Charge Freezing in Zig-zag Chain Cuprates PrBa$_2$Cu$_4$O$_8$ Observed by Cu Nuclear Quadrupole Resonance

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We report nuclear quadrupole resonance (NQR) studies on the chain Cu sites of PrBa$_2$Cu$_4$O$_8$, 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 (EFG). 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.

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 rich phase diagram associated with various instabilities towards Mott localization, spin density wave, charge order, and superconductivity [5, 6]. Pr-based cuprates, PrBa$_2$Cu$_4$O$_8$ in organic Bechgaard salts [4] and cuprate ladder magnets [7, 8] and charge order instability is indicated by 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 (NMR) and nuclear quadrupole resonance (NQR) experiments in Pr$_{123}$ [17] revealed line broadening and anomalies in relaxation rates, which were ascribed to a charge ordering instability.

Although apparent absence of static charge order in Pr$_{124}$ may be due to 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 in Pr$_{124}$, which splits into a zero-energy Drude part with a small weight and a finite energy mode centered at 40 meV [10]. In this letter, we report results of NQR experiments for the chain Cu sites in Pr$_{124}$. We found a pronounced peak in the temperature dependencies 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 Pr$_{124}$ was synthesized by solid state reaction under high pressure as described in [19]. Standard spin-echo pulse technique was used to obtain NMR spectra. The spin-echo decay rate ($1/T_2$) was obtained from the spin-echo intensity measured against the time separation $\tau$ between $\pi/2$ and $\pi$ pulses. The nuclear spin-lattice relaxation rate ($1/T_1$) was measured by inversion recovery method.

The NQR spectra for the chain Cu sites in Pr$_{124}$ 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 as reported elsewhere [8], indicating an antiferromagnetic order of the planer Cu spins. The NQR spectrum for the chain Cu sites shows little change at the Néel temperature of the planar Cu spins ($\sim 220$ K).

The temperature dependence of $1/T_1$ for the chain Cu...
FIG. 1: NQR spectra for the chain Cu sites in Pr124. The peak near 20.2 MHz (18.7 MHz) is due to $^{63}\text{Cu}$ ($^{65}\text{Cu}$) nuclei. The inset shows the temperature dependence of the line width (FWHM) for $^{63}\text{Cu}$.

sites is shown in Fig. 2. Here $1/T_1$ is defined as the inverse time constant for the exponential recovery of the NQR intensity after the inversion pulse, which is three times larger than the standard definition if the relaxation is due to magnetic processes. 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 non-exponential recovery curve. Above 200 K, $1/T_1$ is nearly proportional to $T$, similar to the results in Y124 [20]. Below 200 K, however, $1/T_1$ deviates significantly from the $T$-linear behavior and shows a pronounced peak near 100 K.

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. 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 $1/T_2 \approx 120 \text{ ms}^{-1}$ is more than 5 times larger than the value reported for Y124 [21].

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 $^{65}\text{Cu}$ than for $^{63}\text{Cu}$ 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 gyromagnetic ratio $(^{65}\gamma/^{63}\gamma)^2 = 1.148$, 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 $^{63}\text{Cu}$, 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 electric field gradient (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 $1/T_1$ (s$^{-1}$) and $1/T_2$ (ms$^{-1}$) at different temperatures in Figs. 2 and 3, respectively.

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

FIG. 3: The temperature dependence of $1/T_2$ for $^{63}\text{Cu}$ and $^{65}\text{Cu}$ nuclei.
The 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 \cite{22,23}. 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 $\tau_c$ is the correlation time of the fluctuations. The spin-lattice relaxation rate is given by their Fourier transform at the NQR frequency $\omega_n$ (20 MHz in our case),

\[
\frac{1}{T_1} = \frac{\Delta^2 \tau_c}{1 + \omega_n^2 \tau_c^2},
\]

where $\Delta$ 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 $\Delta$ is constant but $\tau_c$ 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 increase of $\tau_c$ with decreasing temperature, i.e., slowing down 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 as shown in Fig. 4. Although the temperature range is limited (75 K $\leq T \leq 140$ 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 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 as shown in Fig. 4. Although the temperature range is limited (75 K $\leq T \leq 140$ K), we can extract an activation energy 430 K from the temperature dependence of $1/\tau_c$.

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 corresponding to the anomalous nuclear relaxation. 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 down 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 with no line splitting nor fine structure. These are in sharp contrast to what have been observed in charge-density-wave (CDW) materials such as NbSe$_3$ \cite{24}, 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 NQR frequency changes with hole concentration approximately at a rate 20 - 30 MHz/hole \cite{24,27}. 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.

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Although we do not have conclusive evidence concerning the origin of the anomalous EFG fluctuations, 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 de-
scribed here are very similar to what were observed in the lightly hole-doped two-leg ladder compound Sr$_2$Cu$_2$O$_4$$_1$$_2$ [28]. This material is an insulator at low temperatures and there are evidences for charge order in the ladder planes from both the frequency dependent conductivity [24, 31] and the development of fine structure in the NQR spectrum [29]. 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 Pr$_{124}$. However, Pr$_{124}$ is a good metal and dc-transport measurements indicate no sign of static charge order.

The optical conductivity $\sigma(\omega)$ by Takenaka et al [10], 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 [31, 22] and suggests dynamic short range correlation for charge disproportionation. The frequency dependence of 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 [10]. These results altogether point out that Pr$_{124}$ 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 Pr$_{124}$ so far. However, recent neutron diffraction results [34] indicates sudden change of Ba position along the $c$-direction by about 0.05 Å near 160 K. The Raman spectra of Ba-phonon mode also show large frequency shift and sudden narrowing near the same temperature [34]. Although we notice a slight shift of the NQR frequency by about 100 kHz (Fig. 1) from 300 K to 100 K, which may be a consequence of movement of Ba, uniform change of ionic positions do not cause broadening of the spectrum. It is not likely that the static and dynamic NQR anomalies described here are merely lattice effects, since they are not observed in the isostructural Y$_{124}$. 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$_2$Cu$_4$O$_8$ provide evidence for slow fluctuations of electric field gradient. Their correlation time is extremely slow and show glassy freezing at low temperatures. The amplitude of the fluctuations and concomitant freezing is about two orders of magnitude smaller than what we expect when the whole carrier in the Cu$_2$O$_2$ chains participate in charge order.

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