Charge Freezing in the Zigzag Chain $PrBa_2Cu_4O_8$ Cuprate

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We report nuclear quadrupole resonance (NQR) studies on the chain Cu sites of $PrBa_2Cu_4O_8$, a quasi-one-dimensional conductor with a nearly quarter-filled band. The nuclear spin-lattice relaxation rate $1/T_1$ shows a pronounced peak near 100 K caused by fluctuations of electric field gradient. Similar peak was observed for the spin-echo decay rate $1/T_2$, however, at a different temperature near 50 K. These results and broadening of the NQR spectrum at low temperatures indicate that slow charge fluctuations of either electronic or ionic origin freeze gradually at low temperatures.

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There has been increasing interest in quasi-one-dimensional (Q1D) correlated electrons. Theoretical studies on generalized Hubbard or t-J models for chains and ladders have revealed a rich phase diagram associated with various instabilities towards Mott localization, spin density wave, charge order, and superconductivity [1–3]. A variety of phases has indeed been observed in organic Bechgaard salts [4] and cuprate ladder materials [5,6]. Pr-based cuprates, $PrBa_2Cu_3O_7$ (Pr123) and $PrBa_2Cu_4O_8$ (Pr124), also provide good model systems of strongly correlated Q1D electrons. Each of these has an identical structure to the respective Y-based high temperature superconductors, $YBa_2Cu_3O_7$ (Y123) and $YBa_2Cu_4O_8$ (Y124). However, the CuO_2 planes in the Pr-based compounds are insulating as inferred from optical conductivity [7,8] and show antiferromagnetic order [9,10]. This feature was explained by Fehrenbacher and Rice [11] based on a model of the localized hole states made of Pr-4f and O-2p_π hybridized orbitals. Thus the active element for low energy charge excitations in Pr-based cuprates are the Cu-O chains, single chains in Pr123, and double (zigzag) chains in Pr124.

These two compounds show contrasting transport behavior. Pr124 is a highly anisotropic Q1D metal showing extremely large in-plane resistivity anisotropy $\rho_a/\rho_b \sim 1000$ at 4 K [12–14], where b is along the chain direction. Although ρ_b shows monotonic metallic temperature dependence, ρ_a exhibits a broad peak near 130 K, indicating incoherent transport perpendicular to the chains at high temperatures. The angle resolved photoemission spectra (ARPES) [15] also revealed a clear one-dimensional dispersion which crosses the Fermi level near the momentum $k_b \simeq \pi/4$, pointing to a nearly quarter-filled conduction band. In Pr123, the spectral weight of the chain contribution to the optical conductivity [7] and the ARPES spectra [16] are also consistent with an approximately quarter-filled conduction band. However, semiconducting behavior of the dc resistivity, steep suppression of the optical conductivity below 0.1 eV, and vanishing ARPES intensity near the Fermi level all indicate the existence of a charge gap. Nuclear magnetic resonance and nuclear quadrupole resonance (NQR) experiments in Pr123 [17] revealed line broadening and anomalies in relaxation rates, which were ascribed to a charge ordering instability.

The apparent absence of static charge order in Pr124 may be due to a slight deviation from the quarter-filling [15] or to the geometrical frustration of intersite Coulomb interactions in zigzag chains [18]. However, dynamic signature towards charge order instability is indicated by the optical conductivity data [8]. In this Letter, we report results of NQR experiments for the chain Cu sites in Pr124. We found a pronounced peak in the temperature dependences of the nuclear spin-lattice relaxation rate $(1/T_1)$ and spin-echo decay rate $(1/T_2)$, as well as broadening of the NQR spectra, indicating gradual freezing of fluctuations of electric field gradient (EFG) with decreasing temperature. The powder sample of Pr124 was synthesized by a solid state reaction under high pressure as described in [19]. The standard spin-echo pulse technique was used in the NQR experiments.

The NQR spectra for the chain Cu sites in Pr124 are presented in Fig. 1. We observed well resolved resonance lines for both ^{63}Cu and ^{65}Cu isotopes with the full width at half maximum (FWHM) of 560 kHz for ^{63}Cu at 300 K. The resonance signal from the planar Cu sites was observed near 70 MHz at 1.5 K, indicating an antiferromagnetic order of the planar Cu spins [10]. The NQR spectrum for the chain Cu sites shows little change at the Néel temperature of the planar Cu spins (~ 220 K).

The temperature dependence of $1/T_1$ for the chain Cu sites is shown in Fig. 2. Here $1/T_1$ is defined simply as the inverse time constant for the exponential recovery of the NQR intensity after the inversion pulse. The fitting of the recovery curve to an exponential function was satisfactory over two decades except below 100 K, where the distribution of $1/T_1$ results in a slightly nonexponential recovery curve. Above 200 K, $1/T_1$ is nearly proportional to T, similar to the results in Y124 [20,21]. Below 200 K, however, $1/T_1$ deviates significantly from the T-linear behavior and shows a pronounced peak near 100 K.

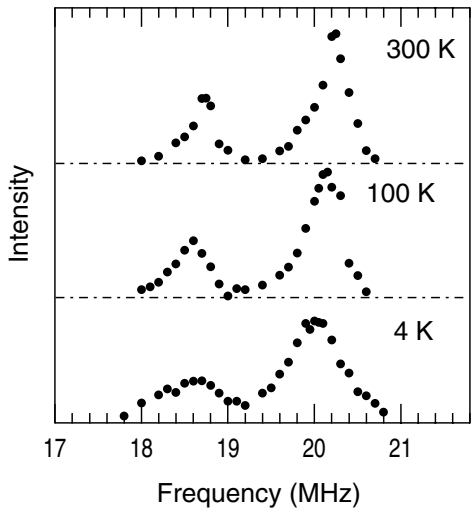

FIG. 1. NQR spectra for the chain Cu sites in Pr124. The peak near 20.2 MHz (18.7 MHz) is due to ^{63}Cu (^{65}Cu) nuclei.

A similar peak was observed also for $1/T_2$ shown in Fig. 3. The spin-echo decay curves can be fit well to an exponential function $\exp(-2\tau/T_2)$ below 200 K, where τ is the time separation between $\pi/2$ and π pulses. At higher temperatures, the spin-echo decay curve contains also a small Gaussian component and the fitting becomes less satisfactory. Although $1/T_2$ is almost independent of temperature above 100 K, there is a strong peak near 50 K. Note that this temperature is lower than the peak of $1/T_1$ by 50 K. The peak value $1/T_2 \simeq 120\ \mathrm{ms}^{-1}$ is more than 5 times larger than the value reported for Y124 [22].

The isotopic ratio of these relaxation rates can be used to identify the relaxation process. Both $1/T_1$ and $1/T_2$ are larger for ^{65}Cu than for ^{63}Cu when the temperature is sufficiently higher or lower than the peak (Figs. 2 and 3). Their ratio is close to the ratio of squared nuclear magnetic moments $(^{65}\gamma/^{63}\gamma)^2 = 1.148$, indicating that relaxation is caused by fluctuations of the local magnetic field acting on nuclei. In the temperature range near the peak, on the other hand, both relaxation rates are larger for ^{63}Cu, with the isotopic ratio close to the ratio of squared nuclear electric quadrupole moments $(^{65}Q/^{63}Q)^2 = 0.856$. Therefore, we conclude that the peaks in the relaxation rates are caused by fluctuations of the EFG tensor, $V_{\alpha\beta} = \partial^2 V/\partial x_\alpha \partial x_\beta$, where V is the electrostatic potential at the nuclear position.

The relaxation rates can then be related to the time correlation functions of EFG components. A simple interpretation of temperature dependences of $1/T_1$ and $1/T_2$, in particular, the difference in their peak temperatures, is given by a classical model of motional narrowing [23,24]. Let us assume a simple exponential form for the correlation functions, $\langle V_{\alpha\beta}(t)V_{\alpha\beta}(0)\rangle = \langle V_{\alpha\beta}^2\rangle \exp(-t/\tau_c)$, where τ_c is the correlation time of the fluctuations. The spin-lattice relaxation rate is given by their Fourier transform at the NQR frequency ω_n (20 MHz in our case),

$$\frac{1}{T_1} = \frac{\Delta^2 \tau_c}{1 + \omega_n^2 \tau_c^2}, \tag{1}$$

where Δ is the magnitude of the transition matrix element of the quadrupolar interaction, which is proportional to the amplitude of the EFG fluctuations $\langle V_{\alpha\beta}\rangle$ appropriately averaged over different tensor components. If Δ is constant but τ_c depends on temperature, $1/T_1$ attains the maximum value when $\omega_n \tau_c = 1$. Thus the peak of $1/T_1$ is naturally understood due to an increase of τ_c with decreasing temperature, i.e., slowing of the EFG fluctuations at low temperatures. By applying Eq. (1) to the experimental data, we deduced $\Delta/2\pi = 170$ kHz and $1/\tau_c$ is obtained as a function of temperature near 100 K

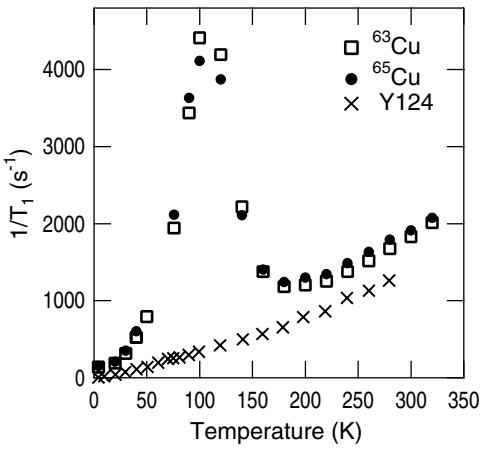

FIG. 2. The temperature dependence of $1/T_1$ for ^{63}Cu and ^{65}Cu. The data for the chain ^{63}Cu sites in Y124 [20] are shown for comparison.

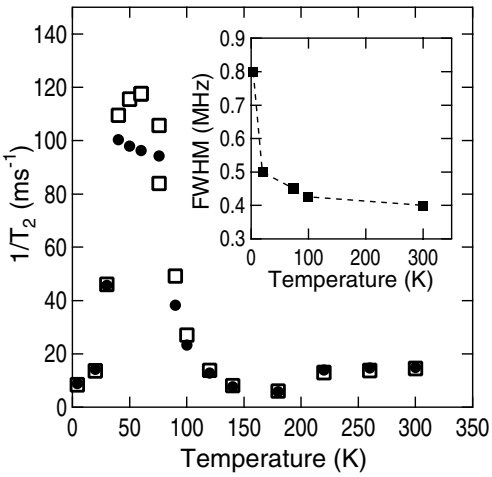

FIG. 3. The temperature dependence of $1/T_2$ for ^{63}Cu (open squares) and ^{65}Cu (closed circles) nuclei. The inset shows the temperature dependence of the linewidth (FWHM) of the ^{63}Cu NQR spectrum (see Fig. 1).

as shown in Fig. 4. Although the temperature range is limited (75 K $\geq T \geq$ 140 K), we can extract an activation energy 430 K from the temperature dependence of $1/\tau_c$.

In contrast, it is known that $1/T_2$ determined from the spin-echo decay curve takes the maximum value $1/T_2 \sim \Delta$ when $\Delta\tau_c \sim 1$ [24–26]. Since Δ is 2 orders of magnitude smaller than ω_n, gradual slowing of the EFG fluctuations accounts for the fact that the peak in $1/T_2$ occurs at a lower temperature than the peak of $1/T_1$. The plot in Fig. 4 indeed shows that $1/\tau_c \sim 10^6$ s$^{-1} \sim \Delta$ near 50 K, where $1/T_2$ shows a peak. The value of $1/T_2$ at the peak (Fig. 3) is also of the same orders of magnitude as Δ, consistent with our model.

If the correlation time continuously grows at lower temperatures, we expect the EFG fluctuations to freeze eventually, resulting in broadening of the NQR spectrum. This is indeed observed as shown in the inset of Fig. 3. The width (FWHM) of ^{63}Cu NQR spectrum is 400 kHz at 300 K, while it increases rapidly below 20 K and reaches 800 kHz at 4.2 K. If we assume two independent contributions to the width, one due to T-independent inhomogeneity which is represented by the spectrum at 300 K and the other due to freezing of EFG fluctuations at low temperatures, and the square of the widths from these sources add to make up the observed value, the FWHM due to EFG freezing at 4.2 K is estimated to be 570 kHz. This value agrees with the second moment $\Delta/2\pi =$ 170 kHz deduced from the $1/T_1$ data, which translates to FWHM of 400 kHz for a Gaussian distribution.

The results of $1/T_1$, $1/T_2$, and the NQR spectra altogether provide convincing evidence for slow EFG fluctuations, which freeze randomly at low temperatures. Such fluctuations must be caused by motion of either electronic or ionic charges. Let us summarize the prominent features that characterize the fluctuations, irrespective of their origin. First, the dynamics is extremely slow, with $1/\tau_c$ ranging from 10^6 to 10^9 sec^{-1} in the temperature range 50–150 K. It is much too slow to be attributed to the transport of individual electrons along the chain. Second is the glassy and random nature. Gradual slowing of the fluctuations without a well defined critical temperature is evidenced by the different peak temperatures of $1/T_1$ and $1/T_2$. Spatial randomness with no signature of a long range order breaking translational symmetry is indicated by the broadening of the NQR spectrum without line splitting or fine structure. These are in sharp contrast to what have been observed in charge-density-wave materials such as $NbSe_3$ [27], where peak temperatures for $1/T_1$ and $1/T_2$ coincide. Third, the amplitude of the fluctuating EFG is rather small, of the order of a few hundred kHz. It is known for high-T_c cuprates that the NQR frequency at the planar Cu sites changes with hole concentration at a rate 20–30 MHz/hole [28,29]. A similar change is expected for the chain Cu sites. Therefore, if the NQR anomalies in Pr124 are due to electronic origin, only a minor fraction of the holes are relevant. The charge distribution at low temperatures must still be largely uniform and only partial random freezing is possible with amplitude of the order of 1% of holes per site.

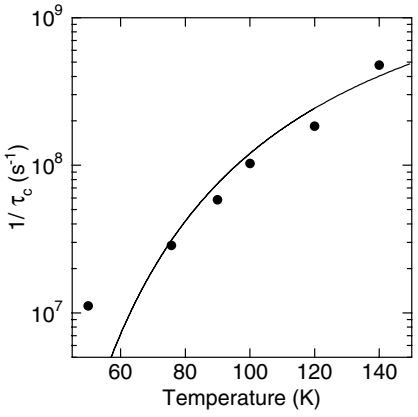

FIG. 4. The temperature dependence of the correlation time for EFG fluctuations. The line shows a fit yielding the activation energy of 430 K.

Although we do not have conclusive evidence concerning the origin of the anomalous EFG fluctuations, the following observations suggest that collective electron-lattice coupled motion is important. The peak in $1/T_1$ and the subsequent spectral change at lower temperatures described here are very similar to what were observed in the lightly hole-doped two-leg ladder compound $Sr_{24}Cu_{24}O_{41}$ [30]. This material is an insulator at low temperatures, and there is evidence for charge order in the ladder planes from both the frequency dependent conductivity [31,32] and the development of fine structure in the NQR spectrum [30]. Thus the peak in $1/T_1$ in this material is most likely caused by collective fluctuations of electronic charge. The similarity of the NQR results suggests that this is also the case for Pr124. However, Pr124 is a good metal and dc-transport measurements indicate no sign of static charge order.

The optical conductivity $\sigma(\omega)$ by Takenaka *et al.* [8], on the other hand, clearly shows dynamical correlation towards charge order instability, as mentioned earlier. The spectrum of $\sigma(\omega)$ along the chain direction splits into the Drude-like zero energy mode with only 2% of the total spectral weight and a gapped finite energy mode centered at 40 meV. The two-component structure resembles that observed in the organic Bechgaard salts [33,34] and suggests dynamic short range correlation for charge disproportionation. The frequency dependence of the high energy part of $\sigma(\omega)$ was analyzed in the framework of the Tomonaga-Luttinger liquid, yielding a small value of the charge correlation exponent $K_\rho \sim 0.24$, which implies strong repulsive interaction [8]. These results altogether point out that Pr124 is in close proximity to charge order; therefore, charge freezing may occur near impurities or can be triggered by a coupling to the lattice.

No structural transition has been reported in Pr124 so far [35]. However, recent neutron diffraction results [36] indicate a sudden change of the Ba position along the c direction by about 0.05 Å near 160 K. The Raman spectra of the Ba-phonon mode also show a large frequency shift and sudden narrowing near the same temperature [37]. Although we notice a slight shift of the NQR frequency by about 100 kHz (Fig. 1) from 300 to 100 K, which may be a consequence of movement of Ba, a uniform change of ionic positions does not cause broadening of the spectrum. It is unlikely that the static and dynamic NQR anomalies described here are merely lattice effects, since they are not observed in the isostructural Y124. On the other hand, when such double-well–type ionic instability is coupled to an electron system close to charge order, we suspect that a static partial charge freezing can occur.

In summary, the pronounced peaks in $1/T_1$ and $1/T_2$ at different temperatures and broadening of the NQR spectrum at lower temperatures for the chain Cu sites in $PrBa_2Cu_4O_8$ provide evidence for slow fluctuations of electric field gradient. Their correlation time is extremely slow and shows glassy freezing at low temperatures. The amplitude of the fluctuations and concomitant freezing is about 2 orders of magnitude smaller than what we expect when the whole carrier in the Cu_2O_2 chains participate in charge order.

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