PHYSICAL REVIEW B **67**, 060404(R) (2003)

Spin dynamics and antiferromagnetic order in $PrBa_2Cu_4O_8$ studied by Cu nuclear resonance

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(Received 21 October 2002; published 25 February 2003)

Results of the nuclear resonance experiments for the planar Cu sites in $PrBa_2Cu_4O_8$ are presented. The nuclear magnetic resonance spectrum at 1.5 K in zero magnetic field revealed an internal field of 6.1 T, providing evidence for an antiferromagnetic order of the planar Cu spins. This confirms that the CuO_2 planes are insulating; therefore, the metallic conduction in this material is entirely due to the one-dimensional zigzag Cu_2O_2 chains. The results of the spin-lattice relaxation rates measured by zero-field nuclear quadrupole resonance above 245 K in the paramagnetic state are explained by the theory for a Heisenberg model on a square lattice.

DOI: 10.1103/PhysRevB.67.060404 PACS number(s): 75.40.Gb, 76.60.Es, 76.60.Gv, 76.60.Jx

There has been increasing interest in quasi-one-dimensional 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 spin density wave, charge order, and superconductivity.[1–3] Experimental studies have been focused mostly on organic and cuprate materials. Many phases including superconducting states were found, for example, in the organic Bechgaard salts[4] and cuprate ladder materials.[5]

Pr-based cuprates also provide model systems of strongly correlated quasi-one-dimensional electrons. The best studied compound is $PrBa_2Cu_3O_7$, which is isostructural to the superconducting $YBa_2Cu_3O_7$ but yet insulating. The antiferromagnetic order in the CuO_2 planes found by nuclear magnetic resonance (NMR) experiments[6] and the large charge transfer energy gap in the optical conductivity spectrum along the *a* direction[7] in $PrBa_2Cu_3O_7$ indicate that the electronic structure of the CuO_2 planes is similar to that in undoped Mott insulators such as $YBa_2Cu_3O_6$. Fehrenbacher and Rice proposed a model including localized hole states made of Pr $4f$ and O $2p_\pi$ hybridized orbitals[8] to explain the insulating nature of the CuO_2 planes. The CuO_2 chains, on the contrary, remain paramagnetic and show a midinfrared optical peak,[7] consistent with the hole concentration of ≈ 0.5 per Cu. Such a quarter-filled one dimensional band was also observed by angle-resolved photoemission experiments.[9] In the NMR/NQR (nuclear quadrupole resonance) experiments for the chain Cu sites, Grévin *et al.* found a large enhancement of the spin-lattice and spin-spin relaxation rates due to electric quadrupole interaction.[10] This suggests that the insulating behavior of the chains is due to charge-ordering (charge density wave) instability.

$PrBa_2Cu_4O_8$ has the same structure as the superconducting $YBa_2Cu_4O_8$ with Cu_2O_2 zigzag chains. This compound is not superconducting but remains metallic down to low temperatures.[11,12] Muon spin relaxation experiments at zero field by Yamada *et al.* revealed the onset of an internal field at 220 K and a second magnetic transition at 17 K, which were ascribed to the order of Cu spins and Pr moments, respectively.[13] Kikuchi *et al.* performed Cu NMR experiments on a powder sample with the *c* axis aligned by magnetic field.[14] They found that the signal from the planar Cu sites disappears below 250 K, which they attributed to the magnetic order of the planar Cu spins, while the signal from chain Cu sites remains intact. Recent resistivity measurements on single crystals by Horii *et al.*[15] and by Hussey *et al.*[16] revealed large in-plane anisotropy, indicating that the conduction is dominantly due to chains. Thus $PrBa_2Cu_4O_8$ provides a unique example of metallic quasi-1D electrons without apparent disorder.

In this paper, we report the results of nuclear resonance experiments on the planar Cu sites in $PrBa_2Cu_4O_8$ at zero magnetic field. The results on the chain Cu sites are reported in a separate paper. The spectrum at 1.5 K revealed an internal field of 6.1 T due to antiferromagnetic order of the planar Cu spins. The nuclear spin-lattice relaxation rate $1/T_1$ was measured using the NQR signal at zero magnetic field in the paramagnetic state above 245 K. The temperature dependence of $1/T_1$ is consistent with the theoretical formula, $1/T_1 \propto T^{1.5}\exp(1.13J/T)$, for the spin-(1/2) Heisenberg model on a square lattice[24] with the exchange integral $J=1230$ K.

The powder sample of $PrBa_2Cu_4O_8$ was synthesized by solid-state reaction under high pressure as described in Ref. 11. The NMR/NQR experiments were performed with the standard spin-echo pulse sequence combined with the inversion recovery method for T_1 measurements.

We show in Fig. 1 the spin-echo NMR spectrum at 1.5 K in zero external field. The spectrum has three distinct peaks

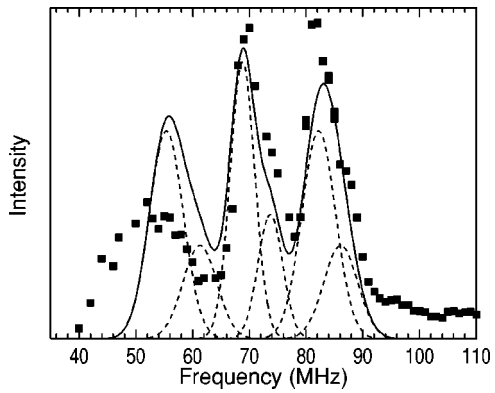

FIG. 1. The spin-echo intensity for the planar Cu sites at zero magnetic field is plotted as a function of frequency at $T=1.5$ K (symbols). The solid line is fit to the spectrum as described in the text, which is the sum of six resonance lines shown by the dashed lines.

at 52, 70 and 82 MHz. Because the spin-echo decay time T_2 is very short, we did not attempt to correct the spin-echo intensity for possible frequency variation of T_2. The spectrum with more than two peaks at frequencies much larger than the typical NQR frequencies of high-T_c cuprates ($\sim$30 MHz) points to the presence of a larger internal magnetic field due to antiferromagnetic order.

To understand the spectrum, we consider the Hamiltonian for spin-(3/2) nuclei in a magnetically ordered state in the presence of electric field gradient (EFG), which is written as

$$\mathcal{H}=\gamma_N\hbar H_{\rm int}I_z+\frac{eQ}{4I(2I-1)}V_{zz}[3I_z^2-I(I+1)]. \qquad (1)$$

Here, γ_N and Q are the gyromagnetic ratio and the quadrupole moment of the nuclei, $H_{\rm int}$ is the magnitude of the internal magnetic field whose direction is taken to be the z direction, and $V_{zz}=\partial^2V/\partial z^2$ is the zz component of the EFG tensor. Since the analysis of the spectrum shown below indicates that the magnetic Zeeman interaction is much larger than the electric quadrupolar interaction, only the first-order effect of the quadrupolar interaction is included in the above Hamiltonian.

When the values of $H_{\rm int}$ and V_{zz} are given for one isotope (^{63}Cu), we can compute positions of all six resonance lines, three lines corresponding to the transitions $I_z=3/2\leftrightarrow1/2$, $1/2\leftrightarrow-1/2$, $-1/2\leftrightarrow-3/2$ for each of the two isotopes (^{63}Cu and ^{65}Cu), by using the known ratios of the gyromagnetic ratios ($^{63}\gamma/^{65}\gamma=0.933$) and electric quadrupolar moments ($^{63}Q/^{65}Q=1.081$) for the two isotopes. The solid line in Fig. 1 is the fit to the experimental spectrum with the values $H_{\rm int}=6.1$ T and $\nu_{zz}=3eQV_{zz}/2hI(2I-1)=13.4$ MHz for ^{63}Cu. The half width at half maximum for ^{63}Cu is 1.5 MHz for the central line ($I_z=1/2\leftrightarrow-1/2$) and 2.1 MHz for the satellite lines ($I_z=\pm3/2\leftrightarrow\pm1/2$). Thus the NMR spectrum provides direct evidence for an antiferromagnetic order of the planar Cu spins.

In the paramagnetic state above 245 K, we observed NQR signal at zero field for ^{63}Cu nuclei at $\nu_Q=31.2$ MHz, which is close to the resonance frequency in $YBa_2Cu_3O_7$ (31.2 MHz) and $YBa_2Cu_4O_8$ (29.7 MHz). Since in both compounds, the EFG tensor is axially symmetric around the c axis, we assume this to be the case in $PrBa_2Cu_4O_8$ as well. Then the angle θ between the c axis and the magnetic hyperfine field in the ordered state is given by the relation $\nu_{zz}=\nu_Q(3\cos^2\theta-1)/2$, leading to the value of $\theta=77°$ or 38°. We adopt the former value, since analysis of the NMR spectra in the antiferromagnetic state of both $YBa_2Cu_3O_6$ (Ref. 17) and La_2CuO_4 (Ref. 18) concluded that the magnetic hyperfine field is parallel to the ab plane within 10°. This is also consistent with the fact that the ordered moment in the parent insulators of the high-T_c cuprates lies approximately in the ab plane. We note, however, that the NMR spectra in the ordered state in $PrBa_2Cu_3O_7$ (Refs. 6 and 19) and $PrBa_2Cu_3O_6$ (Ref. 20) show only one broad peak near 70 MHz with no resolved quadrupolar splitting, leading to a much smaller value of $\theta\sim57°$.[19,21]

If we use the values of the hyperfine coupling constants in the Mila-Rice scheme[22] estimated for $YBa_2Cu_3O_7$,[23] $A_{cc}=-16$, $A_{ab}=3.4$, $B=4\ T/\mu_B$, where A_{cc} and A_{ab} are the hyperfine fields from the onsite spin and B is the supertransferred hyperfine field from a nearest-neighbor spins, the magnitude and the direction of the ordered moment are estimated to be 0.50 μ_B and 4.6° out of the ab plane. The hyperfine coupling constants in $PrBa_2Cu_4O_8$, however, are not accurately known. The magnitude and the direction of the ordered moment thus obtained are subject to rather large uncertainties.

In the paramagnetic state, we measured the nuclear spin-lattice relaxation rate $1/T_1$ by using Cu NQR signal in the temperature range 245–320 K. We could not observe the NQR signal at lower temperatures. This is consistent with the Néel temperature of 220 K revealed by both the disappearance of the planar Cu NMR signal[14] at a high magnetic field and the onset of the internal field at the muon sites.[13]

Nuclear relaxation in two-dimensional quantum antiferromagnets was theoretically studied by Chakravarty and Orbach[24] in the renormalized classical regime, where the ground state is a Néel ordered state. For the case of the spin-(1/2) Heisenberg model on a square lattice with the nearest neighbor exchange J, $1/T_1$ is expressed as

$$\frac{1}{T_1}=\frac{0.134(2A_Q\gamma_N\hbar)^2}{2\pi\rho_s\hbar}\left(\frac{T}{2\pi\rho_s}\right)^{3/2}\left(\frac{1}{1+T/2\pi\rho_s}\right)^3\times\exp\left(\frac{2\pi\rho_s}{T}\right), \qquad (2)$$

where $\rho_s=0.18J$ is the spin-stiffness constant and $A_Q=A_{ab}-4B$. When the temperature is much smaller than $2\pi\rho_s=1.13J$, $1/T_1T^{1.5}$ is expected to be proportional to $\exp(1.13J/T)$.

The observed $1/T_1$ at the planar Cu site includes the contribution from the Pr local moments through dipolar interaction, $(1/T_1)_{4f}$, in addition to the contribution from the planar Cu spins. Thus we must subtract it from the experimental data before comparing with the theory. Since the temperature range of our measurements is higher than the ordering tem-

perature of the Pr moments ($T_{N,4f}=17$ K), $(1/T_1)_{4f}$ can be estimated from the following formula valid in the high temperature limit:[25,26]

$$\left(\frac{1}{T_1}\right)_{4f}=\frac{2\sqrt{2\pi}}{3}\frac{\gamma_N^2(g_J\mu_B)^2}{\omega_{\rm ex}}J(J+1)\Sigma_i\frac{3(5-3\cos^2\theta_j)}{4r_j^6}. \tag{3}$$

where $J=4$, $g_J=0.8$ is the Landés g factor of Pr^{3+}, and θ_j is the angle between the c axis and $\mathbf{r}_j$ connecting a Cu nucleus and a neighboring Pr moment. The exchange frequency $\omega_{\rm ex}$ is given as

$$\omega_{\rm ex}=\sqrt{\frac{2}{3}}\frac{J_{4f}}{\hbar}\sqrt{zS(S+1)}, \tag{4}$$

where $S=1$, $z=4$ is the number of nearest-neighbor Pr sites, and J_{4f} is the exchange interaction among Pr moments that can be estimated from the mean field expression for the ordering temperature, $T_{N,4f}=J_{4f}zS(S+1)/3k_B$. We obtain $\omega_{\rm ex}=1.94\times10^{12}$ s^{-1}. The sum over the Pr sites in Eq. (3) is dominated by the four nearest neighbors. By putting $\gamma_N=2\pi\times1.1285\times10^3$ s^{-1} G^{-1}, $\cos^2\theta_j=0.28$, and $\Sigma_j(1/r_j^6)=3.29\times10^{45}$ cm^{-6}, we obtained $(1/T_1)_{4f}=550$ s^{-1}.

In Fig. 2, we plot $1/T_1T^{1.5}$ against $1/T$ using the corrected data after subtracting $(1/T_1)_{4f}$ (solid squares). As shown by the straight line, our results on $PrBa_2Cu_4O_8$ are compatible with the theoretical prediction. By fitting the data to Eq. (2), we obtained $J=1230$ K and $A_Q=5.6\ T/\mu_B$. Imai *et al.* first presented such an analysis for their experiments on La_2CuO_4.[28] They obtained $J=1590$ K for La_2CuO_4. The smaller J for $PrBa_2Cu_4O_8$ is consistent with the lower Néel temperature. It is quite puzzling, however, that the value of A_Q obtained here is much smaller than the value estimated for $YBa_2Cu_3O_7$.[23] Moreover, when combined with the internal field of 6.1 T, this would lead to the magnitude of the ordered moment approximately equal to $1\mu_B$. We do not have a satisfactory explanation for this yet.

In summary, we have confirmed that the ground state of $PrBa_2Cu_4O_8$ has an antiferromagnetic long-range order of planar Cu spins. From the analysis of the NMR spectrum at 1.5 K, the magnitude and the direction of the internal magnetic field are determined. The direction of the internal field is about 10° out of the ab plane, indicating that the ordered moments lie approximately within the ab plane, similarly to the case of $YBa_2Cu_3O_6$ and La_2CuO_4. This is, however, contrasting to the results reported for $PrBa_2Cu_3O_7$. The nuclear relaxation rate above 245 K follows the relation $1/T_1T^{1.5}\propto1/T$, which is expected for two-dimensional spin-(1/2) Heisenberg antiferromagnets on a square lattice.

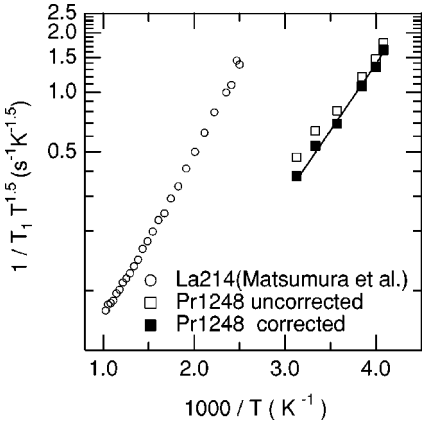

FIG. 2. The nuclear relaxation rate in the paramagnetic state. The data of $1/T_1T^{1.5}$ are plotted against $1/T$. The raw experimental data for $PrBa_2Cu_4O_8$ are shown by open squares. The results after subtracting the temperature independent contribution from Pr moments are shown by solid squares. For comparison, the data for La_2CuO_4 reported by Matsumura *et al.*(Ref. 27) are also shown by open circles.

We acknowledge Dr. Y. Itoh for providing us the data of $1/T_1$ in La_2CuO_4. This work was supported by the Grant-in-Aid of the Ministry of Education, Culture, Sports, Science and Technology. S.F. was supported by the Japan Society for the Promotion of Science.

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