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TITLE Copper NMR and Hole Depletion in the Normal State of $Y_{1-x}Pr_xBa_2Cu_3O_7$

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COPPER NMR AND HOLE DEPLETION IN THE NORMAL STATE OF $Y_{1-x}Pr_xBa_2Cu_3O_7$

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This paper gives a summary of copper NMR measurements in the high T_c superconductor $YBa_2Cu_3O_7$ doped with praseodymium. This element is unique among the rare earths in depressing the superconducting transition temperature T_c, which falls to zero at about 60% Pr doping. The NMR Knight shift and spin-lattice relaxation measurements indicate that Pr doping depletes conduction holes, and in this respect, behaves similarly to oxygen-deficient $YBa_2Cu_3O_{7-y}$. A consistent analysis in the framework of the phenomenological theory of antiferromagnetic fluctuations of Millis, Monien and Pines is given. In the end compound $PrBa_2Cu_3O_7$ the NMR signal from plane Cu sites indicates antiferromagnetic ordering at a Néel temperature of about 280 K.

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COPPER NMR AND HOLE DEPLETION IN THE NORMAL STATE OF $Y_{1-x}Pr_xBa_2Cu_3O_7$

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ABSTRACT

Normal-state copper NMR spectra and spin-lattice relaxation rates $1/T_1$ have been measured in the planar cuprate system $YBa_2Cu_3O_7$. With Pr doping the Knight shift K decreases and develops a temperature dependence at both plane and chain sites. 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 Knight shift behavior resembles that in oxygen-deficient $YBa_2Cu_3O_{7-y}$, as does the temperature dependence of $1/T_1$ for plane Cu sites and magnetic field perpendicular to the c axis. 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. In the end compound $PrBa_2Cu_3O_7$ the NMR signal from plane Cu sites indicates antiferromagnetic (AF) ordering at a Néel temperature ~280 K, and in the AF state yields an internal field similar to those found in AF $YBa_2Cu_3O_6$ and La_2CuO_4.

1. 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]. The superconducting transition temperature T_c decreases monotonically with increasing Pr concentration to 0 K at $x \simeq 0.6$, with an accompanying change from metallic to semiconducting behavior near this concentration. Several investigations [2–4] have concluded that Pr is nearly tetravalent, and depresses T_c by filling or localizing conduction-hole band states. Spectroscopic studies have shown, however, that the Pr valence is close to 3+, which would seem to rule out hole filling or localization. An alternative mechanism would then be depression of T_c by magnetic spin-flip scattering and consequent Cooper-pair breaking. 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. Nevertheless, persuasive arguments for some form of conduction-hole depletion include (a) the fact that T_c is depressed only for Pr doping, (b) the existence of the metal-insulator transition just as T_c is depressed to 0, and (c) recent evidence for a Pr^{4+} crystal-field-split ground state [5].

Nuclear magnetic resonance (NMR) spectroscopy has provided important experimental information on the normal-state properties of high-T_c superconductors [6]. Anomalous behavior of ^{63}Cu and ^{17}O NMR Knight shifts and spin relaxation rates has been observed in the normal states of $YBa_2Cu_3O_7$ [6], $YBa_2Cu_3O_{6.63}$ [7], and $La_{1.85}Sr_{0.15}CuO_4$ [8]. These results have been successfully accounted for by the phenomenological model of Millis, Monien and Pines (MMP) [9], which postulates an antiferromagnetically-correlated Fermi liquid with strong AF Cu spin fluctuations. Although this model is not unique in explaining the data [10] its success gives evidence for the importance of AF fluctuations, whose relation to superconductivity nevertheless remains a matter for speculation.

In this paper we report a study of copper NMR in Pr-doped $YBa_2Cu_3O_7$ [11,12]. 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 which 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 any charge carrier band modification can be studied with a minimum of complication.

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. As in O-deficient $YBa_2Cu_3O_{7-y}$, 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.

We present our results and analysis of the ^{63}Cu Knight shifts and relaxation rates for Y-rich $Y_{1-x}Pr_xBa_2Cu_3O_7$ in Section 2. In Section 3 the MMP model is applied to extract relevant spin-fluctuation parameters. Copper NMR in the end compound $PrBa_2Cu_3O_7$ is described in Section 4, and our findings are summarized in Section 5.

2. ^{63}Cu NMR in Y-rich $Y_{1-x}Pr_xBa_2Cu_3O_7$.

2.1. Cu(2) Knight shift.

The temperature dependence of the Knight shift tensor principal-axis components $K_{2\alpha}$ at Cu(2) (plane) sites is given in Fig. 1. Here $\alpha = (a, b, c)$ indicates the crystal axis along which the external field $\mathbf{H}_{ext}$ is oriented. 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 [13,14]. In contrast, the "planar" shift K_{2ab} exhibits a strong temperature and Pr concentration dependence. The shift decreases with increasing x, and develops a temperature dependence with a downward curvature. Similar behavior of the Cu(2) Knight shift has been reported in oxygen-depleted $YBa_2Cu_3O_{7-y}$, $0.3 \lesssim y \lesssim 0.55$, by several groups [7,15,16], 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 [17].

The Knight shift $K_{2\alpha}(T)$ can be written as the sum of spin and orbital contributions: $K_{2\alpha}(T) = K_{2\alpha}^{(s)}(T) + K_{2\alpha}^{(orb)}(T)$. The constancy of K_{2c} indicates that the orbital shift $K_{2c}^{(orb)}$ is independent of Pr concentration for Cu(2) plane sites. In the undoped compound Mila and Rice [18] have explained the magnitude and anisotropy of $K_{2\alpha}^{(s)}$ by postulating an isotropic transferred hyperfine field from nearest-neighbor plane copper sites. Then

$$K_{2\alpha}^{(s)} = (A_{2\alpha}^{(s)} + 4B)\chi_2^{(s)} , \qquad (1)$$

where $A_{2\alpha}^{(s)}$ is the on-site hyperfine coupling constant and 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 indicate that this relation also holds for Pr-doped samples, and suggest, 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 for $\mathbf{H}_{ext} \parallel \mathbf{c}$ while there is for $\mathbf{H}_{ext} \perp \mathbf{c}$. We note that for the undoped parent compound all components are temperature-independent [6,13].

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 band picture as a decrease of the density of states $\rho(\epsilon_F)$ at the Fermi energy. 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. In the following we consider this possibility and show that it is inconsistent with the data.

In a simple metal a localized spin moment produces a conduction-band spin polarization, which can be monitored by the Knight shift. This Rudermann-Kittel-Kasuya-Yosida (RKKY) mechanism has successfully explained the observed temperature dependence of the Knight shift in several rare-earth intermetallic compounds [19]. The hamiltonian $\mathcal{H}$ which describes exchange between an ensemble of $4f$ moments, each of total angular momentum $\hbar\mathbf{J}_i$, and the conduction-band spin polarization $\mathbf{s}_c$ can be written

$$\mathcal{H} = \sum_i \mathcal{J}_{cf}(g_J - 1)\mathbf{J}_i \cdot \mathbf{s}_c\,\delta(\mathbf{r}_i)\ , \tag{2}$$

where $\mathcal{J}_{cf}$ 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 [19] 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 $\langle\mathcal{J}_{cf}\rangle$ of $\mathcal{J}_{cf}$.

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

$$K_{2ab}(T) = A^{(4f)}_{2ab}\chi_{ab}(T) + \text{const.}\ , \tag{3}$$

so that the exchange parameter can be obtained from a plot of K_{2ab} vs. χ_{ab} with temperature an implicit parameter. This is done in Fig. 2, which reveals a linear relation for most points below 200 K.

The values of $\langle \mathcal{J}_{cf} \rangle$ obtained in this manner [12] are to be compared with the results of calculations by Peng et al. [3] who used the Abrikosov-Gor'kov theory of superconducting pair breaking to fit their $T_c(x)$ data. As pointed out in a preliminary report of this work [11], the value of $\langle \mathcal{J}_{cf} \rangle$ obtained from $T_c(x)$ is substantially smaller than that obtained from $K_{2ab}(T)$. In other words, the depression of T_c should be more drastic than what is actually observed if the exchange interaction is strong enough to cause the observed temperature dependence of the Knight shift. Our results for $\langle \mathcal{J}_{cf} \rangle$ actually underestimate $\mathcal{J}_{cf}$, 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 $\mathcal{J}_{cf}$ and, therefore, increase the estimate of $\mathcal{J}_{cf}$ for a given observed shift. We therefore 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 of Fig. 2 to be more or less fortuitious. It should be emphasized that this conclusion is not *per se* evidence against the importance of pair breaking in the depression of T_c; only that the weak exchange required for the latter would not be observable in the Knight shift.

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 band modification resulting from hole depletion by Pr doping. A more fundamental question is then the origin of the temperature-dependent susceptibility. As an example of an approach to this problem, Kampf and Schrieffer [20] have suggested that a "pseudogap" in the single-particle spin excitation spectrum can form as a result of strong AF correlations. Indeed, as we shall see in Sect. 3, the phenomenological MMP theory yields an increasing AF correlation length for plane-site Cu moments as doping is increased and as temperature is decreased.

2.2. Cu(2) spin-lattice relaxation rate.

The nuclear spin-lattice relaxation rate $1/T_1$ is related to the imaginary (dissipative) component $\chi''(\mathbf{q},\omega)$ of the dynamical spin susceptibility $\chi(\mathbf{q},\omega)$ [21]:

$$1/T_1 = \frac{\gamma_n^2 k_B T}{2\mu_B^2} \sum_{\mathbf{q}} |A(\mathbf{q})|^2 \frac{\chi''(\mathbf{q},\omega_n)}{\omega_n} , \tag{4}$$

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

The temperature dependence of the ^{63}Cu spin-lattice relaxation rate $1/T_1$ at Cu(2) sites, with $\mathbf{H}_{ext} \parallel \mathbf{c}$, is given in Fig. 3. 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 rate for $x = 0.20$ is ~15% slower than for $x = 0$. For all Pr concentrations, as for $x = 0$ [22], the so-called "coherence peak" just below T_c, expected from the standard BCS theory of superconductivity and s-wave pairing, 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. Figure 4 gives the temperature dependence of the quantity $1/T_1T$, where we have also included data for $YBa_2Cu_3O_7$ [13] and $YBa_2Cu_3O_{6.63}$ [7] for comparison.

It is evident that the "Korringa law" $1/T_1T = \text{const.}$ 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. [23] have attributed the decrease of $1/T_1T$ above T_c to a superconducting precursor effect, while Yasuoka et al. [13] 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. [7] have shown that the Cu $1/T_1T$ behavior can be explained as the combined temperature dependences of the spin susceptibility and a short-range AF correlation length.

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

$$(T_1TK^2)^{-1} = (\pi\gamma_n^2/\hbar\mu_B^2)R(\alpha) \; , \tag{5}$$

where $R(\alpha)$ is an enhancement factor which goes to unity in the non-interacting limit [22]. In the $x = 0$ material at 100 K $R(\alpha)$ is about 11 for ^{63}Cu, but only about 1.4 for ^{17}O. This difference has been accounted for by the MMP model of antiferromagnetic correlations among Cu $3d$ spins [9], 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 $1/T_1T$, which varies as a weighted sum of $\chi''(\mathbf{q},\omega_n)$ over all $\mathbf{q}$, unless the form factor $|A(\mathbf{q}\simeq\mathbf{Q})|^2$ vanishes. 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 ^{17}O, due to geometrical cancellation of transferred hyperfine fields from symmetrically-located near-neighbor Cu spins, but that $|A(\mathbf{q}\simeq\mathbf{Q})|^2$ is substantial for ^{63}Cu(2) sites.

Such a picture suggests that in $Y_{1-x}Pr_xBa_2Cu_3O_7$ the change of $1/T_1T$ with Pr doping is due to the x dependence of $\chi(\mathbf{q},\omega)$ itself, and that the decrease of $1/T_1T$ above T_c is due to the suppression of $\chi(\mathbf{q},\omega)$. The consequences of assuming that this suppression is due to AF correlations are investigated in the next section.

3. The antiferromagnetic Fermi liquid.

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

q dependence of the dynamical susceptibility in reciprocal space. Details of the theory can be found in the references.

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

$$\chi(\mathbf{q},\omega) = \chi_{\mathrm{FL}}(\mathbf{q},\omega) + \chi_{\mathrm{AF}}(\mathbf{q},\omega)\ . \tag{6}$$

Here $\chi_{\mathrm{FL}}(\mathbf{q},\omega)$ is a normal Fermi-liquid-like contribution, which is spread broadly over **q** space, and $\chi_{\mathrm{AF}}(\mathbf{q},\omega)$ characterizes the antiferromagnetic fluctuations and is taken to be a Lorentzian centered at $\mathbf{q} = \mathbf{Q}$. The **q** dependence of the antiferromagnetic part is characterized by the AF correlation length ξ, which determines the width of the Lorentzian:

$$\chi_{\mathrm{AF}}(\mathbf{q},\omega) = \frac{\chi_{Q}(\omega)}{1+\xi^2(\mathbf{Q}-\mathbf{q})^2}\ . \tag{7}$$

We are interested in the role played by the AF correlation in determining the relaxation rate. The reader is referred to [9] and [12] for details of the calculation of $1/T_1$. The model yields a value of ξ at each temperature using the experimental data. The results of this procedure are plotted in Fig. 5, where we have also included the result for $x = 0$ [13,21]. The correlation lengths in Fig. 5 are reasonable in value. They grow with decreasing temperature, and saturate before reaching T_c. This behavior indicates that the AF correlations cease to grow just above the point where the systems undergoes the transition to the superconducting phase.

Another important result is the increase of ξ with Pr concentration which emerges from this analysis. This is consistent with the view that mobile holes on the planes destroy the AF correlation of Cu spins, as in the O-deficient compounds. This would then imply that these holes are filled or localized by Pr doping, and that in the end compond $PrBa_2Cu_3O_7$ the absence of holes leads to antiferromagnetic ordering of Cu moments in the planes.

4. NMR and plane-Cu antiferromagnetism in $PrBa_2Cu_3O_7$.

In this section we describe results of Cu NMR experiments in $PrBa_2Cu_3O_7$. A more detailed report of this work will appear elsewhere [24].

Spectra from Cu(2) sites indicate antiferromagnetic (AF) ordering of plane copper magnetic moments, in agreement with recent μSR studies [25]. NMR spectra in the AF state reflect a large internal hyperfine magnetic field $H_{int} \simeq 65\,kOe$ 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 [26], is a signature of the absence of doped holes in the plane conduction band.

Representative field-swept spectra obtained at high temperatures are shown in Fig. 6. The low- and high-field peaks at 300 K have been identified as arising from Cu(1) and Cu(2) sites respectively [13]. The disappearance 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 $280 \pm 10\,K$.

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 $YBa_2Cu_3O_7$ [6], 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 [6], and we interpret the 21-MHz spectrum 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, this indicates that magnetic ordering does not occur on chain sites down to 1.4 K.

The 80-MHz zero-field spectrum, shown in Fig. 7, is attributed to NMR of Cu(2) nuclei in an internal hyperfine field $\mathbf{H}_{int}$ due to AF ordering of Cu moments at plane sites. This 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 [26]. The hyperfine fields are of similar magnitude but details of the spectra are different in the two cases.

The small quadrupole satellite splitting in the spectrum of Fig. 7 leads to acceptable fits to calculated spectra over a wide range of angle θ between $\mathbf{H}_{int}$ and the c axis. For all fits H_{int} is found to be in the vicinity of 65 kOe. To determine θ we have measured frequency-swept NMR spectra for nonzero $\mathbf{H}_{ext} \parallel \mathbf{c}$. The applied field splits the resonances of nuclei on the two AF sublattices, and renders the calculated spectra sensitive to the direction of $\mathbf{H}_{int}$. The best fit was obtained for $\theta = 79° \pm 1°$.

The value of the Cu(2) internal field $H_{int} = 65.2 \pm 0.2$ kOe is comparable to that found in antiferromagnetic $YBa_2Cu_3O_6$ (~79 kOe) [27] and La_2CuO_4 (~78 kOe) [28]. Interestingly, a c-axis angle of ~79° was also found in La_2CuO_4. Assuming the same hyperfine coupling parameters as in $YBa_2Cu_3O_6$, we estimate the magnetic moment to be about $0.5\,\mu_B$ 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 [18] 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 $PrBa_2Cu_3O_7$, our results indicate that the Cu(2) spin orientation is nearly in the ab plane as in $YBa_2Cu_3O_6$.

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 [29]. This suggests a Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange mechanism. But Pr orders at 17 K in $PrBa_2Cu_3O_7$, which is two orders of magnitude higher than would be expected from such a scaling. It seems likely that in $PrBa_2Cu_3O_7$ the Pr-Pr exchange interaction is enhanced by a Suhl-Nakamura-like coupling [30] 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.

5. 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 [3] suggested that pair breaking is important in supressing 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 an indication of tetra- 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 [31].

We note, however, that hole filling is unlikely to be the entire story, if we compare $Y_{1-x}Pr_xBa_2Cu_3O_7$ and $YBa_2Cu_3O_{7-y}$ using a simple hole-counting scheme. If Pr were 4+ the $x = 0.20$ samples would be equivalent to $y = 0.10$, for which T_c is barely depressed from the end compound. To explain the observed T_c pair breaking (or some other mechanism) must be invoked.

The Knight shift results also show that the exchange interaction presumably responsible for pair breaking is very 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. 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.

We have also used copper NMR to confirm antiferromagnetic ordering on planar copper sites in $PrBa_2Cu_3O_7$ 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 $YBa_2Cu_3O_{7-y}$ and $Y_{1-x}Pr_xBa_2Cu_3O_7$ is consistent with the above picture and suggests, as concluded by Neumeier et al. [32] that hole filling as well as pair breaking plays an important role in the destruction of superconductivity in the latter compound. These results all illustrate the importance of the interplay between superconductivity and magnetism in the high-T_c cuprates.

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REFERENCES

[1] Z. Fisk, J.D. Thompson, E. Zirngiebl, J.L. Smith and S.-W. Cheong, Solid State Commun. 62 (1987) 743.

[2] M.B. Maple, J.M. Ferreira, R.R. Hake, B.W. Lee, J.J. Neumeier, C.L. Seaman, K.N. Yang and H. Zhou, J. Less-Comm. Met. 149 (1989) 405.

[3] J.L. Peng, P. Klavins, R.N. Shelton, H.B. Radousky, P.A. Hahn and L. Bernardez, Phys. Rev. B 40 (1989) 4517 and references therein.

[4] A. Kebede, C.-S. Jee, D. Nichols, M.V. Kuric, J.E. Crow, R.P. Guertin, T. Mihalisin, G.H. Meyer, I. Perez, R.E. Salomon and P. Schlottmann, J. Magn. Magn. Mater. 76-77 (1988) 619.

[5] J.E. Crow et al., these proceedings.

[6] For a review of NMR in $YBa_2Cu_3O_7$ see C. Pennington and C.P. Slichter, in Physical Properties of High Temperature Superconductors, ed. D.M. Ginzberg, vol. II (World Scientific, Teaneck, New Jersey, 1990). See also K. Asayama et al., these proceedings.

[7] M. Takigawa, A.P. Reyes, P.C. Hammel. J.D. Thompson, R.H. Heffner, Z. Fisk and K.C. Ott, Phys. Rev. B, to be published.

[8] H. Yasuoka, T. Imai and T. Shimizu, Proceedings of the IBM Japan Int. Symp. on Strong Correlation and Superconductivity, ed. H. Fukuyama, S. Maekawa and A. P. Malozemoff, p. 254 (Springer-Verlag, 1989).

[9] A.J. Millis, H. Monien and D. Pines, Phys. Rev. B, to be published.

[10] C.M. Varma, P.B. Littlewood, S. Schmitt-Rink, E. Abrahams and A.E. Ruckenstein, Phys. Rev. Lett. 63 (1989) 1996; P.B. Littlewood, unpublished.

[11] A.P. Reyes, D.E. MacLaughlin, M. Takigawa, P.C. Hammel, R.H. Heffner, J.D. Thompson, J.E. Crow, A. Kebede, T. Mihalisin and J. Schwegler, J. Appl. Phys. 67 (1990) 5032.

[12] A.P. Reyes, D.E. MacLaughlin, M. Takigawa, P.C. Hammel, R.H. Heffner, J.D. Thompson and J.E. Crow, unpublished.

[13] M. Takigawa, P.C. Hammel, R.H. Heffner, Z. Fisk, J.L. Smith and R.B. Schwartz, Phys. Rev. B 39 (1989) 300.

[14] S.E. Barrett, D.J. Durand, C.H. Pennington, C.P. Slichter, T. Friedmann, J.P. Rice and D.M. Ginsberg, Phys. Rev. B 41 (1990) 6283.

[15] T. Shimizu, H. Yasuoka, T. Tsuda, K. Koga and Y. Ueda, in Proceedings of the Tenth ISMAR Meeting, Morzine, France, 1989 (Bull. Mag. Res., to be published).

[16] R.E. Walstedt, W. Warren, R. Bell, R. Cava, G. Espinosa, L. Schneemeyer and J. Waszczak, Phys. Rev. B, to be published.

[17] H. Alloul, T. Ohno and P. Mendels, Phys. Rev. Lett. 63 (1989) 1700.

[18] F. Mila and T.M. Rice, Physica C 157 (1989) 561.

[19] See, for example, G.C. Carter, L.H. Bennett and D.J. Kahan, Metallic Shifts in NMR, Progr. Mat. Sci. 20 (1977) 1, and references therein.

[20] A. Kampf and J.R. Schrieffer, unpublished.

[21] T. Moriya, J. Phys. Soc. Jpn. 18 (1963) 516.

[22] P.C. Hammel, M. Takigawa, R.H. Heffner, Z. Fisk and K.C. Ott, Phys. Rev. Lett. 63 (1989) 1992.

[23] W.W. Warren, R.E. Walstedt, G.F. Brennert, J.J. Cava, R. Tyco, R.F. Bell and G. Dabbagh, Phys. Rev. Lett. 623 (1989) 1993.

[24] A.P. Reyes, D.E. MacLaughlin, M.Takigawa, P.C. Hammel, R.H. Heffner, J.D. Thompson, J.E. Crow, A. Kebede, T. Mihalisin and J. Schwegler, Phys. Rev. B, in press.

[25] D.W. Cooke, R.S. Kwok, R.L. Lichti, T. Radus, C. Boekema, W.K. Dawson, A. Kebede, J. Schwegler, J.E. Crow and T. Mihalisin, Phys. Rev. B vol41 (1990) 4801.

[26] C.-S. Jee, A. Kebede, D. Nichols, J.E. Crow, T. Mihalisin, G.H. Myer, I. Perez, R.E. Salomon and P. Schlottmann, Solid State Commun. 69 (1989) 379; A. Matsuda, K. Kinoshita, T. Ishii, H. Shibata, T. Watanabe and T. Yamada, Phys. Rev. B 38 (1988) 2910.

[27] H. Yasuoka, T. Shimizu, Y. Ueda and K. Kosuge, J. Phys. Soc. Japan 57 (1988) 2659; Y. Yamada, K. Ishida, Y. Kitaoka, K. Asayama, H. Takagi, H. Iwabuchi and S. Uchida, *ibid.* 57 (1988) 2663; P. Mendels and H. Alloul, Physica C (Amsterdam) 156 (1988) 355.

[28] T. Tsuda, T. shimizu, H. Yasuoka, K. Kishio and K. Kitazawa, J. Phys. Soc. Japan 57 (1988) 2908.

[29] For a review see J.T. Markert, Y. Dalichaouch, and M.B. Maple, in Physical Properties of High Temperature Superconductors, ed. D.M. Ginzberg, vol. 1, p. 265 (World Scientific, Teaneck, New Jersey, 1990).

[30] H. Suhl, Phys. Rev. 109 (1958) 606; T. Nakamura, Progr. Theor. Phys. 20 (1958) 542.

[31] M. E. López-Morales, D. Ríos-Jara, J. Tagüeña, R. Escudero, S. La Placa, A. Bezinge, V.Y. Lee, E.M. Engler and P.M. Grant, Phys. Rev. B 41 (1990) 6655.

[32] J.J. Neumeier et al., unpublished.

FIGURE CAPTIONS

Fig. 1. Temperature dependence of Knight shift components for Cu(2) (plane) sites in yttrium-rich $Y_{1-x}Pr_xBa_2Cu_3O_7$.

Fig. 2. Planar ($\mathbf{H}_{ext} \perp c$) Knight shift at Cu(2) sites vs. bulk susceptibility, with temperature an implicit parameter, in $Y_{1-x}Pr_xBa_2Cu_3O_7$. Solid lines: fits to the data for $T \leq 200$ K.

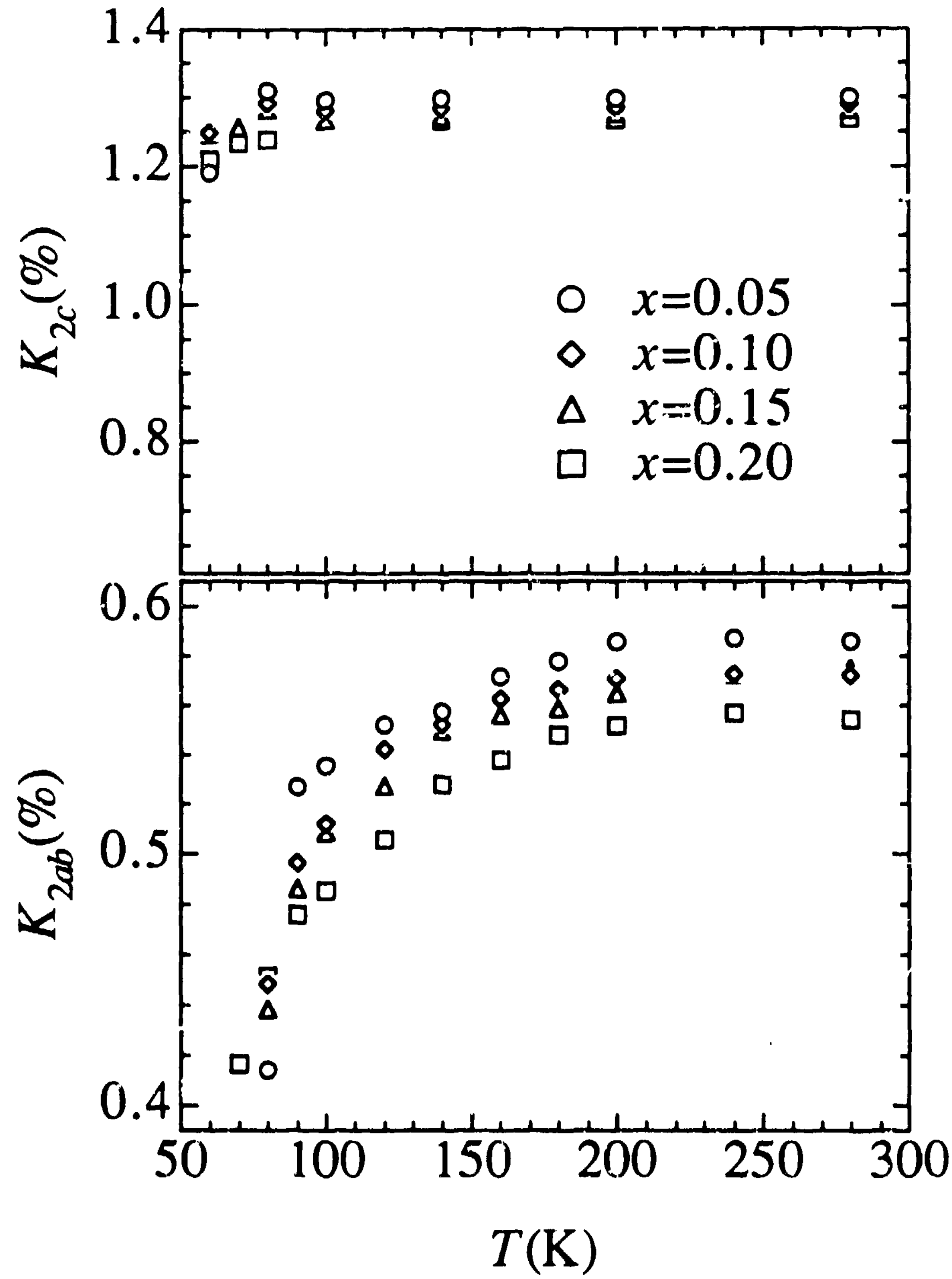
Fig. 3. Temperature dependence of the ^{63}Cu spin-lattice relaxation rate at Cu(2) sites in $Y_{1-x}Pr_xBa_2Cu_3O_7$.

Fig. 4. ^{63}Cu spin-lattice relaxation rate divided by temperature in the normal states of $Y_{1-x}Pr_xBa_2Cu_3O_7$ and oxygen-deficient $YBa_2Cu_3O_{7-y}$. Data for $x=0$, $y=0$ are taken from [13], and data for $x=0$, $y=0.37$ are taken from [7].

Fig. 5. Temperature and Pr concentration dependence of the correlation length ξ, in units of the lattice constant a, for $Y_{1-x}Pr_xBa_2Cu_3O_7$ as derived from the antiferromagnetic Fermi liquid theory of Millis, Monien, and Pines [9].

Fig. 6. High-temperature field-swept ^{63}Cu NMR spectra in $PrBa_2Cu_3O_7$. Spectrometer frequency 85 MHz. The peaks near 73.9 kOe and 74.5 kOe are due to Cu(1) and Cu(2) nuclei respectively [6]. The disappearance of the Cu(2) signal near 280 K indicates magnetic ordering of Cu(2) moments at this temperature.

Fig. 7. Zero-field NMR spectra of Cu(2) nuclei in $PrBa_2Cu_3O_7$ at 1.4 K. The dotted curves correspond to Lorentzian-broadened quadrupole-split ^{63}Cu and ^{65}Cu lines. The solid curve gives the resultant spectrum.



1.4
1.2
1.0
0.8
K_{2c}(%)
x=0.05
x=0.10
x=0.15
x=0.20
0.6
0.5
0.4
K_{2ab}(%)
50
100
150
200
250
300
T(K)

Fig. 1

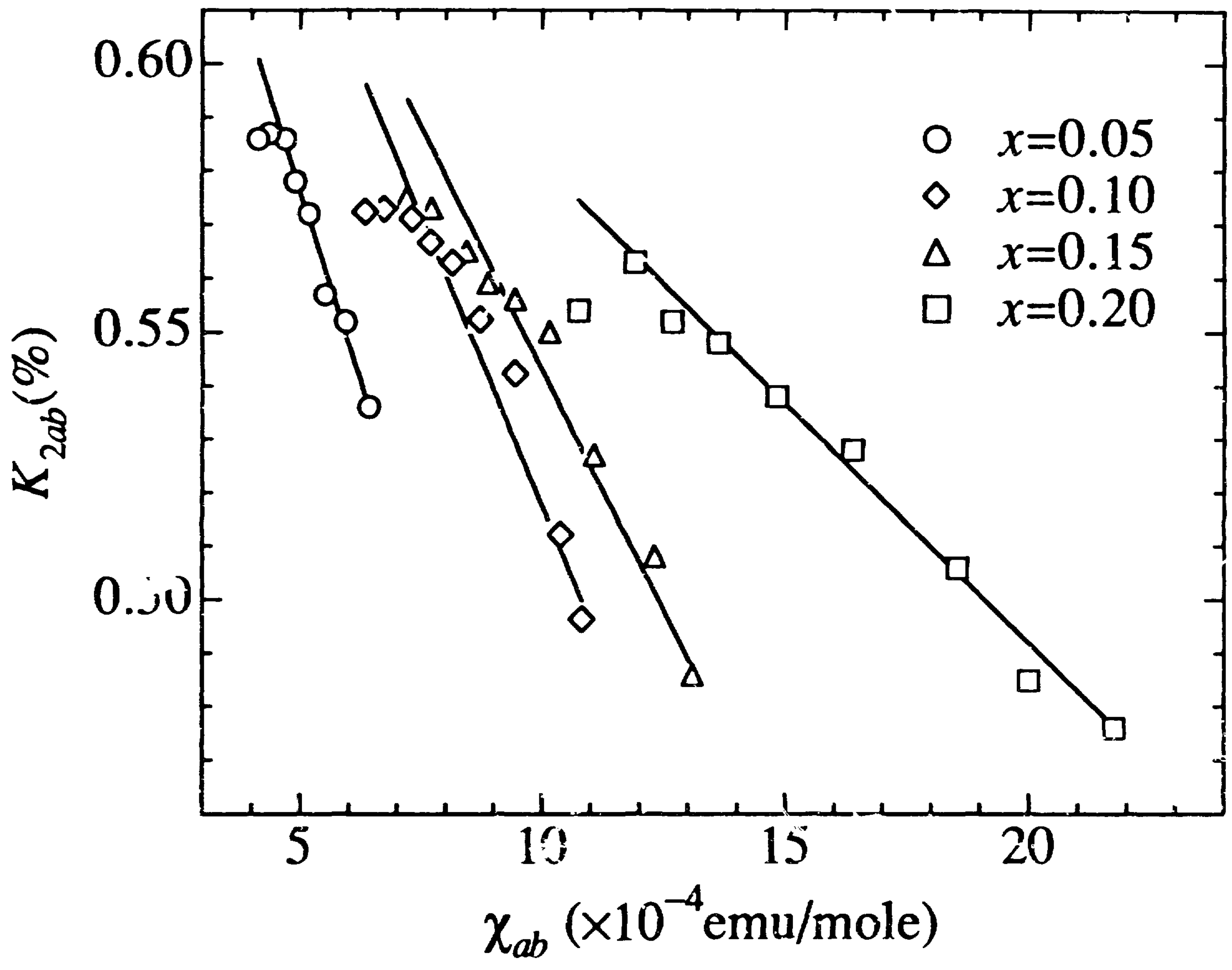

0.60
0.55
0.50
K_{2ab}(%)
5
10
15
20
χ_{ab} (×10^{-4}emu/mole)
x=0.05
x=0.10
x=0.15
x=0.20

Fig. 2

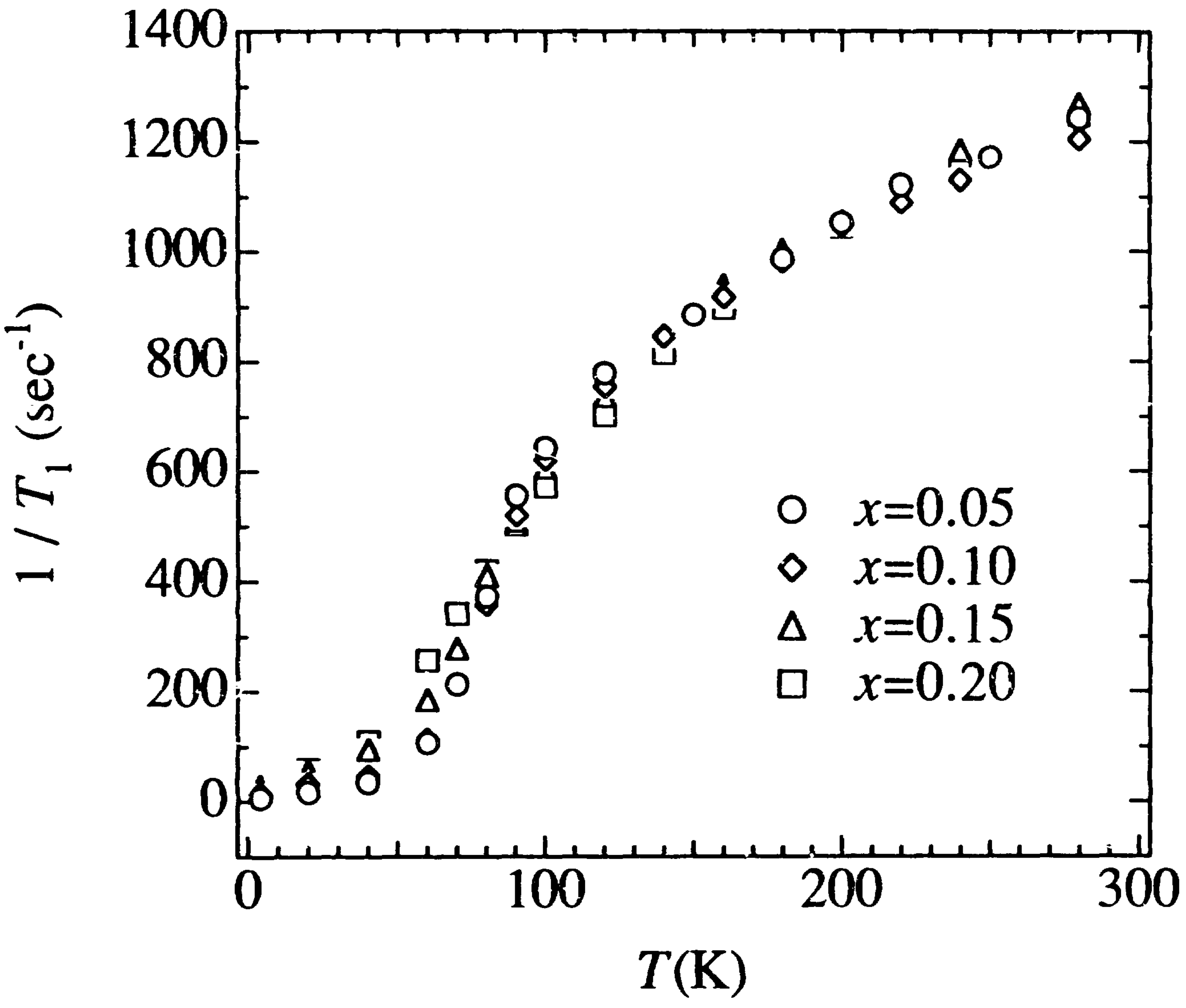

1400
1200
1000
800
600
400
200
0
0
100
200
300
1 / T_1 (sec^{-1})
T(K)
x=0.05
x=0.10
x=0.15
x=0.20

Fig. 3

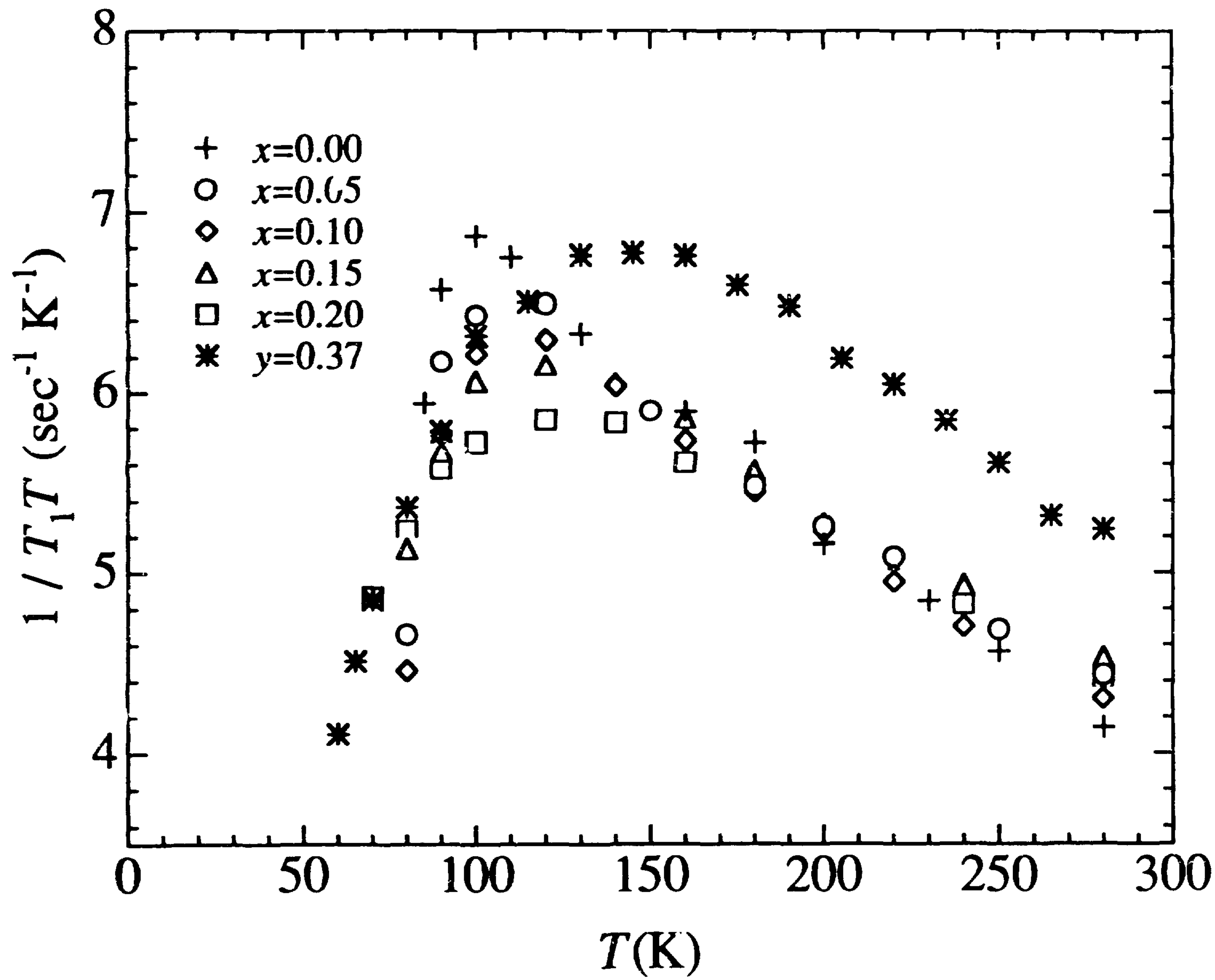

x=0.00
x=0.05
x=0.10
x=0.15
x=0.20
y=0.37
1 / T1T (sec-1 K-1)
T(K)
0
50
100
150
200
250
300
4
5
6
7
8

Fig. 4

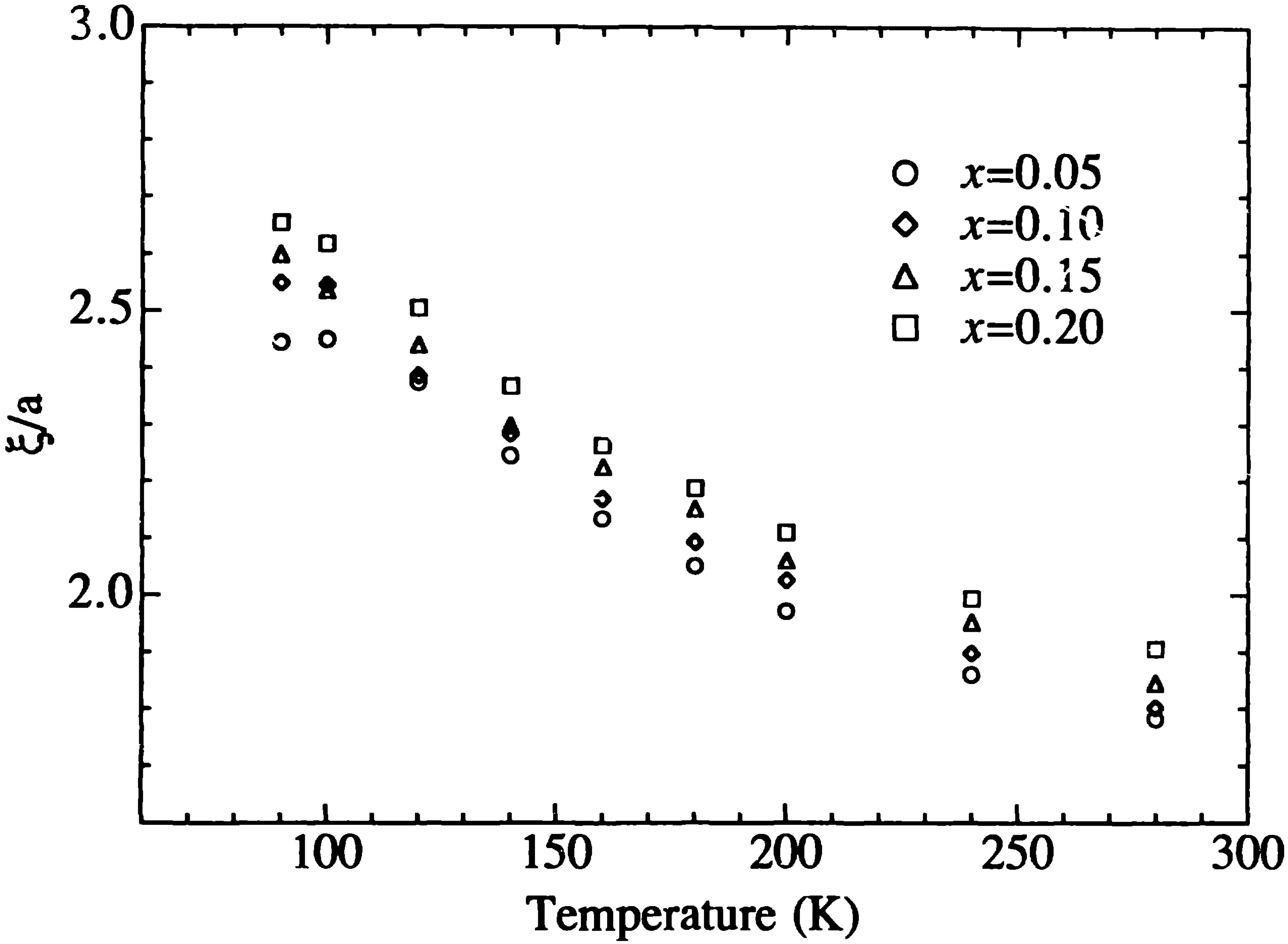

3.0
2.5
2.0
ξ/a
100
150
200
250
300
Temperature (K)
x=0.05
x=0.10
x=0.15
x=0.20

Fig. 5

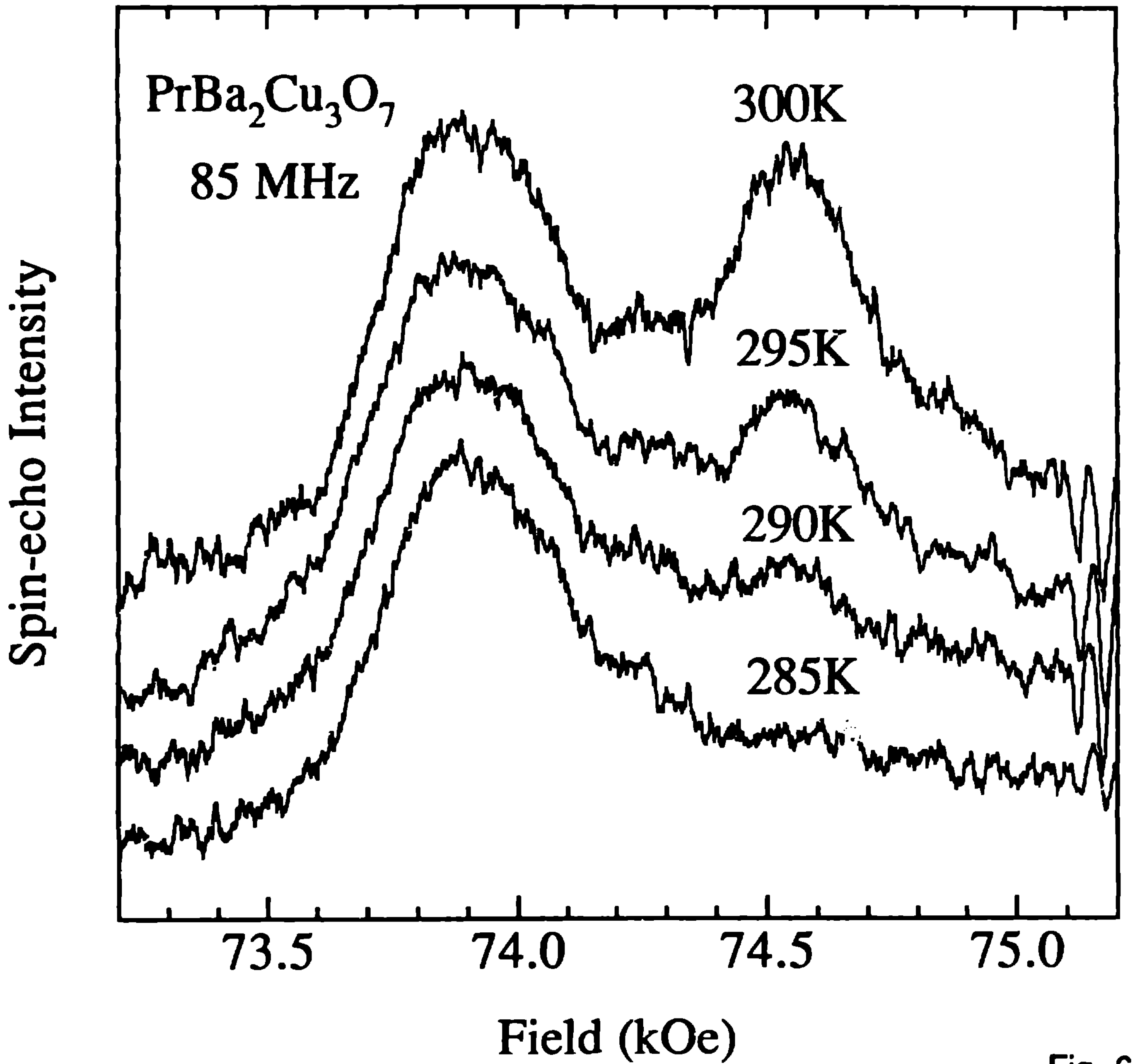

PrBa$_2$Cu$_3$O$_7$
85 MHz
300K
295K
290K
285K
Spin-echo Intensity
73.5
74.0
74.5
75.0
Field (kOe)

Fig. 6

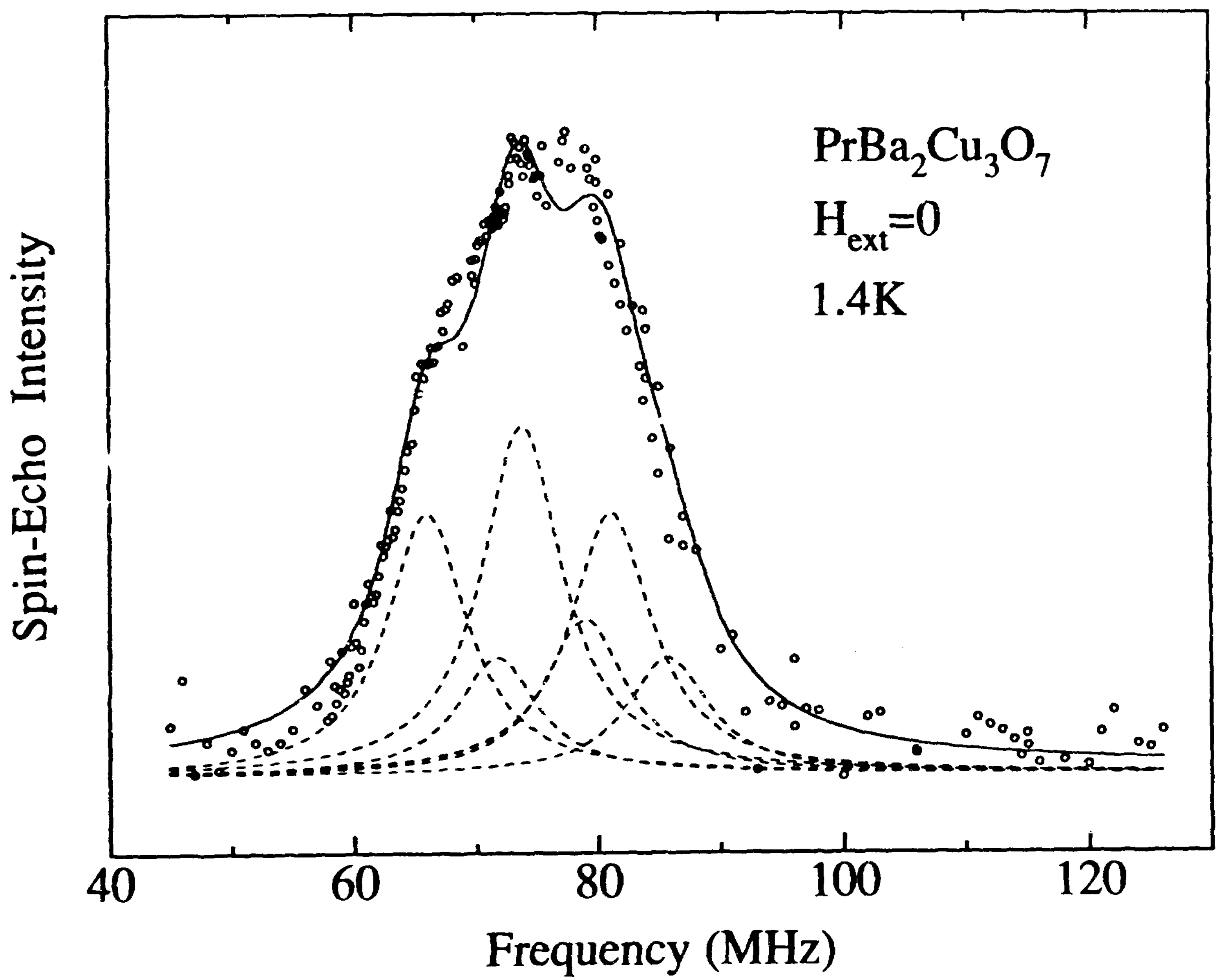

PrBa2Cu3O7
Hext=0
1.4K
Spin-Echo Intensity
40
60
80
100
120
Frequency (MHz)

Fig. 7