PHYSICAL REVIEW B VOLUME 43, NUMBER 4 1 FEBRUARY 1991

^{63}Cu NMR and hole depletion in the normal state of yttrium-rich $Y_{1-x}Pr_xBa_2Cu_3O_7$

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(Received 18 September 1990)

The ^{63}Cu Knight shift K and spin-lattice relaxation rate $1/T_1$ have been measured in the superconducting cuprate system $Y_{1-x}Pr_xBa_2Cu_3O_7$, $0.05 \leq x \leq 0.20$. With Pr doping K decreases and develops a temperature dependence at both plane and chain sites. This resembles the behavior of the Cu and Y Knight shifts as well as the bulk susceptibility in oxygen-deficient $YBa_2Cu_3O_{7-y}$. The orbital contribution to K and the anisotropy of the Cu hyperfine coupling remain essentially unchanged over the entire Pr concentration range. No appreciable direct effect of Pr magnetism on the conduction-band susceptibility was found. Instead, analysis of the bulk susceptibility and NMR data indicate that pair breaking and hole depletion both take part in the suppression of the superconducting transition temperature T_c. The temperature dependence of $1/T_1$ for magnetic field parallel to the c axis is also similar to that for the oxygen-deficient compound. This agreement leads to a consistent picture of the role of antiferromagnetic fluctuations in these materials. An analysis of the data in the framework of the phenomenological theory of Millis, Monien, and Pines is given.

I. INTRODUCTION

Praseodymium is unique among rare-earth dopants in suppressing superconductivity in the high-T_c cuprate $YBa_2Cu_3O_7$ while maintaining the orthorhombic structure of the host.[1] This property has motivated many investigators to study the $Y_{1-x}Pr_xBa_2Cu_3O_7$ system.[2-5] The superconducting transition temperature T_c decreases monotonically with increasing Pr concentration from 93 K at $x=0$ to 0 K at $x \simeq 0.6$, with an accompanying change in electrical behavior from metallic to semiconducting near the latter concentration. In these compounds several investigations[3-5] have concluded that Pr is nearly tetravalent and depresses T_c by filling or localizing conduction-hole band states. Spectroscopic studies[6,7] have indicated, however, that the Pr valence is close to 3+, so that magnetic spin-flip scattering and consequent Cooper-pair breaking depresses T_c. This interpretation is supported by the fact that $T_c(x)$ agrees well with the behavior predicted by the Abrikosov-Gor'kov theory of pair breaking by paramagnetic impurities.[4,5]

Nuclear magnetic resonance (NMR) spectroscopy has provided important experimental information on the normal-state properties of high-T_c superconductors.[8] Anomalous behavior of ^{63}Cu and ^{17}O NMR Knight shifts and spin relaxation rates has been observed in the normal states of $YBa_2Cu_3O_7$,[8] $YBa_2Cu_3O_{6.63}$,[9] and $La_{1.85}Sr_{0.15}CuO_4$.[10] These results have been successfully accounted for by the phenomenological model of Millis, Monien, and Pines (MMP),[11] which postulates an antiferromagnetically correlated Fermi liquid with strong antiferromagnetic (AF) Cu spin fluctuations. Although this model is not unique in explaining the data,[12] its success gives evidence for the importance of AF fluctuations, whose relation to superconductivity, nevertheless, remains a matter for speculation.

Preliminary ^{63}Cu NMR experiments[13] suggest a striking similarity between the behavior of the local magnetic susceptibilities in $Y_{1-x}Pr_xBa_2Cu_3O_7$ and oxygen-deficient $YBa_2Cu_3O_{7-y}$. The CuO_2-plane AF ordering observed in insulating members ($x \gtrsim 0.6$) of the $Y_{1-x}Pr_xBa_2Cu_3O_7$ series[14,15] is microscopically similar to that for $YBa_2Cu_3O_{7-y}$, $0 \lesssim y \lesssim 0.4$,[16,17] which gives strong evidence that the same mechanism for antiferromagentism is involved in both systems and probably in planar cuprates in general. Indeed, the proximity of these materials to a magnetic instability has long been thought to play a key role in their superconductivity.[18] Experimental data on normal-state properties of lightly doped $Y_{1-x}Pr_xBa_2Cu_3O_7$, which retains its metallic and superconducting nature, are therefore desirable to provide information on the relation, if any, between superconductivity and antiferromagnetism in planar cuprates.

In this paper we report an extensive study of ^{63}Cu NMR in Pr-doped $YBa_2Cu_3O_7$. A preliminary report of this work has appeared elsewhere.[19] Praseodymium doping offers a unique opportunity to study the depression of superconductivity without introducing structural disorder on either the chains or the planes in the $YBa_2Cu_3O_7$ crystal structure. Substitution of transition metals, e.g., Zn, Mn, Co, or Fe for Cu strongly disorders either the chains or the planes, and oxygen depletion ($YBa_2Cu_3O_{7-y}$, $y > 0$) results in a phase that is structurally different from the end compound. $Y_{1-x}Pr_xBa_2Cu_3O_7$ is, therefore, a useful system in that effects of disorder appear to be small, and the effect of charge carrier band modification can be studied with a minimum of complications.

In the present NMR experiments we have found that, to a considerable extent, the microscopic behavior at copper sites mimics that of oxygen-deficient $YBa_2Cu_3O_{7-y}$. Temperature-dependent Knight shifts were observed at chain and plane Cu sites, for which the hyperfine coupling remains almost the same as in undoped $YBa_2Cu_3O_7$. This latter result suggests that Pr doping has little effect on the Cu wave function at either site. Comparison of local susceptibilities derived from NMR Knight shifts shows that the chain and plane susceptibilities are not proportional, which implies, within mean-field theory, that the chain susceptibility possesses an intrinsic temperature dependence. As with increasing oxygen deficiency in $YBa_2Cu_3O_{7-y}$, the nuclear spin relaxation rate $1/T_1$ monotonically decreases with Pr concentration x at low temperatures, which suggests depression of the density of low-lying states. Analysis of these results has been carried out in the framework of the MMP model, with consistent and reasonable values of the parameters involved.

In Secs. II and III we discuss the preparation of our samples and experimental details, respectively. Then we present our results and analysis of the copper Knight shifts and relaxation rates in Sec. IV . In Sec. V, the MMP model is applied to extract relevant spin-fluctuation parameters. Our findings are summarized in Sec. VI.

II. SAMPLE PREPARATION

The samples used in this experiment were prepared using a standard solid-state reaction technique as follows. Stoichiometric amounts of high-purity Y_2O_3, Pr_6O_{11}, $BaCO_3$, and CuO were thoroughly mixed and fired for 2 h at 950 °C for initial reaction and calcination. The reacted samples were powdered and reheated for 12 h at least three times to assure even distribution of the reactants and to minimize the formation of unwanted phases. They were then pressed into pellets for a final 12-h sintering. These pellets were then powdered and heated in flowing oxygen to 600 °C, cooled to 520 °C over 10 h, annealed at 420 °C for 40 h and, finally, cooled slowly to room temperature over 10 h. X-ray powder diffraction patterns revealed samples consisting of a single orthorhombic phase, with lattice constants consistent with those of Kebede and co-workers.[20]

Figure 1 gives diamagnetic shielding curves for each Pr concentration, corrected for demagnetizing fields, at an applied field of 10 Oe. The transition temperatures for our samples are in substantial agreement with other work.[2–5,20] The transitions widths, estimated from the slope of the shielding curves at T_c, depend on x but are typically 3–5 K. The shielding fraction depends on Pr concentration and varies between 40 and 70%. Small shielding fractions are sometimes taken to indicate sample inhomogeneity, but NMR and other data on these specimens are consistent with homogeneous samples and intrinsic behavior. Although not visible in the x-ray patterns, a very small amount of pure $YBa_2Cu_3O_7$ phase ($\lesssim 2\%$) manifests itself as a slight diamagnetic tail in the shielding curve just below ~92 K. This is followed by a sharp transition at a lower temperature when the doped $Y_{1-x}Pr_xBa_2Cu_3O_7$ phase becomes superconducting. This small amount of second phase does not affect NMR measurements, however, since most of the signal comes from the doped phase.

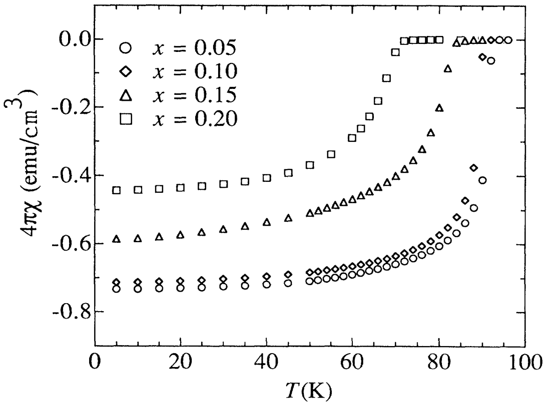

FIG. 1. Diamagnetic shielding (zero-field-cooled magnetization) curves for $Y_{1-x}Pr_xBa_2Cu_3O_7$ samples used in the present work. $H_{\mathrm{appl}} = 10$ Oe.

The oxygen stoichiometry was verified by the sharpness of the Cu(1) (chain) NMR and nuclear quadrupole resonance (NQR) lines. In oxygen-deficient $YBa_2Cu_3O_{7-y}$ samples, oxygen vacancies on the chains result in three configurations of chain Cu sites with distinct NQR and quadrupole-split NMR frequencies. The sharp peaks observed in our samples were similar to those obtained for $YBa_2Cu_3O_7$,[21] and there was a marked absence of lines corresponding to two- or three-oxygen coordinated chain Cu sites as seen in $YBa_2Cu_3O_{6.63}$.[9] This analysis gives a rough estimate, $y \lesssim 0.1$,[22] for which T_c would not be severely depressed. Magnetization measurements in the normal state yielded Curie-Weiss-like susceptibilities in good agreement with other reports.[19]

III. EXPERIMENT

The powdered samples were aligned with their c axes parallel to a 4.2-T magnetic field while being cast in epoxy at room temperature. This procedure allows us to obtain relatively narrow Cu NMR lines even in the presence of the large quadrupole splitting. A conventional NMR spectrometer was used to determine the ^{63}Cu Knight shift K and spin-lattice relaxation rate $1/T_1$ at plane and chain copper sites. The NMR spectra were obtained by integrating the NMR spin-echo signal while sweeping the magnetic field. Knight shifts were obtained from the observed fields for resonance and corrected for the quadrupolar shifts.[21] Relaxation data were obtained by digitizing the spin echo from the central ($\frac{1}{2}\leftrightarrow-\frac{1}{2}$) transition for increasing delay times following a single 90° saturating pulse. The integrated spin-echo amplitudes were then fit to a standard three-parameter multiexponential recovery curve[23] to obtain T_1. The fits were good at high temperatures, but the assumed functional form deviated from the data near and below T_c, which indicates a distribution of T_1's under these conditions. At low temperatures, where the central transitions from the plane and chain sites broaden and overlap, relaxation data were obtained from the quadrupole satellites instead.

IV. RESULTS AND DISCUSSION

A. Cu spectra

Figure 2 shows field-swept spectra of the ^{63}Cu central lines at 100 K and 85 MHz for plane and chain sites, each with **H**||**c** and **H**⊥**c**. The shapes of the spectra are essentially unchanged compared with undoped $YBa_2Cu_3O_7$ (Ref. 21) except for a slight broadening as Pr concentration is increased; this indicates an introduction of some disorder by Pr doping. For **H**||**c**, the two sharp lines at 73.7 and 74.4 kOe are identified as the Cu(1) and Cu(2) (plane Cu) central transitions, respectively. The small peaks at around 75 kOe are Cu(1) satellites that are not clearly resolved. For **H**⊥**c**, the sharp peak is due to Cu(2) nuclei, and the broad signal between 74 and 77 kOe matches the quadrupolar powder pattern with asymmetry parameter $\eta\sim1$ appropriate to Cu(1) nuclei. Weak signals in the spectra are spurious and arise from nuclei in the probe.

Our measurements indicate a slight temperature dependence of the quadrupole coupling frequency ν_Q at Cu(2) sites, similar to that originally observed by Riesemeier *et al.*[24] We also observed a slight change of ν_Q with Pr concentration, of about 2% for $x=0.2$ and monotonically decreasing with increasing x. This is several times larger than one would expect from the expansion of the lattice[20] on the basis of a point charge calculation and opposite to what would be expected from the picture of Shimizu *et al.*,[25] assuming that the on-site contribution does not change with doping. The asymmetries of the electric field gradients remain essentially unchanged for both copper sites over the range of Pr concentrations studied.

B. Cu(1) Knight shift

The principal-axis Knight shift tensor components at Cu(i) sites ($i=1,2$) will be denoted by $K_{i\alpha}$, where $\alpha=(a,b,c)$ indicates the crystal-axis direction. For chain sites ($i=1$), the temperature dependences of the Knight shifts are given in Fig. 3. For all α, $K_{1\alpha}(x,T)$ decreases with increasing x and develops a temperature dependence that is almost linear above T_c. Although the temperature

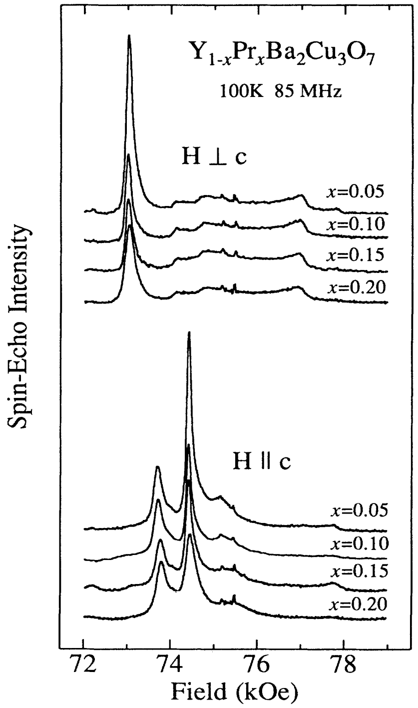

FIG. 2. Field-swept ^{63}Cu NMR spectra of aligned $Y_{1-x}Pr_xBa_2Cu_3O_7$ powders at 100 K and 85 MHz. See text for identification of resonance lines. The small peaks between 75 and 76 kOe are spurious signals from the probe.

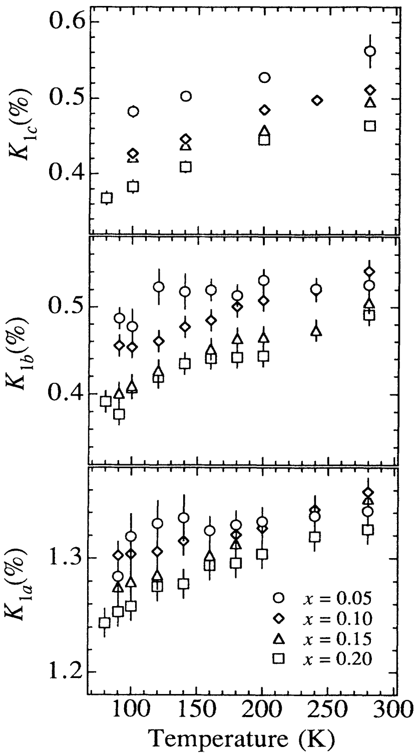

FIG. 3. Temperature dependence of the principal-axis Knight-shift tensor components for Cu(1) (chain) sites in the normal state of $Y_{1-x}Pr_xba_2Cu_3O_7$. The errors are statistical only.

variation of the resonance peak is small compared with the linewidth, the consistent behavior observed across the range of Pr concentrations suggests that it is intrinsic to the system. This temperature dependence is to be contrasted with the Cu(1) Knight shifts in undoped $YBa_2Cu_3O_7$, which are temperature independent above T_c.[8,21,26] Similar behavior has also been observed in $YBa_2Cu_3O_{6.45}$ (Ref. 25) and $YBa_2Cu_3O_{6.63}$ (Ref. 27) for Cu(1) sites with four oxygen neighbors and **H**||**c**. It should be noted that it is more difficult to obtain these data in oxygen-deficient samples because of the wide distribution of quadrupole frequencies associated with chain-oxygen vacancies and also because of linewidth anomalies that smear out the Cu(1) signal at low temperatures.[28] These difficulties are considerably reduced in $Y_{1-x}Pr_xBa_2Cu_3O_7$.

Formally, the Knight shift at each site i can be written as the sum of spin and orbital contributions

$$K_{i\alpha}=K_{i\alpha}^{(s)}+K_{i\alpha}^{(\mathrm{orb})}\ , \tag{1}$$

where the superscripts (s) and (orb) refer to spin and Van Vleck orbital paramagnetic contributions, respectively. Each component is proportional to a corresponding susceptibility, i.e.,

$$K_{i\alpha}^{(s,\mathrm{orb})}=A_{i\alpha}^{(s,\mathrm{orb})}\chi_{i\alpha}^{(s,\mathrm{orb})}\ , \tag{2}$$

where the A_α's are the principal-axis components of the hyperfine coupling tensors. We will assume that the spin susceptibility is isotropic and gives rise to the temperature dependence of the Knight shift in the following analysis, and we will demonstrate consistency with this assumption at the end.

Figure 4 gives plots of K_{1a} and K_{1b} versus K_{1c} with temperature as an implicit parameter. From this plot we can determine the orbital contributions to the Knight shifts as follows: In the absence of strong spin-orbit scattering, the freezing out of spin paramagnetism in the superconducting state yields $K_{i\alpha}^{(s)}(T=0)=0$. This allows one to read off the temperature-independent orbital contribution from the measured zero-temperature shift.[8,21,26] Due to difficulties associated with the field correction for diamagnetic shielding by supercurrents, we will not do this directly but will assume instead that the orbital contribution to K_{1c} does not change from its value in the undoped compound. This assumption is reasonable because $K_\alpha^{(\mathrm{orb})}$ is mainly ionic in nature and is relatively unaffected by changes in electronic structure outside the Cu ion, unless the latter changes valence appreciably.

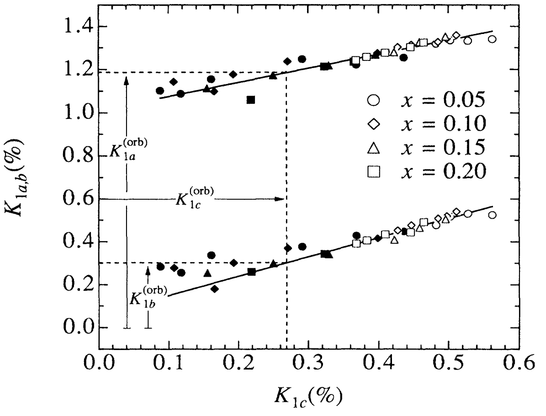

FIG. 4. Planar (**H**⊥**c**) vs c-axis (**H**||**c**) Knight shifts at Cu(1) sites in the normal (open symbols) and superconducting (solid symbols) states of $Y_{1-x}Pr_xBa_2Cu_3O_7$, with temperature an implicit parameter. Upper line: K_{1a}. Lower line: K_{1b}. Some shifts in the superconducting state are smaller than the orbital values because no diamagnetic correction has been made. The straight lines are fits to normal-state data. The value $K_{1c}^{(\mathrm{orb})}$ is that found for $x=0$ (Ref. 26).

If we then take $K_{1c}^{(\mathrm{orb})}=0.27\%$, as obtained for $x=0$,[26] we find $K_{1a}^{(\mathrm{orb})}=(1.17\pm0.02)\%$ and $K_{1b}^{(\mathrm{orb})}=(0.29\pm0.03)\%$. These values are relatively unchanged from those in the $x=0$ compound and remain essentially constant ($\pm10\%$) over the Pr concentration range. This anisotropy of the orbital Knight shift has been accounted for by the Cu $3d$-state crystal-field splitting,[29] which also justifies the validity of the assumption of vanishing spin shift at $T=0$.

The linearity of the relations of Fig. 4 is consistent with temperature-independent hyperfine couplings and an isotropic temperature-dependent susceptibility over the entire Pr concentration range. Indeed, the uniform slopes in Fig. 4 indicate that the anisotropy of the Cu(1) hyperfine coupling is independent of temperature and doping. From these slopes we obtain $A_{1a}^{(s)}/A_{1c}^{(s)}=0.65\pm0.10$ and $A_{1b}^{(s)}/A_{1c}^{(s)}=0.90\pm0.19$. These are to be compared with the corresponding values[26] 0.75 ± 0.13 and 0.90 ± 0.13, respectively, in $YBa_2Cu_3O_7$. We conclude that both the spin and orbital hyperfine coupling constants at Cu(1) sites are temperature independent.

A temperature dependence of the anisotropy would be expected only if a transferred hyperfine coupling to the temperature-dependent Pr magnetization existed. This is seen not to be the case here, nor is it the case for Cu(2) as will be shown shortly. The absence of such a coupling to Cu(1) sites is not surprising, given the remoteness of the Pr ions.

C. Cu(2) Knight shift

The temperature dependence of the Knight shift tensor principal-axis components $K_{2\alpha}(T)$ at Cu(2) (plane) sites is given in Fig. 5. Within errors, K_{2c} is independent of temperature and very close to its undoped value. This is as expected, since, for $x=0$, the spin hyperfine coupling along the c direction is fortuitously small, and K_{2c} is dominated by the orbital contribution.[21,26]

In contrast, the in-plane shift K_{2ab} exhibits a strong temperature and Pr concentration dependence. As for Cu(1) (Sec. IV B) the Cu(2) shifts decrease with increasing x, but their temperature dependence exhibits downward curvature rather than being linear. Similar behavior of the Cu(2) Knight shift has been reported in oxygen-depleted $YBa_2Cu_3O_{7-y}$, $0.3\lesssim y\lesssim0.55$, by several groups,[9,25,28] and also in ^{89}Y Knight shift data taken over the entire range $y<0.6$, for which $YBa_2Cu_3O_{7-y}$ is superconducting.[30] Measurements on Sr- and O-doped

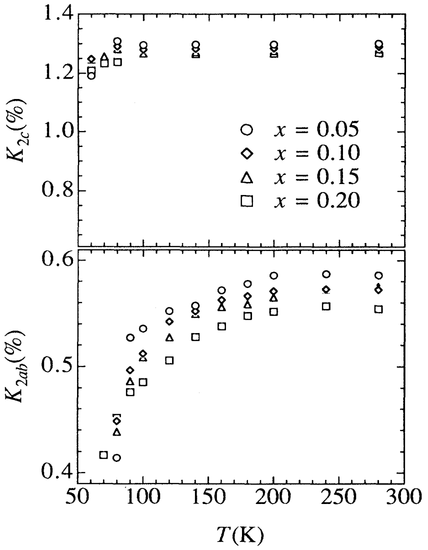

FIG. 5. Temperature dependence of ^{63}Cu Knight-shift components at Cu(2) (plane) sites in $Y_{1-x}Pr_xBa_2Cu_3O_7$.

La_2CuO_4 also indicate temperature-dependent Knight shifts.[31]

The constancy of K_{2c} indicates that the orbital shift $K_{2c}^{(\mathrm{orb})}$ is independent of Pr concentration for Cu(2) plane sites, as was shown in Sec. IV B for Cu(1) chain sites. As for $x=0$, this yields $K_{2c}^{(s)} \simeq 0$. In the undoped compound, Mila and Rice[29] have explained the magnitude and anisotropy of $K_{2\alpha}^{(s)}$ by adding a second term to the spin component of Eq. (1) due to an isotropic transferred hyperfine field from nearest-neighbor plane copper sites. Then

$$K_{2\alpha}^{(s)} = (A_{2\alpha}^{(s)} + 4B)\chi_2^{(s)} , \tag{3}$$

where B is the transferred hyperfine coupling constant. The vanishing c-axis spin Knight shift is, therefore, the result of a balance between on-site and transferred hyperfine contributions: $A_{2c}^{(s)} + 4B \simeq 0$. The present results show that this relation also holds for Pr-doped samples, and indicates, therefore, that the Cu(2) hyperfine constants are substantially independent of Pr doping. This cancellation of contributions to the hyperfine field is also necessary to explain why there is no T dependence of K_2 of $\mathbf{H}\|\mathbf{c}$, while there is for $\mathbf{H}\perp\mathbf{c}$. We note that such a temperature independence is not found for K_1, and that, for the undoped parent compound, all components are temperature independent.

Close inspection of Fig. 5 reveals a small x dependence to K_{2c}, $\sim 2\%$, which could be due to systematic errors in determining the peak frequencies but might also be real. If this x dependence is real, the fact that it is not accompanied by the development of a temperature dependence indicates by the above argument that the orbital shift, but not the spin shift, is affected by Pr doping.

Based on the Mila-Rice model, one might ascribe the x dependence of K to a transferred hyperfine field from Pr spins via planar oxygens. It can be argued, however, that if the decrease of K_{2ab} with both x and T is due to Pr, it should also give at least a noticeable effect on K_{2c}, which is inconsistent with the present data. This suggests that hyperfine coupling to Pr spins is negligible, as for chain Cu sites, even though Pr is close to the planes. We consider this point in more detail below.

If we adopt the view that Pr removes holes from the conduction band, possibly because it is close to a tetravalent state, the decrease of the magnitude of Knight shifts on both planes and chains with increasing x can be understood in a simple rigid-band picture as a decrease in the number of conduction-band carriers and, hence, of the density of states at the Fermi energy. The decrease at *both* plane and chain sites then implies that mobile holes are present on both structural entities.

Another possible interpretation of the change of $K_{2ab}(T)$ with Pr doping is suggested by the shape of its temperature dependence and the Curie-Weiss-like behavior of the Pr-dominated bulk susceptibility, viz., a transferred hyperfine interaction between Pr spins and Cu nuclei. Such a picture might be more appropriate for Pr close to a 3+ state, which has a more extended wave function that would be capable of stronger hybridization. In the following we consider this possibility and show that it is inconsistent with the data.

In a simple metal, a local spin moment produces a conduction-band spin polarization, which can be monitored by the Knight shift of the host nuclei. This Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism has successfully explained the observed temperature dependence of the host-nuclei Knight shift in several rare-earth intermetallic compounds.[33] The Hamiltonian $\mathcal{H}$, which describes exchange between the conduction-band spin polarization $\mathbf{s}_c$ and an ensemble of $4f$ moments, each of total angular momentum $\hbar\mathbf{J}_i$, can be written

$$\mathcal{H} = \sum_i \mathcal{J}_{\mathrm{CF}}(g_J - 1)\mathbf{J}_i \cdot \mathbf{s}_c \delta(\mathbf{r}_i) , \tag{4}$$

where $\mathcal{J}_{\mathrm{CF}}$ is the exchange constant, and g_J is the Landé g factor. The sum is over all $4f$-moment sites. In the uniform conduction-band polarization model,[33] it is assumed that the local moments uniformly polarize the band carriers. The hyperfine coupling constant $A^{(4f)}$ between the local-moment spin and a nucleus is then related to a spatially averaged estimate $\langle \mathcal{J}_{\mathrm{CF}} \rangle$ of $\mathcal{J}_{\mathrm{CF}}$ and is given by

$$A^{(4f)} = \frac{K^{(s)} \langle \mathcal{J}_{\mathrm{CF}} \rangle (g_J - 1)}{2N_A g_J \mu_B} . \tag{5}$$

Here $K^{(s)}$ is the spin Knight shift due to conduction electrons, which can be taken from a nonmagnetic reference compound or from the high-temperature limit of the observed Knight shift, N_A is Avogadro's number, and μ_B is the Bohr magneton.

We now assume that the temperature dependences of both K_{2ab} and the bulk susceptibility are dominated by that of the $4f$ susceptibility, i.e.,

$$K_{2ab}(T) = A_{2ab}^{(4f)} \chi_{ab}(T) + \mathrm{const} , \tag{6}$$

so that the exchange parameter can be obtained from a plot of K_{2ab} versus χ_{ab}, with temperature as an implicit parameter. This is done in Fig. 6, which reveals a linear relation for most points below 200 K. With $K^{(s)}$ taken from the high-temperature extrapolation (~280 K), and $K^{(\rm orb)}$ taken from the end compound $YBa_2Cu_3O_7$,[26] the fits for $T \leq 200$ K yield coupling parameters, which are summarized in Table I.

As pointed out in a preliminary report of this work,[13] the values of $\langle \mathcal{J}_{\rm CF} \rangle$ obtained in this manner are substantially larger than usually found in ordinary metals containing $4f$ ions. They are also substantially larger than the values obtained by Peng *et al.*,[4] who used the Abrikosov-Gor'kov theory of superconducting pair breaking to fit their $T_c(x)$ data. In other words, the depression of T_c should be more drastic than is actually observed if the exchange interaction were strong enough to cause the observed temperature dependence of the Knight shift. Our results for $\langle \mathcal{J}_{\rm CF} \rangle$ actually underestimate $\mathcal{J}_{\rm CF}$, because the uniform-polarization approximation breaks down in the dilute limit, where the finite-ranged RKKY spin polarization would decrease the average shift for a given value of $\mathcal{J}_{\rm CF}$ and, therefore, increase the estimate of $\mathcal{J}_{\rm CF}$ for a given observed shift. Thus we consider the RKKY-like scenario for the shift variation to be less likely than band modification, specifically hole depletion by Pr doping, and we take the linear relation in Fig. 6 to be fortuitous. It should be emphasized that this conclusion is not *per se* evidence against the importance of pair breaking in the depression of T_c. We can only say that the weak exchange required for the latter would not be observable in the Knight shift, which we ascribe to conduction-band modification resulting from hole depletion by Pr impurities. The parallel behavior of the Knight shift in $Y_{1-x}Pr_xBa_2Cu_3O_7$ and oxygen-deficient $YBa_2Cu_3O_{7-y}$ is also suggestive of such hole depletion.

A fundamental question that then arises is the origin of the temperature-dependent reduction of the susceptibility with increasing x. Pines[33] has suggested that this is a consequence of the increasing strength of antiferromagnetic correlations with hole depletion, whereas Kampf and Schrieffer[34] have considered a "pseudogap" in the single-particle spin excitation spectrum, which can form as a result of strong AF correlations. We shall see in Sec. V that the phenomenological MMP theory yields an increasing AF correlation length for plane-site Cu moments as doping is increased and as temperature is decreased.

TABLE I. Quantities required for estimation of the exchange coupling constant $\mathcal{J}_{\rm CF}$ between Pr local moments and conduction-band spins in $Y_{1-x}Pr_xBa_2Cu_3O_7$ from Cu(2) Knight-shift data and comparison with estimates of $\mathcal{J}_{\rm CF}$ from the depression of T_c. Symbols are defined in the text. The host spin Knight shift $K^{(s)}_{2ab}$ is obtained from the observed Knight shift at 280 K minus the orbital shift of 0.28% (Ref. 26). In Eq. (5) we use $g_J = 0.8$ appropriate to Pr^{3+}. The result $\langle \mathcal{J}_{\rm CF} \rangle_K \gg (\mathcal{J}_{\rm CF})_{T_c}$ is evidence that the observed temperature dependence of $K^{(s)}_{2ab}$ is not due to RKKY coupling to Pr spins.

x	0.05	0.10	0.15	0.20
$K^{(s)}_{2ab}$ (%)	0.306	0.292	0.295	0.274
$dK/d\chi$ (mol emu^{-1})	−2.849	−2.153	−1.081	−0.895
$A^{(4f)}$ (kOe/μ_B)	−15.9	−12.0	−6.04	−5.00
$\langle \mathcal{J}_{\rm CF} \rangle_K$ (eV)[a]	0.241	0.191	0.095	0.084
$(\mathcal{J}_{\rm CF})_{T_c}$ (eV)[b]		0.026		0.025

[a] Calculated from Knight-shift data [Eqs. (5) and (6)].

[b] Calculated from depression of T_c (Ref. 4).

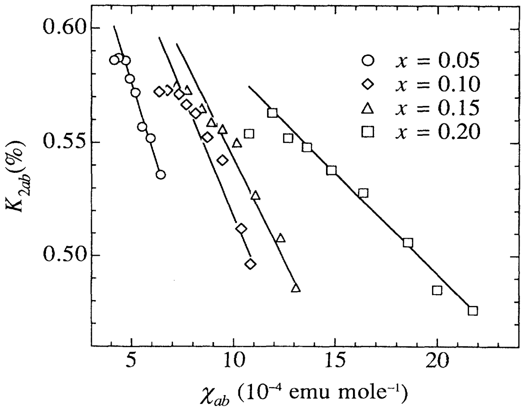

FIG. 6. Planar (H⊥c) Knight shift at Cu(2) sites vs bulk susceptibility in $Y_{1-x}Pr_xBa_2Cu_3O_7$. Solid lines: fits to the data for $T \leq 200$ K.

D. Chain-plane coupling; temperature dependence of chain susceptibility

Is the temperature dependence of the spin susceptibility (as measured by K) on the chain sites influenced by the planes, or is it at least in part intrinsic? Proportionality between chain and plane susceptibilities, which would seem to imply some form of strong chain-plane coupling, was assumed by Walstedt *et al.*[28] for $YBa_2Cu_3O_{6.7}$; using this assumption they found $\chi^{(s)}_1 \approx 2\chi^{(s)}_2$. In their analysis of NMR in $YBa_2Cu_3O_7$, Mila and Rice[29] assumed that the chains and planes have equal susceptibilities: $\chi^{(s)}_1 = \chi^{(s)}_2$. We examine this question by plotting the chain Knight shift versus the plane Knight shift, each normalized to its value at 280 K, in Fig. 7, where it can be seen that the shifts (and, therefore, the susceptibilities) are not proportional.

In a mean-field theory, the effective chain ($i = 1$) and plane ($i = 2$) spin susceptibilities $\chi^{(s)}_{i,\rm eff}$ can be written in the presence of coupling between chain and plane magnetism as

$$\chi^{(s)}_{i,\rm eff} = [1 + \Gamma_{ij}\chi^{(s)}_{j,\rm eff}(T)]\chi^{(s)}_{i,\rm loc}, \quad (i \neq j) \ . \tag{7}$$

Here Γ_{ij} is a mean-field coupling parameter (Γ_{12} need not be equal to Γ_{21}), and $\chi^{(s)}_{i,\rm loc}$ would be the local spin susceptibility at site i if chains and planes were uncoupled. If $\chi^{(s)}_{1,\rm loc}$ were independent of temperature, we would expect a linear relationship between $\chi^{(s)}_{1,\rm eff}$ and $\chi^{(s)}_{2,\rm eff}$. This would yield linearity between $K^{(s)}_{1c}(T)$ and $K^{(s)}_{2ab}(T)$, which is not observed (Fig. 7). We conclude that both the chain and plane susceptibilities are intrinsically temperature depen-

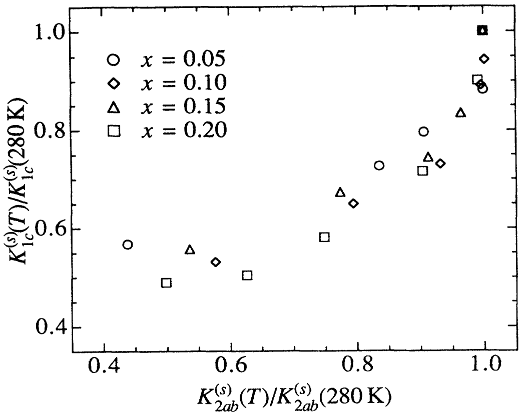

FIG. 7. Cu(1) (chain) spin Knight shift vs Cu(2) (plane) Knight shift, with temperature as an implicit variable, in $Y_{1-x}Pr_xBa_2Cu_3O_7$. The shifts are normalized to their respective values at 280 K. The lack of linearity indicates that the chain susceptibility is intrinsically temperature dependent.

dent in $Y_{1-x}Pr_xBa_2Cu_3O_7$. The data do not permit us to decide whether the coupling between chains and planes is weak or strong nor to determine the intrinsic temperature dependence.

E. Corrected Pr magnetic susceptibility

With the information on the Cu spin susceptibility available from the Knight shifts, we can further analyze the bulk susceptibility data to obtain the Pr contribution separately. The results of this analysis differ from those of previous work[4,5] in which the band susceptibility was taken to be temperature and concentration independent because we have shown this not to be so and obtained the temperature dependence from our Knight shift measurements. We do invoke the apparent Pr-concentration independence of the hyperfine couplings in order to estimate their value in the doped materials using data from the end compound $YBa_2Cu_3O_7$.

We write the susceptibility for $\mathbf{H}\perp\mathbf{c}$ as the sum of conduction-band, praseodymium, and diamagnetic contributions:

$$\chi_{ab}(x,T)=\chi_{ab}^{(\text{band})}(x,T)+\chi_{ab}^{(\text{Pr})}(x,T)+\chi^{(\text{dia})} . \tag{8}$$

The temperature-independent core diamagnetic susceptibility $\chi^{(\text{dia})}$ is not expected to be very different from the value of -1.75×10^{-4} emu mol^{-1} in the undoped compound.[35] The term labeled (band) is understood to be that from the hybridized Cu-O plane and chain bands, the predominant contribution to which comes from Cu spin and orbital paramagnetism. In fact, we write

$$\chi_{ab}^{(\text{band})}(x,T)=\chi_{1ab}^{(s)}(x,T)+2\chi_{2ab}^{(s)}(x,T)+\chi_{ab}^{(\text{orb})} , \tag{9}$$

where $\chi_{ab}^{(\text{orb})}$ is the orbital Van Vleck paramagnetic susceptibility that we argued earlier is independent of temperature and Pr doping.

Using Eq. (2) we can write

$$\chi_{ab}^{(\text{orb})}=(2K_{2ab}^{(\text{orb})}+K_{1ab}^{(\text{orb})})N_A\mu_B/A^{(\text{orb})} , \tag{10}$$

with the isotropic orbital hyperfine field $A^{(\text{orb})}=2\mu_B\langle r^{-3}\rangle$. Using $\langle r^{-3}\rangle=6.1$ a.u.,[36] and the orbital shift values $K_{2ab}^{(\text{orb})}=0.28\%$ and

$$K_{1ab}^{(\text{orb})}=(K_{1a}^{(\text{orb})}+K_{1b}^{(\text{orb})})/2=0.74\%$$

for the undoped compound,[24] we obtain $A^{(\text{orb})}=759$ kOe/μ_B and $\chi_{ab}^{(\text{orb})}=0.96\times10^{-4}$ emu mol^{-1}. The spin contribution $\chi_{ab}^{(s)}$ to the susceptibility from the planes can now be obtained directly from Eq. (3) using $A_{2ab}^{(s)}+4B=198.4$ kOe/μ_B.[11]

There are no published data for the hyperfine fields at chain sites, but we can make estimates based on results for the undoped compound. We first use the anisotropy of K_1 given in Fig. 4 to write

$$\chi_{1ab}^{(s)}=(0.77K_{1a}^{(s)}+0.56K_{1b}^{(s)})N_A\mu_B/A_{1c}^{(s)} . \tag{11}$$

Assuming $A_{1c}^{(s)}$ is independent of x and T, we can estimate it following the analysis of Ref. 18. We also assume that the spin density is equally shared by the two sites, i.e., $\chi_{1c}^{(s)}=\frac{1}{3}\chi_c^{(s)}$ in the undoped compound. Then, $\chi_c^{(s)}$ is obtained from the measured susceptibility after subtracting the Van Vleck and core diamagnetic terms; we refer the reader to Ref. 18 for details of the calculation. Using the best available values of the Knight shift,[26] we obtain $\chi_c^{(s)}=3.09\times10^{-4}$ emu mol^{-1} and $A_{1c}^{(s)}=173$ kOe/μ_B.

The contribution from Pr ions is assumed to be of the Curie-Weiss form

$$\chi_{ab}^{(\text{Pr})}(T)=\mathcal{C}/(T-\Theta)+\chi_0 . \tag{12}$$

Here $\mathcal{C}$ is the Curie constant, and χ_0 consists of all temperature-independent Van Vleck orbital and core diamagnetic contributions from Pr ions and, in principle, any other temperature-independent susceptibility not included in $\chi^{(\text{dia})}$ in Eq. (8). Even though this Curie-Weiss form might be modified by any crystal-field splitting of the $(2J+1)$-fold Pr degeneracy, it is still of interest to subtract our estimate for the conduction-band susceptibility from the measured bulk susceptibility and compare the resulting Pr susceptibility with Eq. (12).

The result of this procedure is shown in Fig. 8, which gives the temperature dependence of the measured bulk susceptibility for an aligned powder with $\mathbf{H}\perp\mathbf{c}$ together with the temperature dependence of the Pr contribution to the susceptibility obtained as described above. It is evident that the temperature-dependent Cu contribution cannot be ignored. The parameters that result from the fits are given in Table II. It is clear that the effective moment μ_{eff} is underestimated if one fits Eq. (12) directly to the bulk susceptibility. For smaller x, μ_{eff} is slightly larger, which could perhaps indicate a tendency toward lower than tetravalency (the Hund's-rule values are $\mu_{\text{eff}}=3.58\mu_B$/Pr for Pr^{3+} and $\mu_{\text{eff}}=2.54\mu_B$/Pr for Pr^{4+}) for lower Pr concentrations. We note that this tendency for small x toward trivalence and reduced hole filling could be related to the result of Neumeier *et al.*,[37] who concluded from their experiments on Ca-doped $Y_{1-x}Pr_xBa_2Cu_3O_7$ materials that most of the initial drop

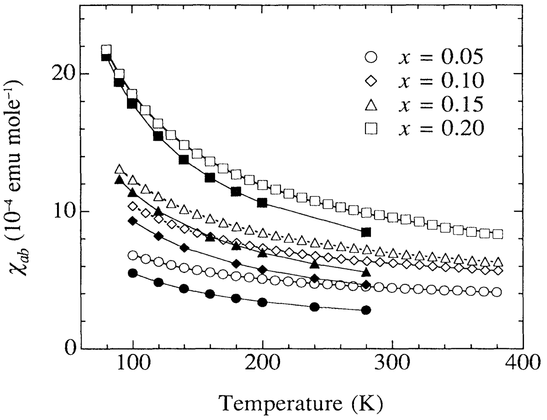

FIG. 8. Temperature dependence of the measured bulk susceptibility (open symbols) and Pr susceptibility obtained as described in the text (solid symbols). Solid lines: fits to Eq. (12).

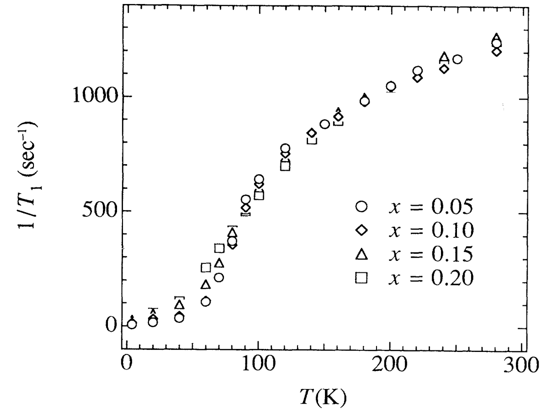

FIG. 9. Temperature dependence of the ^{63}Cu spin-lattice relaxation rate at Cu(2) sites in $Y_{1-x}Pr_xBa_2Cu_3O_7$.

in T_c for small x is due to pair breaking rather than hole filling. More trivalent behavior for small x was also concluded by Sankar *et al.*[38] from their specific-heat study of $Y_{1-x}Pr_xBa_2Cu_3O_7$.

F. Cu(2) spin-lattice relaxation rate

The temperature dependence of the ^{63}Cu spin-lattice relaxation rate $1/T_1$ at Cu(2) (planar) sites, with H‖c, is given in Fig. 9. With Pr doping, $1/T_1$ increases slightly at room temperature but decreases markedly at lower temperatures just above T_c. For example, at 100 K the relaxation rate for $x=0.20$ is $\sim 15\%$ slower than for $x=0$. For all Pr concentrations, as for $x=0$,[39] the so-called "coherence peak" expected from the standard BCS theory of superconductivity and s-wave pairing[40] is absent. The change in slope of $1/T_1(T)$ at T_c becomes smaller as x is increased and, for $x=0.20$, is hardly noticeable. For the latter sample, the relaxation rate for H⊥c was found to be about 4.25 times faster than for H‖c. (For $x=0$, this ratio is about 3.8.[26])

Figure 10 gives the temperature dependence of the quantity $1/T_1T$, where we have also included data for $YBa_2Cu_3O_{6.63}$ for comparison. It is evident that the "Korringa relation" $1/T_1T=\text{const}$ is not obeyed. For increasing Pr concentration, $1/T_1T$ exhibits a rounded maximum near 100 K, followed by a sharp decrease at lower temperatures. As x increases, the maximum becomes broader and shifts slightly to higher temperatures, reaching ~ 130 K for $x=0.20$. This behavior is qualitatively similar to that for $y=0.37$, except that the relaxation rate in the latter material is considerably enhanced at high temperatures. Warren *et al.*[41] have attributed the decrease of $1/T_1T$ above T_c to a superconducting precursor effect, whereas Yasuoka *et al.*[10] suggested the opening of a spin gap just below the peak temperature. With the aid of ^{17}O NMR results, and based on an antiferromagnetic Fermi-liquid model similar to that proposed for the $x=0$ material, Takigawa *et al.*[9] and Monien, Pines, and Takigawa[42] have shown that the Cu $1/T_1T$ behavior in $YBa_2Cu_3O_{6.63}$ can be explained as the combined temperature dependences of the spin susceptibility and a short-range AF correlation length.

Before proceeding to a similar analysis of our relaxation data, we first estimate the direct Pr-spin contribution to the observed relaxation rate. We note at the outset that one would expect such an additional mechanism to increase $1/T_1$ with increasing x, so that the observed decrease for $T \gtrsim T_c$ appears instead to reflect the reduction

TABLE II. Parameters obtained from Curie-Weiss fits [Eq. (12)] to bulk susceptibility data before and after correction for conduction-band contributions. Symbols are defined in the text. Errors are statistical only.

x		0.05	0.10	0.15	0.20
χ_0 (10^{-4} emu mol^{-1})	a	2.94±0.02	3.72±0.03	3.70±0.09	4.81±0.05
	b	1.06±0.11	1.63±0.02	1.78±0.06	2.96±0.05
Θ (K)	a	−22.1±2.2	−17.5±1.8	−22.4±1.1	−6.5±0.7
	b	−11.7±6.4	−16.1±0.5	−16.8±1.4	−5.9±0.5
$\mathcal{C}$ (10^{-4} emu K mol^{-1})	a	476±11	787±15	1054±12	1466±15
	b	495±20	890±6	1123±20	1572±13
μ_{eff} [μ_B (Pr ion)$^{-1}$]	a	2.76±0.03	2.51±0.03	2.37±0.02	2.42±0.01
	b	2.81±0.05	2.67±0.01	2.45±0.02	2.51±0.01

[a] Before correction for band contribution.
[b] After correction for band contribution.

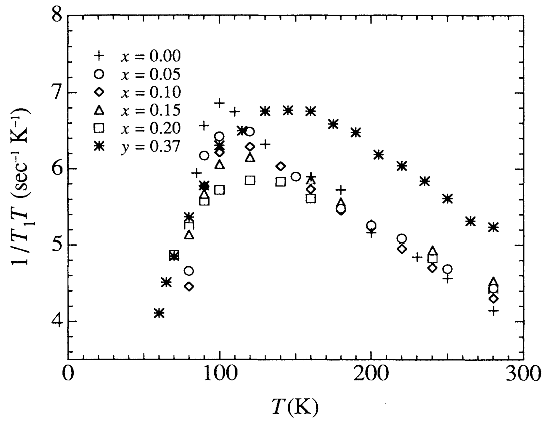

FIG. 10. Relaxation rate divided by temperature in the normal states of $Y_{1-x}Pr_xBa_2Cu_3O_7$ and oxygen-depleted $YBa_2Cu_3O_{7-y}$. Data for $x=0$ are taken from Ref. 21, and data for $y=0.37$ are taken from Ref. 9.

of conduction-hole concentration previously seen in the Knight shift.

Coupling between Cu nuclei and Pr ions could be via either direct dipolar interaction or indirect RKKY exchange. In the first case, the average relaxation rate due to a single Pr local moment is given by

$$1/T_1 \sim \gamma_n^2 \mu_{\mathrm{eff}}^2 \langle r^{-6} \rangle / \omega_{\mathrm{ex}} , \tag{13}$$

where γ_n is the nuclear gyromagnetic ratio, μ_{eff} is the effective Pr magnetic moment, ω_{ex} is the fluctuation frequency associated with the Pr-Pr exchange interaction, r is the distance between the Pr ion and the nuclear spin, and the angular brackets indicate a spatial average. Using the Néel temperature T_N to estimate ω_{ex}, Hammel *et al.*[43] have calculated and experimentally verified that the relaxation rate at Cu(2) sites due to dipolar coupling to Gd spins in $GdBa_2Cu_3O_7$ is about 20 times the rate in $YBa_2Cu_3O_7$. A similar calculation for Pr spins in $PrBa_2Cu_3O_7$ ($x=1$), using $T_N=17$ K, yields Cu(2) relaxation rates of 50 and 150 sec^{-1} for Pr^{4+} and Pr^{3+} ions, respectively. With dilution $\langle r^{-6}\rangle \propto x^2$ which, assuming that ω_{ex} is roughly linear in x, leads to $1/T_1 \propto x$. We use this admittedly severe extrapolation to estimate a Pr-spin contribution for $x=0.20$ of 10–30 sec^{-1}, which is quite negligible compared with the observed values in the normal state.

Estimates can also be made from our data in the superconducting state well below T_c (Fig. 9), where relaxation by superconducting excitations vanishes. This contribution was found to be at most only 3% of $1/T_1$ at 100 K. Crystal-field effects could, however, increase this contribution at higher temperatures, as seen, e.g., in unstable-moment systems.[44] We will, nevertheless, neglect direct Pr-spin relaxation in the following analysis.

The nuclear spin-lattice relaxation rate is related to the imaginary (dissipative) component $\chi''(\mathbf{q},\omega)$ of the dynamical spin susceptibility $\chi(\mathbf{q},\omega)$:[45]

$$1/T_1 = \frac{\gamma_n^2 k_B T}{2\mu_B^2} \sum_{\mathbf{q}} |A(\mathbf{q})|^2 \frac{\chi''(\mathbf{q},\omega_n)}{\omega_n} , \tag{14}$$

where ω_n is the nuclear Larmor frequency and $A(\mathbf{q})$ is the Fourier transform of the hyperfine coupling $A(\mathbf{r})$. The quantity $1/T_1T$ is, therefore, a measure of $\chi''(\mathbf{q},\omega)$, summed (with a weighting factor) over all fluctuation wave vectors $\mathbf{q}$ and evaluated at the nuclear resonance frequency ω_n.

For a Fermi liquid coupled to nuclei via the contact hyperfine interaction, the form factor is constant, and the Korringa relation[46] is satisfied:

$$(T_1TK^2)^{-1} = (\pi\gamma_n^2\hbar/\mu_B^2)R(\alpha) , \tag{15}$$

where $R(\alpha)$ is an enhancement factor that goes to unity in the noninteracting limit.[45] In the $x=0$ material, at 100 K, $R(\alpha)$ is about 11 for ^{63}Cu at Cu(2) sites but only about 1.4 for ^{17}O at plane oxygen [O(2),O(3)] sites.[39] This difference has been accounted for by AF correlations among Cu $3d$ spins,[11,39] which give rise to a peak in $\chi(\mathbf{q},\omega)$ for $\mathbf{q}$ near the AF wave vector $\mathbf{Q}=(\pi/a,\pi/a)$. This peak in turn enhances $1/T_1T$ [Eq. (14)], unless the form factor $|A(\mathbf{q})|^2$ is small for $\mathbf{q}\simeq\mathbf{Q}$. Copper AF spin fluctuations can be made to account for the NMR data, then, by noting that $|A(\mathbf{q}\simeq\mathbf{Q})|^2\simeq 0$ for plane oxygen sites, due to geometrical cancellation of transferred hyperfine fields from symmetrically located near-neighbor Cu spins but that $|A(\mathbf{q}\simeq\mathbf{Q})|$ is substantial for Cu(2) sites.

Our data suggest the change of Cu $1/T_1T$ with Pr doping in $Y_{1-x}Pr_xBa_2Cu_3O_7$ is due to the x dependence of $\chi(\mathbf{q},\omega_n)$ for the conduction band, and the above results for undoped $YBa_2Cu_3O_7$ suggest the importance of AF correlations, i.e., of the behavior of $\chi(\mathbf{q}\simeq\mathbf{Q},\omega)$. In the next section we apply the MMP theory, in which AF correlations are a central feature, to the case of $Y_{1-x}Pr_xBa_2Cu_3O_7$.

V. THE ANTIFERROMAGNETIC FERMI LIQUID

The dynamical behavior of ^{63}Cu and ^{17}O NMR in $YBa_2Cu_3O_7$, $YBa_2Cu_3O_{6.63}$, and $La_{1.85}Sr_{0.15}CuO_4$ is accounted for quantitatively[11,42,47] by a phenomenological theory developed by MMP.[11] In this section we apply the MMP theory to the case of $Y_{1-x}Pr_xBa_2Cu_3O_7$. The essential feature of the theory is the assumption that spins on Cu sites are correlated antiferromagnetically. The finite range of this correlation in real space leads to a broadened $\mathbf{q}$ dependence of the dynamical susceptibility in reciprocal space. Details of the theory can be found in Ref. 11.

A one-component form for $\chi(\mathbf{q},\omega)$ is assumed, which for convenience is written as the sum of two parts:

$$\chi(\mathbf{q},\omega) = \chi_{\mathrm{FL}}(\mathbf{q},\omega) + \chi_{\mathrm{AF}}(\mathbf{q},\omega) . \tag{16}$$

Here $\chi_{\mathrm{FL}}(\mathbf{q},\omega)$ is a normal Fermi-liquid-like contribution, which is spread broadly over $\mathbf{q}$ space, and $\chi_{\mathrm{AF}}(\mathbf{q},\omega)$ characterizes the antiferromagnetic fluctuations and is taken to be a Lorentzian centered at $\mathbf{q}=\mathbf{Q}$. For small energies the frequency-dependent imaginary part of $\chi_{\mathrm{FL}}(\mathbf{q},\omega)$ is of the form

$$\chi''_{\mathrm{FL}}(\mathbf{q},\omega) = \pi\omega\tilde{\chi}_0/\Gamma , \tag{17}$$

where Γ is a characteristic spin-fluctuation energy and

$\bar{\chi}_0=\chi_{\rm FL}(\mathbf{q}=0,\omega=0)$. The $\mathbf{q}$ dependence of the antiferromagnetic part is characterized by the AF correlation length ξ, which determines the width of the Lorentzian:

$$\chi''_{\rm AF}(\mathbf{q},\omega)=\frac{\chi_Q(\omega)(\pi\omega/\Gamma)(\xi^2/\xi_0^2)}{[1+\xi^2(\mathbf{Q}-\mathbf{q})^2]^2}\ , \tag{18}$$

where

$$\chi_Q\equiv\chi(\mathbf{q}=\mathbf{Q})=\bar{\chi}_0(\xi/\xi_0)^2\ ,$$

and ξ_0 is a parameter of the order of the inverse wave vector for which $\chi_{\rm AF}$ begins to dominate $\chi_{\rm FL}$. The temperature dependence of the correlation length is assumed to be of the mean-field form

$$\xi^2(T)=\xi^2(0)\frac{T_x}{T+T_x}\ , \tag{19}$$

where T_x is a characteristic temperature, and a is the lattice parameter.

We are interested in the role played by the AF correlation in determining the relaxation rate. The reader is referred to Ref. 42 for details of the calculation of the Cu(2) relaxation rate ${}^{63{\rm Cu}(2)}T_{1_\parallel}^{-1}$ for $\mathbf{H}\parallel\mathbf{c}$, based on the single-band model, which gives

$${}^{63{\rm Cu}(2)}T_{1_\parallel}^{-1}(T)=\frac{8\pi}{\mu_B^2\hbar^2}B^2k_BT\frac{\bar{\chi}_0(T)}{\Gamma(T)}\left\{0.294+\frac{\beta}{\pi^2}\left[0.49\left[\frac{\xi(T)}{a}\right]^2-0.62\log\left[\frac{\xi(T)}{a}\right]+0.0175\right]\right\}\ , \tag{20}$$

where B is the hyperfine coupling constant, a is the $\rm CuO_2$ square-planar lattice constant, and the parameter $\beta\equiv(a/\xi_0)^4$. For the undoped compound, typical values are $B=41$ kOe/μ_B, $\beta\approx10$, and $\Gamma=0.4-0.5$ eV, the last being almost temperature independent.

Equation (20) can be solved for ξ/a at each temperature using the experimental data. The results of this procedure are plotted in Fig. 11, where we have also included the result for $x=0$.[21,39] The correlation length ξ is of the same order of magnitude as the lattice parameter a, which is a reasonable value for a strongly hole-doped material. ξ increases with decreasing temperature and saturates before reaching T_c. This behavior indicates that the AF correlations cease to grow just above the point where the system undergoes the transition to the superconducting phase.

Another result of this analysis is the increase of ξ with Pr concentration. This is consistent with the view that the reduction of mobile-hole concentration on the planes, due to Pr doping, results in an increase of AF correlation of Cu spins as in the O-deficient compounds. Then one might expect that the absence of holes could lead to antiferromagnetic ordering of Cu moments in the planes in the end compound $\rm PrBa_2Cu_3O_7$. This is indeed the case, as has been shown by μSR (Ref. 14) and NMR (Ref. 15) experiments.

The enhancement $R_{\rm AF}$ of the relaxation rate [Eq. (15)] can now be calculated. It is most easily obtained from Eq. (20) by noting that the case $\beta=0$ is the usual Fermi-liquid result, viz, no enhancement. Hence,

$$R_{\rm AF}(T)={}^{{\rm Cu}(2)}T_{1_\parallel}^{-1}(\beta,T)/{}^{{\rm Cu}(2)}T_{1_\parallel}^{-1}(0,T)\ . \tag{21}$$

We note the importance of the leading ξ^2 term in Eq. (20), which plays a dominant role in determining $1/T_1$, and, from Figs. 11 and 12, we see that indeed the

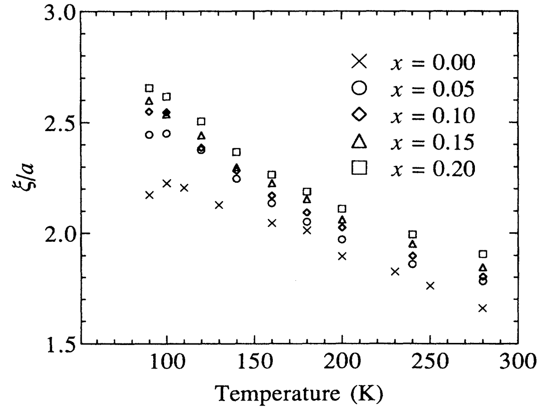

FIG. 11. Temperature and concentration dependence of the correlation length ξ, in units of the lattice constant a, for $\rm Y_{1-x}Pr_xBa_2Cu_3O_7$ as derived from the antiferromagnetic Fermi liquid theory of Millis, Monien, and Pines (Ref. 11); from Eq. (20).

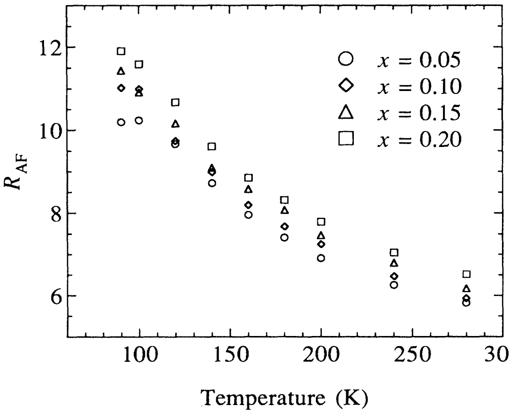

FIG. 12. Enhancement of the ^{63}Cu relaxation rate in $\rm Y_{1-x}Pr_xBa_2Cu_3O_7$. From Eq. (21).

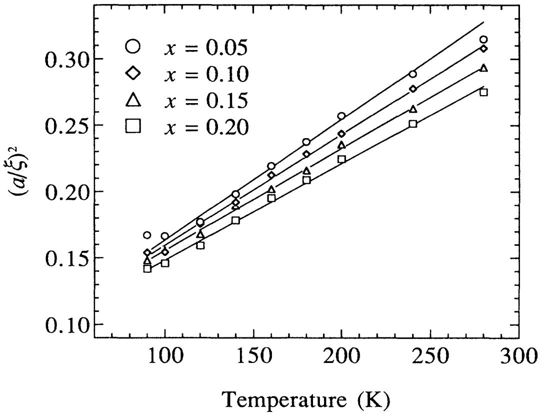

FIG. 13. Temperature dependence of $(a/\xi)^2$ in $Y_{1-x}Pr_xBa_2Cu_3O_7$ for various Pr concentrations. The lines are linear fits.

enhancement of $1/T_1$ behaves like the correlation length. At 100 K, R_{AF} is almost twice its room-temperature value. The peaking of $1/T_1T$ above T_c is, therefore, due to a competition between the antiferromagnetic enhancement and the temperature dependence of the static spin susceptibility.

Finally, Fig. 13 gives the temperature dependence of the quantity $[a/\xi(T)]^2$. The linearity of this behavior agrees with Eq. (19), which shows the consistency of assuming the mean-field temperature dependence of the correlation length. The value of T_x obtained from linear fits to these plots increases with increasing Pr concentration.

VI. CONCLUSIONS

The NMR results in $Y_{1-x}Pr_xBa_2Cu_3O_7$ presented in this paper provide clues to the nature of the depression of T_c and other effects of Pr doping in this system. Previous analyses[4] ,suggested that pair breaking is important in suppressing superconductivity, but the striking resemblance of the local magnetic behavior to that found in oxygen-deficient $YBa_2Cu_3O_{7-y}$ provides evidence that removal of hole carriers is also important. This in turn is a strong indication of tetravalent or mixed-valent behavior of praseodymium in this system, although Pr^{3+} ions, through modification of the local electronic structure on the planes, might also provide a hole localization mechanism.[48]

We can see that hole filling may not be the entire story, however, if we compare T_c depression in $Y_{1-x}Pr_xBa_2Cu_3O_7$ and $YBa_2Cu_3O_{7-y}$ using a simple hole-counting scheme. If Pr were 4+ and the doped-hole distributions are similar for the two systems, the hole concentration for $x=0.20$ would be equal to that for $y=0.10$. In the latter case, T_c is barely depressed from the end compound $y=0$, however, whereas, for $x=0.2$, the depression is significant. Different hole distributions, such as filling of chain holes by Pr doping, may also play some role, but this argument suggests that pair breaking (or some other mechanism) may need to be invoked to explain the observed T_c depression in $Y_{1-x}Pr_xBa_2Cu_3O_7$. The inadequacy of hole filling as the only mechanism for T_c depression is further indicated by the tendency towards Pr^{3+} for low x (Sec. IV B), so that initial Pr doping can only fill less than one hole per Pr ion.

The Knight-shift results also show that the exchange interaction presumably responsible for pair breaking is weak, and that the paramagnetism of the conduction band is not directly affected by Pr doping. The insensitivity of the hyperfine coupling parameters to Pr concentration attests to this conclusion. Analysis of Cu(1) and Cu(2) Knight shifts also shows that the plane and chain susceptibilities are not proportional to each other but exhibit significantly different temperature dependences. This result, which contradicts the assumption of proportionality between chain and plane susceptibilities used to treat $YBa_2Cu_3O_7$ (Ref. 29) and $YBa_2Cu_3O_{6.64}$ (Ref. 28) implies, within mean-field theory, that the chain Cu susceptibility possesses its own independent temperature dependence regardless of the strength of the chain-plane interaction. It should be noted that a significant chain-plane interaction is indicated by the appearance of superconductivity on both chains and planes.[8]

Finally, from an analysis of ^{63}Cu(2) shift and relaxation rate data, we have demonstrated that reasonable values of spin fluctuation parameters, whose dependence on temperature and Pr doping follows naturally from the effect of conduction-hole concentration on antiferromagnetic correlations, can be obtained using an antiferromagnetic Fermi-liquid phenomenology.

ACKNOWLEDGMENTS

We acknowledge stimulating discussions with D. Pines, H. Monien, P. Monthoux, T. M. Rice, and G. A. Sawatsky. We also thank Z. Fisk and S.-W. Cheong for their assistance in sample preparation. Work at U.C. Riverside was supported by National Science Foundation (NSF) Grant No. DMR-8814783, by the U.C. Riverside Academic Senate Committee on Research, and by the U.C. Inter-Institutional Collaborative Research (INCOR) Program in High-Temperature Superconductivity. Work at Los Alamos was supported in part by the INCOR program, and was carried out under the auspices of the Department of Energy. Work at Temple University was supported by NSF Grant No. DMR-8802401 and the Temple University Center for Materials Research.

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