RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 42, NUMBER 4 1 AUGUST 1990

Observation of Cu NMR in antiferromagnetic $PrBa_2Cu_3O_7$: Evidence for hole-band filling

A. P. Reyes and D. E. MacLaughlin
University of California, Riverside, California 92521

M. Takigawa, P. C. Hammel, R. H. Heffner, and J. D. Thompson
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

J. E. Crow,* A. Kebede, T. Mihalisin, and J. Schwegler
Temple University, Philadelphia, Pennsylvania 19122
(Received 23 April 1990)

Copper nuclear magnetic resonance (NMR) has been observed at plane and chain Cu sites in $PrBa_2Cu_3O_7$. The field-swept NMR signal from plane Cu sites disappears due to magnetic ordering below ~280 K. In the antiferromagnetic state ($T=1.4$ K) quadrupole-split NMR spectra from plane-site Cu nuclei can be fit using an axial electric-field gradient ($\nu_Q=17\pm2$ MHz) and an internal field $H_{int}=65.2\pm0.2$ kOe directed at an angle $79°\pm1°$ to the c axis. The observation of plane-Cu magnetism is consistent with the absence of doped holes on CuO_2 planes in $PrBa_2Cu_3O_7$, which supports the view that hole filling is important in suppressing superconductivity in $Y_{1-x}Pr_xBa_2Cu_3O_7$.

Copper antiferromagnetism plays an important role in the electronic properties and superconductivity of the high-T_c cuprates. The systems $YBa_2Cu_3O_{6+x}$ and La_2CuO_{4+x} are insulators and exhibit long-range antiferromagnetism for zero or low doped-hole concentrations, but become metallic and superconducting with increasing hole concentration from the added oxygen.[1] Previous nuclear magnetic resonance (NMR) experiments[2] in $Y_{1-x}Pr_xBa_2Cu_3O_7$ provided evidence that Pr doping, like oxygen depletion, reduces the CuO_2-plane hole concentration. This Rapid Communication reports NMR studies of the end compound $PrBa_2Cu_3O_7$, which is insulating and which was found in recent μSR experiments[3] to exhibit plane-Cu antiferromagnetic order.

The superconducting properties of most $RBa_2Cu_3O_7$ compounds (R=lanthanide) isomorphic to $YBa_2Cu_3O_7$ are remarkably insensitive to the large magnetic moments of the rare earths.[4] An important exception is the case R=Pr: praseodymium impurities in $Y_{1-x}Pr_xBa_2Cu_3O_7$ depress T_c significantly,[5] and a metal-insulator transition occurs for $x\simeq0.6$.[6] Two alternative pictures have been proposed for this depression.[7,8] In one of these, Pr is a nearly tetravalent ion which contributes essentially one extra electron per unit cell, thereby filling CuO_2-plane holes. In the other picture, Pr is essentially trivalent, and the T_c depression results from magnetic spin-flip scattering and consequent Cooper-pair breaking.

In this paper we report the first observation of Cu NMR in $PrBa_2Cu_3O_7$. Spectra from planar copper [Cu(2)] sites indicate antiferromagnetic (AF) ordering below a Néel temperature $T_N\simeq280$ K, in agreement with recent μSR studies.[3] NMR spectra in the AF state reflect a large internal hyperfine magnetic-field $H_{int}\simeq65$ kOe at an angle of ~79° with respect to the crystalline c axis, due to AF alignment of Cu(2) moments. This Cu(2) ordering, which is distinct from the AF transition of the Pr ions at ~17 K,[9] is a signature of the absence of doped holes, and is consistent with near tetravalency of Pr in $Y_{1-x}Pr_xBa_2Cu_3O_7$.

The sample used in this experiment was prepared by a standard solid-state-reaction method.[10] A powder sample with field-aligned c axes was prepared as described previously.[11] Representative field-swept spectra obtained at high temperatures with external field $\mathbf{H}_{ext}$ parallel to the crystalline c axis are shown in Fig. 1. The low- and high-field peaks at 300 K have been identified as arising from Cu(1) (chain) and Cu(2) sites, respectively.[11] The disap-

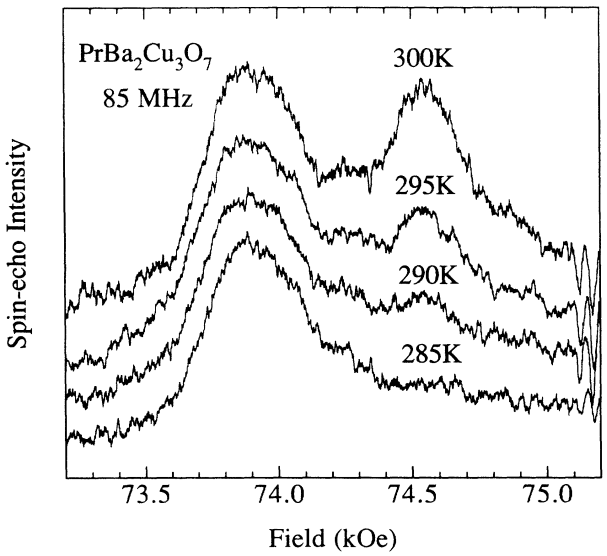

FIG. 1. High-temperature field-swept NMR spectra in $PrBa_2Cu_3O_7$ at 85 MHz. The peaks near 73.9 and 74.5 kOe are due to Cu(1) and Cu(2) nuclei, respectively (Ref. 15). The disappearance of the Cu(2) signal near 280 K indicates magnetic ordering of Cu(2) moments at this temperature.

pearance of the Cu(2) signal with decreasing temperature indicates the onset of large internal fields at nuclear sites. The Néel temperature T_N obtained from these data is 280 ± 10 K.

Frequency-swept spectra were obtained over the frequency range 18–130 MHz at 1.4 K in zero external field. No signal was found near the Cu(2) nuclear quadrupole resonance (NQR) frequency of 31.5 MHz in undoped Y-Ba-Cu-O,[12] but two broad spectra were observed for frequencies around 21 and 80 MHz. The NQR frequencies for Cu(1) sites in fully oxygenated $YBa_2Cu_3O_7$ are in the former range,[12] and we interpret the 21-MHz spectrum (not shown) as arising from unresolved ^{63}Cu and ^{65}Cu NQR lines at Cu(1) sites. Together with the unshifted high-field Cu(1) line observed below T_N for both high (Fig. 1) and low temperatures (not shown), this indicates that magnetic ordering does not occur on chain sites down to 1.4 K.

The 80-MHz spectrum, shown in Fig. 2, is then taken to be the NMR of Cu(2) nuclei in an internal hyperfine field due to AF ordering of Cu moments at plane sites.[13] This attribution is supported by the observation of a zero-field Cu(2) resonance in the undoped AF parent compound $YBa_2Cu_3O_6$ in the same frequency range.[14] The hyperfine fields are of similar magnitude but details of the spectra are different in the two cases: in Pr-Ba-Cu-O the spectrum exhibits broad overlapping central and satellite lines, whereas in $YBa_2Cu_3O_6$ the satellite structure is well resolved. The transverse relaxation time T_2 at 1.4 K was found to be very short (~ 35 μs) and almost independent of frequency across the spectrum. This implies (1) that the entire signal comes from a single site, and (2) that the line shape is relatively free from systematic distortion.

The parameters which determine zero-field NMR spectra in magnetically ordered materials are (1) the magnitude and direction of the internal field $\mathbf{H}_{\text{int}}$, (2) the quadrupole tensor parameters ν_Q (quadrupole frequency) and η (asymmetry parameter) for both ^{63}Cu and ^{65}Cu isotopes, and (3) the parameters required to define the intrinsic line shape. We assume that the quadrupole tensor is nearly axial ($\eta \approx 0$) as in Y-Ba-Cu-O,[11,12] in which case the direction of the in-plane component of $\mathbf{H}_{\text{int}}$ cannot be determined. We also assume for simplicity that the intrinsic line shape is Lorentzian, with a full width at half maximum (FWHM) Γ which is the same for all transitions. This assumption fits our data well, but the fits are not sensitively dependent on it. The gyromagnetic ratios and quadrupole moments of the two Cu isotopes are known. The parameters which are then free to be varied for the best fit are the ^{63}Cu quadrupole frequency $^{63}\nu_Q$, the linewidth Γ, and the internal-field magnitude H_{int} and its angle θ with respect to the c axis.

The small quadrupole satellite splitting in the spectrum of Fig. 2 leads to acceptable fits to calculated spectra in three ranges of the c-axis angle θ. For all three fits H_{int} is found to be in the vicinity of 65 kOe. Range A is for $\theta = 0°$–$10°$; we rule this out because the fit values of $^{63}\nu_Q \sim 6$–8 MHz are much lower than values found in other cuprates. Range B is for θ near the "magic angle" ($\sim 55°$) where the quadrupole splitting almost vanishes; this range results if $^{63}\nu_Q$ is fixed at the $YBa_2Cu_3O_7$ value

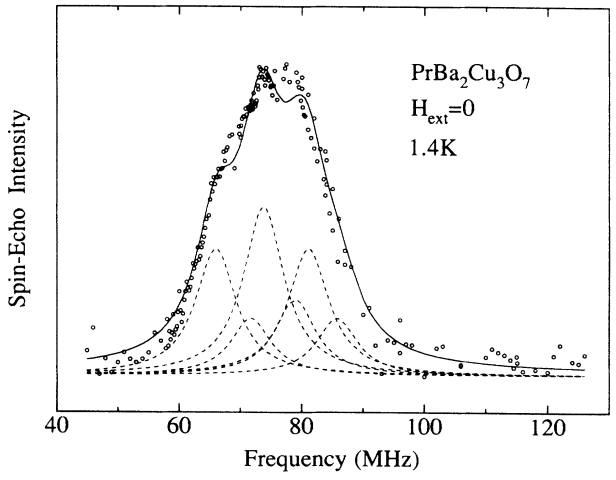

FIG. 2. Zero-field NMR spectra of Cu(2) nuclei in $PrBa_2Cu_3O_7$ at 1.4 K. The dashed curves correspond to Lorentzian-broadened quadrupole-split ^{63}Cu and ^{65}Cu lines, with fit parameters given in Table I (range C in the text). The solid curve gives the resultant spectrum.

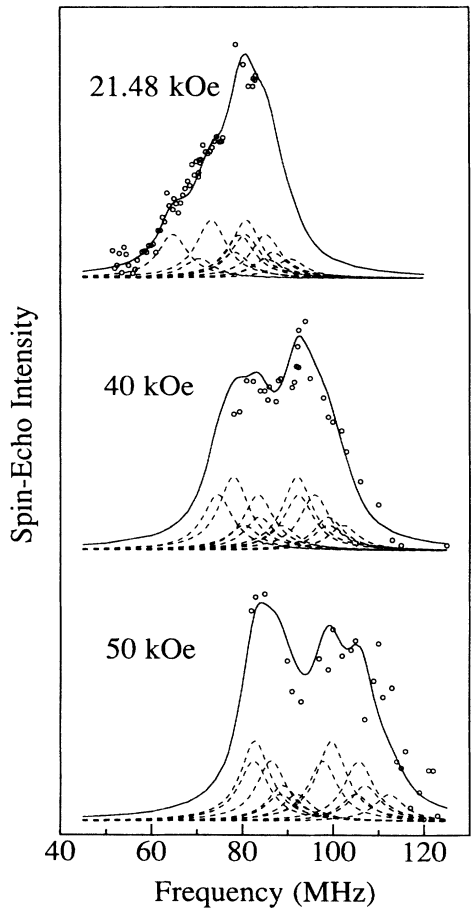

FIG. 3. Cu(2) NMR spectra in $PrBa_2Cu_3O_7$ at nonzero external field H_{ext} and 1.4 K. Dashed and solid curves as in Fig. 2.

TABLE I. NMR parameters obtained from fits to spectra of Figs. 2 and 3. See text for definitions. The final column gives weighted mean values. Indicated errors are statistical only.

H_{ext} (kOe)	0	21.48	40	50	Mean
H_{int} (kOe)	65.1±0.2	64.9±1.6	65.3±0.4	65.5±1.9	65.1±0.2
θ (deg)	79.0±3.0	79.2±2.3	79.2±2.0	77.7±2.2	78.8±1.1
Γ (MHz)	8.0±0.4	9.0±2.5	7.6±0.9	8.0±2.1	8.0±0.5
$^{63}\nu_Q$ (MHz)	17.0±2.0	16.9±4.4	17.5±3.4	18.3±5.5	17.2±1.5

of ~33 MHz, since then the quadrupole splitting is small enough only near the magic angle. Range *C* is for θ=75°-90°; here a value $^{63}\nu_Q \approx$ 15–19 MHz, which is not far from the corresponding value in $YBa_2Cu_3O_6$, is found.

To determine which of the latter two possibilities is correct, we have measured frequency-swept NMR spectra for nonzero $\mathbf{H}_{ext} \| c$. The applied field splits the resonances of nuclei on the two AF sublattices, and renders the calculated spectra sensitive to the direction of $\mathbf{H}_{int}$. Figure 3 shows spectra taken with external field H_{ext}=21.48, 40, and 50 kOe using an aligned powder sample. With the constraints provided by this additional information we found the fits to be significantly better in range *C*, shown in Fig. 3, than in range *B*. Due to spectrometer limitations, the data of Fig. 3 provide only partial coverage of the spectra, but the good fits for all three applied fields are convincing. Fits (not shown) using parameters from range *B* are much wider than the observed spectra for nonzero H_{ext}.

Table I gives the NMR parameters obtained in range *C*. We note that the value of the Cu(2) internal field H_{int}, 65.2 kOe, is comparable to that found in antiferromagnetic $YBa_2Cu_3O_6$ (~79 kOe) (Ref. 14) and La_2CuO_4 (~78 kOe).[15] Interestingly, a *c*-axis angle of ~79° was also found in La_2CuO_4.[15] Assuming the same hyperfine coupling parameters as in $YBa_2Cu_3O_6$, we estimate the magnetic moment to be about 0.5 μ_B on Cu(2) sites.

The orientation of the Cu(2) spins in the AF state can be deduced from the orientation of $\mathbf{H}_{int}$ if the anisotropy of the Cu(2) hyperfine interaction is known. Mila and Rice[16] have analyzed NMR and NQR data from $YBa_2Cu_3O_7$ to provide, among other results, estimates of the hyperfine coupling parameters of a Cu(2) nucleus to its own and near-neighbor-Cu(2) spins. Their results imply an in-plane coupling to an AF Cu(2) spin configuration about three times weaker than the out-of-plane coupling. If it is assumed that the hyperfine coupling is similar in Pr-Ba-Cu-O, our results indicate that the Cu(2) spin orientation is nearly in the *ab* plane as in $YBa_2Cu_3O_6$.

The fit value of $^{63}\nu_Q$, 17.2 MHz, is small compared to that for $YBa_2Cu_3O_7$ (31.5 MHz), but not far from the $YBa_2Cu_3O_6$ value of 22 MHz.[14] The change of $^{63}\nu_Q$ from 31.5 MHz in $YBa_2Cu_3O_7$ to 22 MHz in $YBa_2Cu_3O_6$ has been attributed to the absence of oxygen at the O(1) site.[12] Shimizu *et al.*[17] have obtained a universal relation between $^{63}\nu_Q$ and the calculated lattice contribution to the electric-field gradient (EFG) at Cu sites for a number of cuprates. Our results do not fall on this curve, but we expect a lattice contribution close to that of $YBa_2Cu_3O_7$ since the chains are full in both compounds. On these grounds, and in the absence of a more accurate description of the EFG in these systems, we speculate that the change in $^{63}\nu_Q$ is mainly due to the decreased hole concentration on the plane as x and y are increased in $Y_{1-x}Pr_xBa_2Cu_3O_7$ and $YBa_2Cu_3O_{7-y}$, respectively, and perhaps only to a lesser extent to the oxygens in the chains.

In $RBa_2Cu_3O_7$ compounds other than $PrBa_2Cu_3O_7$, the rare-earth ions order antiferromagnetically at temperatures which scale with the de Gennes factor.[4] This suggests a Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange mechanism. But Pr orders at 17 K in Pr-Ba-Cu-O, which is 2 orders of magnitude higher than would be expected from such a scaling. It seems likely that in Pr-Ba-Cu-O the Pr-Pr exchange interaction is enhanced by a Suhl-Nakamura-like[18] coupling via ordered Cu spins. As far as we are aware AF ordering at Cu(2) sites has not been observed in $RBa_2Cu_3O_7$ for $R \neq$Pr, so that the Suhl-Nakamura mechanism would not be available in these systems.

In summary, we have used copper NMR to confirm antiferromagnetic ordering on planar copper sites in Pr-$Ba_2Cu_3O_7$ below $T_N \simeq$ 280 K, and to determine the direction of the ordered Cu(2) moments. No ordering was found at Cu(1) sites down to 1.4 K. The similarity of this behavior to that of $YBa_2Cu_3O_6$ suggests that the absence of doped holes causes the lack of metallic behavior in both compounds. The similar behavior of the doped systems $YBa_2Cu_3O_{6+x}$ and $Y_{1-x}Pr_xBa_2Cu_3O_7$ is consistent with the above picture and suggests, as concluded by Neumeier *et al.*,[19] that hole filling as well as pair breaking plays an important role in the destruction of superconductivity in the latter compound. These results illustrate the importance of the interplay between superconductivity and magnetism in the high-T_c cuprates.

We are grateful for useful discussions with H. Yasuoka and Z. Fisk. This work was supported by NSF Grants No. DMR-8814783 and No. DMR-8802401, the University of California Institutional Collaborative Research Program in High-Temperature Superconductivity, the University of California, Riverside, Academic Senate Committee on Research, and the Temple University Center for Materials Research, and was performed in part under the auspices of the Department of Energy.

*Present address: Center for Materials Science Research and Development, Florida State University, Tallahassee, FL 32306.

[1]See, for example, *Physical Properties of High Temperature Superconductors,* edited by D. M. Ginsberg (World Scientific, Teaneck, NJ, 1989), Vol. I; *Physical Properties of High Temperature Superconductors,* edited by D. M. Ginsberg (World Scientific, Teaneck, NJ, 1990), Vol. II.

[2]A. P. Reyes *et al.*, in *Proceedings of the Thirty Fourth Conference on Magnetism and Magnetic Materials, Boston, 1989* [J. Appl. Phys. **67**, 5032 (1990)]; and (unpublished).

[3]D. W. Cooke *et al.*, Phys. Rev. B **41**, 4801 (1990).

[4]Z. Fisk *et al.*, Solid State Commun. **62**, 743 (1987); M. B. Maple *et al.*, J. Less-Common Met. **149**, 405 (1989). For a review see J. T. Markert, Y. Dalichaouch, and M. B. Maple, in *Physical Properties of High Temperature Superconductors* (Ref. 1), Vol. I, p. 265.

[5]L. Soderholm *et al.*, Nature (London) **328**, 604 (1987); A. Kebede *et al.*, Solid State Commun. **65**, 1001 (1988).

[6]See, for example, M. B. Maple *et al.*, Physica B **148**, 155 (1987).

[7]A. Kebede *et al.*, J. Magn. Magn. Mater. **76–77**, 619 (1988).

[8]J. L. Peng *et al.*, Phys. Rev. B **40**, 4517 (1989).

[9]C.-S. Jee *et al.*, Solid State Commun. **69**, 379 (1989); A. Matsuda *et al.*, Phys. Rev. B **38**, 2910 (1988).

[10]A. Kebede *et al.*, Phys. Rev. B **40**, 4453 (1989).

[11]M. Takigawa *et al.*, Phys. Rev. B **39**, 300 (1989); M. Takigawa, P. C. Hammel, R. H. Heffner, and Z. Fisk, *ibid.* **39**, 7371 (1989).

[12]For a review of NMR in $YBa_2Cu_3O_{7-y}$ see C. H. Pennington and C. P. Slichter, in *Physical Properties of High Temperature Superconductors* (Ref. 1), Vol. II.

[13]The signal from ^{141}Pr nuclei due to Pr AF ordering at 17 K would be found at a much higher frequency (of the order of GHz) due to the large ^{141}Pr orbital hyperfine field.

[14]H. Yasuoka *et al.*, J. Phys. Soc. Jpn. **57**, 2659 (1988); Y. Yamada *et al.*, *ibid.* **57**, 2663 (1988); P. Mendels and H. Alloul, Physica C **156**, 355 (1988).

[15]T. Tsuda *et al.*, J. Phys. Soc. Jpn. **57**, 2908 (1988).

[16]F. Mila and T. M. Rice, Physica C **157**, 61 (1989).

[17]T. Shimizu *et al.*, in *Proceedings of the Tenth ISMAR Meeting, Morzine, France, 1989* [Bull. Mag. Res. (to be published)].

[18]H. Suhl, Phys. Rev. **109**, 606 (1958); T. Nakamura, Prog. Theor. Phys. **20**, 542 (1958).

[19]J. J. Neumeier *et al.* (unpublished).