$ per Cu(2)] [19] and using the charge neutrality rules, we expect a chain hole doping of 1.5 holes per Cu(1) [average charge $+2.5e$ for Cu(1) [14]]. For this chain doping level, the most probable CDW wavelength (in agreement with scanning tunneling microscopy [2,3] and neutron diffraction [4] data) is $q_{CDW} = 2\pi/2k_F = 4b$, where b is the Cu(1)-Cu(1) distance along the chain axis.

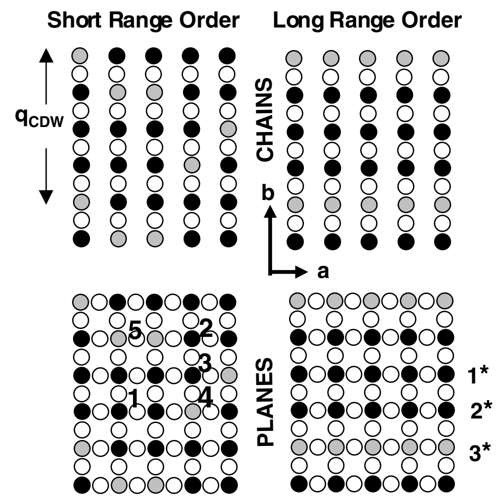

FIG. 3. Upper panel: SRO (left) and LRO (right) CDW states in the Cu-O chain layers. Black and grey circles stand, respectively, for Cu(1) sites with an average point charge $(2.5 + q/3)e$ and $(2.5 - q)e$ (see text). Open circles represent the oxygen O(1) sites. The corresponding CDW charge modulation periodicity q_{CWD} is also shown. Lower panel: In-plane charge modulations induced by the chain CDW states. Black and grey circles represent, respectively, the Cu(2) sites with an average point charge $(2.25 - q/6)e$ and $(2.25 + q/2)e$. In the SRO regime (left), many Cu(2) sites differ from their first and second neighbors charge environment (some of these nonequivalent sites are indicated by labels from 1 to 5). In the LRO regime (right), only three different Cu(2) sites (1*, 2*, and 3*) remain.

With the aim to clarify the discussion, we use a simple point charge picture for the CDW state similar to the one initially proposed in Ref. [14] with the two following hypotheses: (i) on the interval of four Cu(1) sites along the chain axis, the charges $+(2.5 - q)e$ (where q stands for the charge modulation amplitude), and $+(2.5 + q/3)e$ are attributed to the first Cu(1) site and to the three others, respectively, (ii) the Cu(2) sites point charges are simply related to the Cu(1) sites point charges by the neutrality rules. Our discussion, however, is not restricted to this simple charge modulation model, and the forthcoming arguments should be valuable in the case of more complex

CDW states. Following our simple CDW picture, it is important to emphasize the major difference between the respective effects of the chains SRO and LRO regimes upon the induced charge modulation in the Cu(2) plane sites. Indeed, there are actually several Cu(2) sites which differ from their first and second neighbors charge environment in the SRO regime case ($T > 60$ K), whereas there remain three nonequivalent Cu(2) sites with different charge states in the LRO regime case ($T < 60$ K). In the SRO regime, for example, the Cu(2) site labeled 1 with charge $+(2.25 - q/6)e$ has four Cu(2) first neighbors with the same $+(2.25 - q/6)e$ charge, whereas the Cu(2) labeled 2 has three first neighbors charged $+(2.25 - q/6)e$ and one charged $+(2.25 + q/2)e$. The Cu(2) sites charge modulation associated to this SRO regime corresponds to the increase of the $\Delta^{63}\nu_Q(2)$ parameter below T_c. For a correct description of the SRO regime, we must be aware of the limitations of our oversimplified point charge model. Indeed, the charge state is not fully localized on each Cu(2) site, because they are connected in a 2D network through the hybridization via O_{2p} orbitals. Thus, different local charge states occupy the nonequivalent Cu(2) sites previously mentioned in the SRO regime and the charge distribution will be more homogeneous in the LRO regime. As a consequence the Cu(2) NQR linewidth decreases for $T < 60$ K, following the transition between the SRO and the LRO CDW states in the chains. In the frame of this crossover, we note that a small dip is observed on $\Delta^{63}\nu_Q(1)$ at 70 K near the temperature at which the Cu(1) SLRR begin to decrease. Its small amplitude reflects the small interchain coupling in the Cu-O layers. Moreover, the temperature at which this anomaly appears is very near that where $\Delta^{63}\nu_Q(2)$ presents a maxima. This shows the close relation between the chain's behavior and the Cu(2) plane charge modulation.

Last, the low-temperature regime raises some interesting questions. One is the increase of $\Delta^{63}\nu_Q(2)$ below 40 K. We suggest that the in-plane charge modulation should be partially dynamic and that its motion slows down at low temperatures, due, for example, to pinning by local defects such as oxygen vacancies. A second puzzling feature is the absence of a detectable quadrupole intensity pattern which must result from the particular pattern in the LRO case giving a commensurate CDW. Three distinct NQR lines should be observed in the low-temperature spectrum with the respective amplitude a: ($a = 1$) for the shaded Cu(1), ($a = 1$) for the middle of the three solid Cu(1)'s, and ($a = 2$) for the solid Cu(1)'s which are adjacent to the shaded ones. The nondetectability of such a pattern in our Cu(1) NQR spectrum at 4.2 K is unfortunately a consequence of the broadening of the quadrupolar linewidth which gives a low resolution incompatible with such observation.

In summary, our results provide an interesting clue to understanding the nature of the chain ground state and its interaction with the in-plane charge dynamic in Y-123. They reveal unambiguously that a CDW state sets in Cu-O chains below the superconducting transition in fully doped Y-123. The puzzling temperature dependence of Cu(2) and Cu(1) NQR linewidths is interpreted within the scenario of a crossover between SRO and LRO CDW states in the chains which is associated to a transition between an inhomogeneous charge state and a low-temperature ordered charge state in the planes.

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