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Magnetic ordering in $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ as observed by muon-spin relaxation

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Zero-field positive muon-spin-relaxation (μ^+SR) measurements on $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ ($x=1.0$, 0.8, 0.6, 0.58, and 0.54) show clear evidence for antiferromagnetic ordering of the Cu moments within the Cu-O planes. Néel temperatures are approximately 285, 220, 35, 30, and 20 K for $x=1.0$, 0.8, 0.6, 0.58, and 0.54, respectively. For $x=0.50$ we observe a fast-relaxing component and a long-time tail of the muon polarization, reminiscent of spin-glass behavior. Superconductivity and spin-glass-like magnetism appear to coexist for x near 0.50. For $x=1.0$ the fully developed local magnetic field is ~ 16 mT, but decreases to ~ 12 mT at $T=17$ K, presumably due to the onset of additional ordering. The Néel temperature for oxygen-reduced $PrBa_2Cu_3O_6$ is approximately 325 K.

In spite of voluminous data accumulated during the last three years on high-temperature superconducting oxides, the nature of the superconducting ground state and the pairing mechanism remain unclear. Models based on both conventional phonon-mediated pairing[1] and nonconventional mechanisms[2-4] have been proposed to account for the high transition temperatures T_c. The discovery of antiferromagnetism with strong superexchange interactions between the Cu^{2+} ions in insulating La_2CuO_4 (Ref. 5) and in oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ (Y-Ba-Cu-O) (Refs. 6 and 7) has focused attention on magnetic or spin-fluctuation-mediated BCS-like models[3] and on new "magnetic pairing" models.[4] Experimental information on the interplay between superconductivity and magnetism may, therefore, provide clues pertaining to formation of the superconducting ground state.

It is well known that rare-earth R substitution for Y in $RBa_2Cu_3O_7$ does not affect superconductivity except for $R=$Ce, Tb, Pm, and Pr. Ce- and Tb-based compounds yield multiphase samples, and Pm is radioactively unstable,[8] thus rendering these compounds difficult to study. However $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ exhibits superconductivity and magnetism for certain values of x, retains the orthorhombic structure, and is oxygen stable for all values of x.[9] These properties make this an attractive system for investigating the interplay between superconductivity and magnetism in high-temperature superconductors (HTS).

In this work we report zero-field muon-spin-relaxation (ZF-μSR) observations of static magnetic ordering in $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ for $x \geq 0.54$. For $x=1.0$, $T_{N1} \cong 285$ K. A lower magnetic ordering transition T_{N2} is also observed, which is consistent with the magnetic phase determined by specific-heat and magnetic-susceptibility measurements.[9] Results of these latter measurements, in addition to neutron-diffraction results,[10] suggest that T_{N2} is associated with the magnetic ordering of Pr^{4+} ($J=\frac{5}{2}$) ions on the Y sublattices. The μSR results, however, do not rule out the possibility of magnetic ordering of Cu ions within the Cu-O *chains*. The upper magnetic ordering temperature T_{N1} reported here is presumably associated with Cu^{2+} ordering of the Cu ions within the Cu-O *planes*, which is consistent with recent Mössbauer results.[11] This study is unique in that the interplay between magnetism and superconductivity in the archetypal HTS, Y-Ba-Cu-O, can be examined without complications associated with structural changes or variable oxygen content.

Polycrystalline samples of $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ ($0 \leq x \leq 1.0$) were prepared using conventional solid-state reaction techniques.[9] No evidence for phase separation was found.[8] X-ray- and neutron-diffraction studies indicated that the samples crystallized in an orthorhombic structure with less than 2% impurity phases for all values of x. The cell volume V_c vs x followed Vegard's law for $0 \leq x \leq 1$. The Pr concentration dependence of V_c and the effective paramagnetic moment μ_{eff} suggest that the Pr valence is reasonably independent of x. A graph of μ_{eff} vs x indicates that the Pr ions are close to 4^+.

The μSR experiments were done at the stopped muon channel of the Los Alamos Clinton P. Anderson Meson Physics Facility using standard zero-field (ZF) techniques.[12] Briefly, spin-polarized positive muons are implanted into a sample and the decay positrons are detected by counters located in the forward (direction of initial muon momentum) and backward directions. In a zero external field (in the experiment the field was nulled to ± 2 μT by trim coils) the muon experiences only the internal magnetic field. Consequently, in an antiferromagnet one should observe one (or more) discrete frequencies determined by the magnitude of the local magnetic field at the muon site, i.e., $\omega_\mu = \gamma_\mu H_{loc}$ ($\gamma_\mu/2\pi = 1.355$ MhzT^{-1}).

Representative ZF-μSR spectra for $PrBa_2Cu_3O_7$ taken at 300 and 180 K are shown in Figs. 1(a) and 1(b). At 300 K the internal magnetic field is due to randomly oriented, quasistatic Cu nuclear moments, which depolarize the muon according to $G(t) = \exp(-\frac{1}{2}\sigma^2 t^2)$, where σ is a Gaussian depolarization rate related to the second moment of the local-field distribution at the muon site. The solid line of Fig. 1(a) is a Gaussian fit to the data with $\sigma = 0.36\ \mu s^{-1}$. In contrast, the spectrum taken at 180 K shows oscillatory behavior with a well-defined muon frequency at 1.85 MHz. This is clear evidence for the existence of an ordered, local magnetic field. Similar results were obtained for $x = 0.54$, 0.58, 0.6, and 0.8. Muon precessional frequencies for $x = 1.0$, 0.8, and 0.6 are shown in Fig. 2; for clarity the $x = 0.58$ and 0.54 data are not plotted. The Néel temperatures are approximately 285, 220, 35, 30, and 20 K for $x = 1.0$, 0.8, 0.6, 0.58, and 0.54, respectively.

Neutron-scattering measurements on oxygen-deficient $YBa_2Cu_3O_{6+\Delta}$ (Ref. 13) and $NdBa_2Cu_3O_{6+\Delta}$ (Ref. 14) have established that for $\Delta \leq 0.4$ antiferromagnetic ordering of the Cu atoms within the CuO_2 *planes* occurs. The magnetic structure is composed of strong nearest-neighbor antiferromagnetic couplings of the Cu spins within the Cu-O_2 layers with antiferromagnetic alignment of the nearest-neighbor spins in adjacent layers. The magnetic

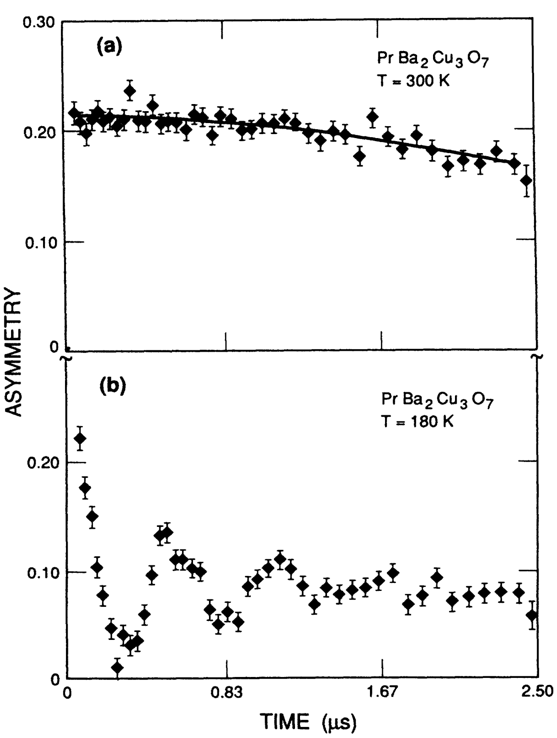

FIG. 1. ZF-μSR spectra for $PrBa_2Cu_3O_7$ taken at (a) 300 K and (b) 180 K. The oscillatory pattern in (b) is clear evidence for magnetic ordering. No ordering is evident in (a).

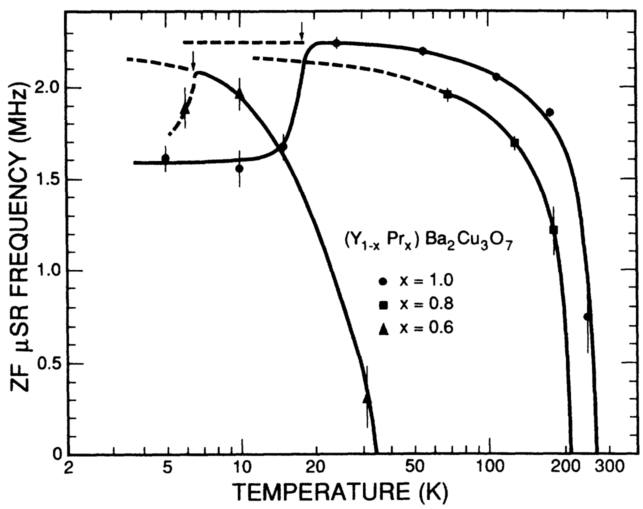

FIG. 2. Zero-field μSR frequencies for $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ ($x = 1.0$, 0.8, and 0.6) as a function of temperature. Néel temperatures are $T_{N1} \sim 285$, 220, and 35 K, respectively. The reduction in frequency near 20 K (for $x = 1.0$) and 7 K (for $x = 0.6$) is due to additional magnetic ordering.

moments are constrained to lie in the plane. Evidence for antiferromagnetic ordering of the Cu moments within the oxygen-deficient *chains* of these systems has also been given.[7,14] Based on these results we conclude that the magnetic ordering in $(Pr_xY_{1-x})Ba_2Cu_3O_7$ as observed by ZF-μSR is associated with the Cu^{2+} ordering of the Cu ions within the Cu-O planes, which is consistent with similar conclusions that have been derived from Mössbauer studies.[11]

A second magnetic ordering transition occurs for $x = 1.0$ at $T_{N2} \approx 20$ K, as shown in Fig. 2. This is consistent with the transition observed by magnetic susceptibility, specific heat, and neutron scattering, and has been associated with the magnetic ordering of Pr^{4+} ($J = \frac{5}{2}$) ions on the Y sublattice.[9,10] The available μSR data ($x = 1.0$ and 0.6) indeed suggest that additional magnetic ordering is occurring at these temperatures (~ 20 and 7 K) with the result that the magnitude of H_{loc} is reduced from ~ 16 to ~ 12 mT. This ordering may be due to Pr moments as suggested above; however, our data do not preclude the possibility that it could also be associated with ordering of Cu moments within the chains, and note that several experimental results[9] are inconsistent with the notion of conventional antiferromagnetic Pr-moment ordering. The 16-mT field associated with the Cu-plane ordering in this system is comparable to the 20- to 30-mT field observed in $YBa_2Cu_3O_6$ (Ref. 6).

The experimentally determined phase diagram for $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ is shown in Fig. 3. T_{N1} is derived from zero-field μSR data and is attributed to antiferromagnetic ordering of Cu within the Cu-O planes. Notice that for $x < 0.54$ (intersection of the T_{N1} and T_c vs x curves) we show a dashed-dotted line indicating that spin-glass-like magnetism (as discussed below) rather than antiferromagnetism is observed in this region. The T_c vs x curve is based on susceptibility and resistivity measurements, and T_{N2} is deduced from μSR, susceptibil-

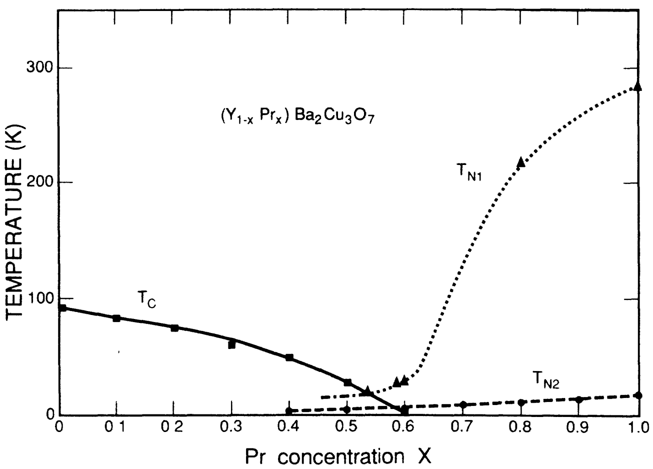

FIG. 3. Phase diagram for $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$. T_{N1} corresponds to antiferromagnetic ordering of Cu moments within the Cu-O planes as determined by ZF-μSR. Spin-glass-like magnetism occurs for $x<0.54$ (dashed-dotted line).

ity, specific-heat, and neutron-scattering measurements. μSR data taken in a 100-mT transverse field confirm the T_c vs x curve.

The region of the phase diagram corresponding to $x \sim 0.50$ is of special interest because it represents a crossover of the ground state from magnetism to superconductivity. In Fig. 4 we show the muon depolarization for $x=0.60$, 0.58, and 0.50 at a fixed temperature of 5 K. A well-defined frequency exists for $x=0.60$ and 0.58, but not for $x=0.50$. For the latter concentration there is a very fast relaxing component of the muon polarization in addition to a long-time tail. We attempted to fit the data of Fig. 4(c) with various known muon relaxation functions. The best fit [shown as the solid line of Fig. 4(c)] was obtained with a spin-glass function, which assumed slow fluctuations of the time-varying local magnetic field,[15]

$$G_z(t)=\tfrac{2}{3}(1-a_0t)\exp(-a_0t)+\tfrac{1}{3}\exp[-(2t/3\tau)]\,, \quad (1)$$

where a_0 is the width of the muon precession frequency distribution and τ is the correlation time. From the fitted data we obtained a fluctuation rate of $10^5\ s^{-1}$. However, the goodness of this fit alone does not prove that the underlying magnetism is that of a spin glass, although it would not be unreasonable to assume that the crossover from antiferromagnetism to superconductivity produced a complex magnetic state that was spin-glass like. This is especially true near $T=5$ K where the Pr-moment ordering and/or Cu-chain ordering may also be contributing to the formation of this complex ground state, although the extrapolated Néel temperature for $x=0.50$ is only 3.4 K (Ref. 1). Nevertheless, this region of the phase diagram presents a rich arena for investigating the interplay between magnetism and superconductivity in oxide superconductors, especially in $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ because it retains the orthorhombic structure for $0 \le x \le 1$.

Based on our μSR data we conclude that no clear signature of antiferromagnetism exists in $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ for a concentration of $x<0.54$. Thus the conclusion that

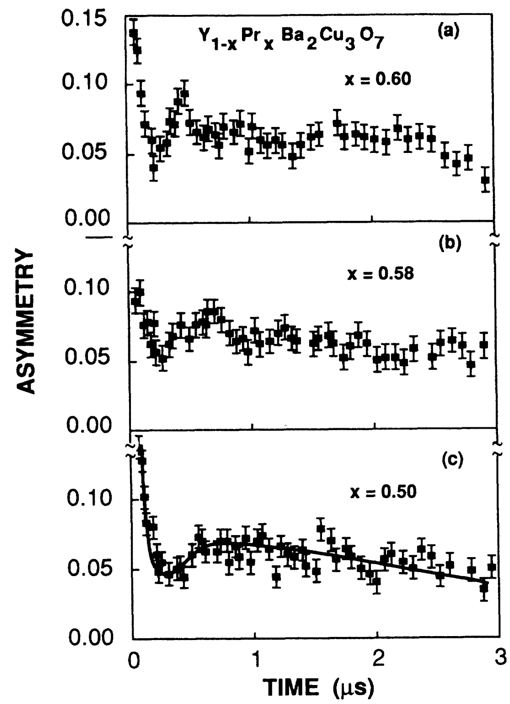

FIG. 4. Zero-field μSR spectra for $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ taken at $T=5$ K. The concentrations are (a) $x=0.60$, (b) $x=0.58$, and (c) $x=0.50$.

antiferromagnetism and superconductivity do not coexist in this system, as suggested by Felner *et al.*,[11] is in agreement with our observations. On the other hand, we suggest that spin-glass-like magnetism and superconductivity do indeed coexist.

Zero-field μSR data taken on $PrBa_2Cu_3O_6$ show that magnetic ordering occurs in this system at a temperature higher than room temperature, which is the highest operating point of our spectrometer. However, by extrapolating the values taken at and below room temperature we estimate the Néel temperature to be approximately 325 K. Interestingly, two distinct frequencies are observed in $PrBa_2Cu_3O_6$, which we attribute to the existence of two magnetically inequivalent muon stopping sites. For $T=250$ and 15 K the measured muon precessional frequencies are $\nu_1=1.5$ MHz and $\nu_2=3.5$ MHz; $\nu_1=2.2$ MHz and $\nu_2=4.7$ MHz, respectively.

In summary, zero-field μSR experiments have been conducted on $(Y_{1-x}Pr_x)Ba_2Cu_3O_7$ as a function of concentration and temperature. The results suggest that antiferromagnetic ordering of the Cu moments within the Cu-O planes occurs for $x=1.0$, 0.80, 0.60, 0.58, and 0.54 with Néel temperatures of 285, 220, 35, 30, and 20 K, respectively. For $x=1$ the magnitude of the fully developed local magnetic field at the muon site is ~ 16 mT, but is reduced to ~ 12 mT near 20 K due to the onset of additional magnetic ordering, which is probably associated with Pr-moment ordering and/or Cu ordering within the Cu-O chains. Additionally, coexistent spin-glass-like magnetism and superconductivity occur for $x=0.50$. Zero-field μSR data taken on $PrBa_2Cu_3O_6$ show that it is also antiferromagnetic with an estimated Néel temperature of 325 K.

[1]W. Weber, Phys. Rev. Lett. **58**, 1371 (1987); B. Ashauer, W. Lee, and J. Rammer, Z. Phys. B **67**, 147 (1987).

[2]C. M. Varma, S. Schmitt-Rink, and E. Abrahams, Solid State Commun. **62**, 681 (1987).

[3]V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987); J. R. Schrieffer, X-G. Wen, and S-C. Zhang, *ibid.* **60**, 944 (1988).

[4]P. W. Anderson, G. Baskaran, Z. Zou, and T. Hsu, Phys. Rev. Lett. **58**, 2790 (1987).

[5]D. Vaknin *et al.*, Phys. Rev. Lett. **58**, 2802 (1987).

[6]N. Nishida *et al.*, Jpn. J. Appl. Phys. Part 2 **26**, L1856 (1987).

[7]J. W. Lynn and W-H. Li, J. Appl. Phys. **64**, 6055 (1988); J. M. Tranquada, *ibid.* **64**, 6071 (1988).

[8]J. L. Peng, P. Klavins, R. N. Shelton, H. B. Radousk, P. A. Hahn, and L. Bernardez, Phys. Rev. B **40**, 4517 (1989).

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

[10]W-H. Li *et al.*, Phys. Rev. B **40**, 5300 (1989).

[11]I. Felner, U. Yaron, I. Nowik, E. R. Bauminger, Y. Wolfus, E. R. Yacoby, G. Hilscher, and N. Pillmayr (unpublished).

[12]A. Schenck, *Muon Spin Rotation Spectroscopy* (Adam Hilger, Bristol, 1986).

[13]J. M. Tranquada *et al.*, Phys. Rev. Lett. **60**, 156 (1988); W-H. Li *et al.*, Phys. Rev. B **37**, 9844 (1988); J. M. Tranquada *et al.*, *ibid.* **38**, 2477 (1988).

[14]J. W. Lynn *et al.*, Phys. Rev. Lett. **60**, 2781 (1988); A. H. Moudden *et al.*, Phys. Rev. B **38**, 8720 (1988); W-H. Li *et al.* (unpublished).

[15]R. H. Heffner *et al.*, J. Appl. Phys. **53**, 2174 (1982).