Low-Temperature Charge Ordering in the Superconducting State of $YBa_2Cu_3O_{7-\delta}$

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(Received 26 February 1999)

Measurements of the nuclear quadrupole resonance (NQR) transverse relaxation rate of $^{63,65}Cu$ and of the NQR linewidths in $YBa_2Cu_3O_{7-\delta}$ in the superconducting state reveal unusual features below $T = 35$ K. A narrow peak in the transverse relaxation rate and an increased quadrupolar line broadening with decreasing temperature are attributed to a charge density wave ordered state below $T = 35$ K.

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

It is well established that the copper-oxygen planes in cuprate superconductors are doped by an intra-unit-cell charge reservoir comprised of copper-oxygen chains in $YBa_2Cu_3O_{7-\delta}$ ($YBCO_{7-\delta}$) or oxygen planes in the case of Bi or Tl cuprates. The doping level of the copper-oxygen planes is determined by the oxygen concentrations in the reservoir. By varying this concentration the doping level of the charge carriers and correspondingly the density of states at the Fermi level and consequently many electronic properties, including the superconducting transition temperature T_{sc}, can be varied. This type of reasoning usually implies homogeneous doping; i.e., all unit cells are considered to be essentially equivalent.

There has been evidence, however, for quite some time that doping proceeds inhomogeneously [1] and modulated structures can appear and have indeed been observed in the Bi cuprates [2,3] and more recently in La cuprates [4,5]. In $YBCO_{7-\delta}$ there is some evidence for a charge density wave (CDW) state in the copper-oxygen-chain layers from scanning tunneling microscopy at 20 K [6] and neutron scattering measurements [7]. Some chain-oxygen ordering was reported from nuclear quadrupole resonance (NQR) measurements in strongly underdoped $YBCO_{7-\delta}$ [8]; however, no collective charge ordering was observed. More recently Brinkmann and co-workers [9,10] proposed a charge density gap state in $YBa_2Cu_4O_8$ with a transition temperature $T^\dagger = 180$ K near the spin-gap temperature T^* as seen by an anomalous behavior in the NMR/NQR relaxation, linewidth, and magnetic shift data, and they observed an isotope effect in the ^{63}Cu NQR relaxation in this compound [11]. However, no ordering of the proposed CDW state was observed so far.

In this Letter we present clear evidence for a transition into an ordered charge density wave state below $T_c = 35$ K in highly doped $YBCO_{7-\delta}$ with a superconducting transition temperature $T_{sc} \approx 90$ K. The evidence is provided by an increasing quadrupolar broadening of the $^{63,65}Cu(2)$ NQR lines below 35 K (Fig. 1) and a λ-like peak in the spin-spin relaxation rate T_2^{-1} at 35 K (Fig. 2). The relaxation peak has been observed by us [12,13] and others [14–17] already for quite some time, but its origin was never clarified and investigated in detail. It was sometimes attributed to some unknown defect or not discussed at all. The increasing quadrupolar broadening of the NQR line for decreasing temperatures below 35 K, as reported here, sheds some new light on this phenomenon and will be argued below in favor of a charge density ordered state.

The experiments were performed on a homebuilt pulsed NQR spectrometer equipped with a continuous flow cryostat which contains the probe and the sample. In order to minimize the influence of external static magnetic fields, such as the earth magnetic field and stray fields, the complete setup was shielded by a μ-metal surrounding [18]. By using a high-power pulse amplifier we were able to achieve a π-pulse length at the ^{63}Cu NQR transition as short as 2 μs. In the superconducting state the dependence of the transverse relaxation rate on the rf-field strength H_1 was checked by applying different rf-field strengths and we found no change of the transverse relaxation rate after reducing H_1 up to a factor of 2. In addition to this we checked the T_{2g} rate at different spectral positions of the line near the center and found the rate to be independent of the frequency within the experimental error. This implies that our spectral excitation is strong enough for observing reliable transverse relaxation data. The spectra were measured by taking subspectra (Fourier transform of echo half) at different carrier frequencies and summing the echo spectra after phase correction. Spin-spin relaxation measurements were performed by using a Hahn-echo sequence ($\pi/2 - \tau - \pi$).

The samples used were unoriented powder samples prepared in a solid state reaction, with an average grain size of 4 μm. Sample *A* was annealed in oxygen at $T = 450$ °C and slowly cooled to room temperature. In sample *B* the oxygen content was slightly reduced by annealing under reduced oxygen partial pressure. The transition temperature of the samples was determined by the detuning of the NQR probe at the superconducting transition temperature. The measured transition temperatures T_{sc} are 89.9 K (sample *A*) and 89.2 K (sample *B*). Both samples show a monoexponential T_1^{-1} behavior over the whole temperature range between room temperature and 10 K which is indicative of single phase composition.

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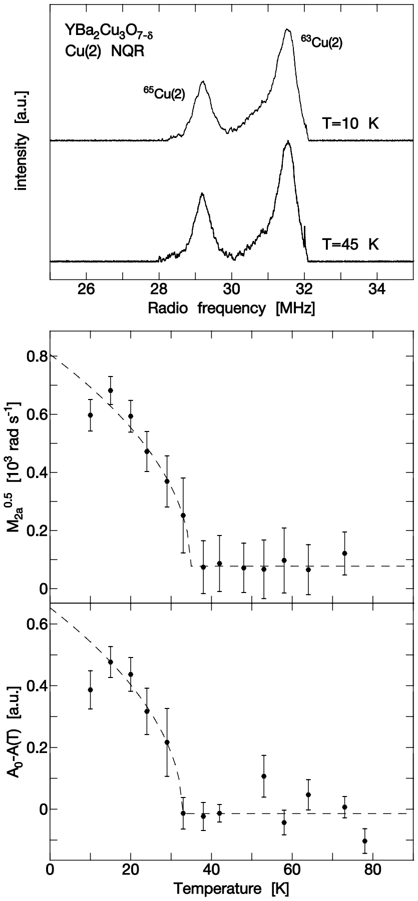

FIG. 1. Top: ^{63,65}Cu(2) spectra of $YBCO_{7-\delta}$ (sample B) at 45 and 10 K. A broad temperature independent background signal was subtracted. A temperature dependent broadening of the narrow component is clearly visible at 10 K. The integral intensity of the spectra has been normalized. The additional broadening occurs only for the narrow components. Middle: Temperature dependence of the line broadening observed in the spectra below 35 K of the ^{63}Cu(2) line in the $YBCO_{7-\delta}$ (sample B) represented by the square root of the additional second moment. Bottom: Temperature dependence of the peak intensity of the normalized spectra. The dashed lines correspond to a mean field order parameter $(T - T_c)^\beta$ with a critical exponent $\beta = 0.5$.

In Fig. 1 we present NQR spectra above and below the characteristic temperature (35 K) (top) together with the temperature dependence of the second moment due to the additional broadening of the ^{63,65}Cu(2) NQR spectrum of $YBCO_{7-\delta}$ (sample B) below $T = 35$ K (Fig. 1, middle). The temperature dependent broadening was determined from the experimental spectra (Fig. 1, top) by convoluting the spectrum above $T = 40$ K with a Gaussian broadening function in order to reproduce the spectra at lower temperatures. In addition to the broadening of the spectrum we have observed a decrease of the peak amplitude of the normalized spectrum (Fig. 1, bottom), which is just another measure of the additional broadening. Both coincide with the onset of the peak in the additional relaxation rate to be discussed in the following.

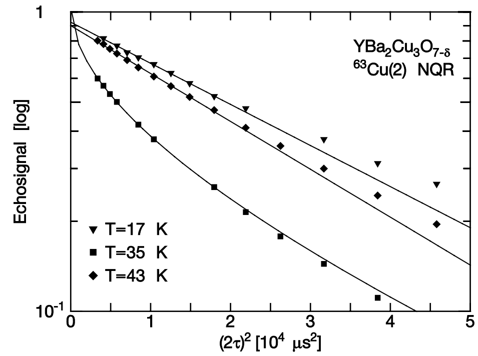

FIG. 2. Spin-echo decay function of ^{63}Cu(2) in $YBCO_{7-\delta}$ (sample B) after T_{2R} correction at different temperatures plotted in a logarithmic intensity scale versus $(2\tau)^2$. Note that the character of the decay changes near 35 K and becomes more exponential.

Spin-spin relaxation measurements were performed on both samples. The echo decay function can be expressed as

$$M(\tau) = M_0 \exp\left(-\frac{2\tau}{T_{2R}}\right) \exp\left(-\frac{1}{2}\frac{(2\tau)^2}{T_{2g}^2}\right) \exp\left(-\frac{2\tau}{T_{2a}}\right)$$

where the first exponential factor represents the spin-lattice or Redfield contribution T_{2R} whereas the second factor represents the Gaussian decay function due to the spin-spin interaction. The Gaussian contribution probes the real part $\chi'(\vec{q}, \omega)$ of the (magnetic) spin susceptibilities [19,20] which is essentially temperature independent. Usually the Gaussian part is of interest only because of its relevance for distinguishing s- and d-wave pairing [20,21]. We remark that the rather weak temperature dependence of the Gaussian part below $T_{\rm sc}$ is indicative of d-wave pairing as demonstrated before [18,21,22].

The third factor is introduced by us in order to account for an additional relaxation mechanism. Its functional form is expected to be exponential in the case of rapid motion but might assume a different nonexponential functional form for slow or correlated motion. Here we have found it to be exponential which will be demonstrated in the following. In this case the additional relaxation mechanism adds a relaxation rate T_{2a}^{-1} to the Redfield contribution. The temperature dependence of the Redfield contribution is known because it can be related to the spin-lattice relaxation rate T_1^{-1} in the case of NQR by [18]

$$T_{2R}^{-1} = (2 + R)\frac{1}{3T_{1,\rm NQR}},$$

where R is the NMR-anisotropy ratio of the spin-lattice relaxation rates between applying the external field perpendicular to the CuO_2 plane or in plane. We assumed for R the value of 3.6 [18]. This leads to $T_{2R}^{-1} = 1.9T_{1,\rm NQR}^{-1}$. The spin-lattice relaxation rate decreases rapidly with decreasing temperature and gives no significant contribution below $T = 40$ K.

After subtracting the T_{2R}^{-1} contribution from the echo decay we are left with the Gaussian decay together with the additional exponential contribution. In this way modified spin-echo decay functions are shown for three different temperatures in Fig. 2.

Around 35 K a significant deviation from the Gaussian behavior occurs and a non-Gaussian component can be extracted from the data. A detailed analysis shows that the additional contribution is truly exponential. We have extracted the additional contribution T_{2a} from the Gaussian decay according to the equation and plotted it in Fig. 3 (bottom) together with the total decay rate (Fig. 3, top) where the Redfield contribution has been subtracted. Sample A, with slightly higher oxygen content, shows the same behavior in the same temperature range.

In order to understand these features we first wanted to clarify the question whether the additional relaxation is of magnetic or quadrupolar (i.e., charge) origin. This is readily established by comparing the behavior of ^{63}Cu and ^{65}Cu. The two isotopes possess slightly different magnetic and quadrupolar parameters. The ^{63}Cu isotope ($I = 3/2$) with a natural abundance of 69.1% has a gyromagnetic ratio $\gamma = 11.28$ MHz T^{-1} and a quadrupole moment $Q = -0.222 \times 10^{-24}$ cm^2, whereas the ^{65}Cu isotope ($I = 3/2$) with a natural abundance of 30.1% has a *larger* gyromagnetic ratio $\gamma = 12.09$ MHz T^{-1} and a *smaller* quadrupole moment $Q = -0.195 \times 10^{-24}$ cm^2. Comparing the additional broadening of the ^{65}Cu(2) line with the ^{63}Cu(2) line we find a significantly larger increase of the ^{63}Cu second moment with decreasing temperature below 35 K than for the ^{65}Cu line. This strongly supports a quadrupolar line broadening mechanism which suggests charge ordering.

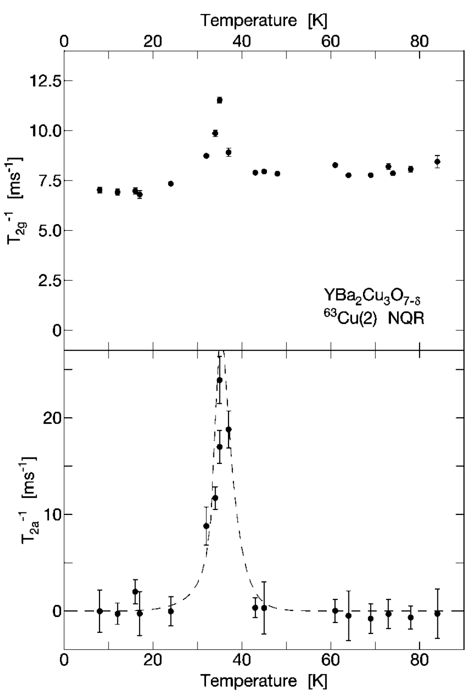

FIG. 3. Top: Temperature dependence of the spin-echo decay rate of ^{63}Cu(2) in $YBCO_{7-\delta}$ (sample B) after T_{2R} correction. Besides the almost temperature independent Gaussian decay rate an additional decay rate is seen around 35 K. Bottom: Additional transverse relaxation rate T_{2a} of ^{63}Cu(2). The dashed line corresponds to a power law $|T - T_c|^{-\nu}$ with $\nu = 0.7$.

Similar results were obtained for the comparison of the relaxation rates of both Cu isotopes at $T = 35$ K under the same experimental conditions. This additional relaxation turns out to be exponential for both isotopes and scales with the square of the quadrupolar moments of the different Cu isotopes as expected for purely quadrupolar relaxation. This provides further support for a quadrupolar, i.e., charge fluctuation driven phase transition at $T_c = 35$ K. In order to emphasize the order parameterlike behavior of the additional broadening we have included in Fig. 1 the expression $A_0(T_c - T)^{\beta}$ with $\beta = 0.5$. At the moment we cannot distinguish between a commensurate and an incommensurate CDW.

There have been theoretical discussions of a possible formation of a CDW in YBCO and its connection with superconductivity [10,23–27]. So far no clear evidence for an ordering phenomenon of the CDW in terms of a phase transition has been reported. We therefore believe that our observation might trigger intense theoretical investigations and further experimental search to verify our proposal.

In summary our analysis of the magnetic and quadrupolar contributions to the line shape and the relaxation clearly indicates that the additional features observed in both the line shape and the relaxation below 35 K is of quadrupolar origin, i.e., it is connected with a redistribution of charges. The order parameterlike behavior of the broadening together with the critical peak in the spin-echo relaxation rate leads us to propose a charge density wave ordered state below 35 K with an ordering temperature of $T_c = 35$ K. We note that the features attributed here to a CDW state are seen at nuclear positions both in the copper oxygen plane and in other parts of the unit cell. It is possible that these other nuclei show these features due to their magnetic coupling to the Cu and O nuclei in the plane.

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