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ANTIFERROMAGNETIC ORDER IN $PrBa_2Cu_3O_x$ ($x \approx 6, 7$)

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Zero and weak transverse field μ^+SR measurements on $PrBa_2Cu_3O_x$ samples with $x \approx 6$ and $x \approx 7$ show ordered magnetism in both oxygen concentration limits. As expected for equivalent doping (nominally $PrBa_2Cu_3O_x \sim YBa_2Cu_3O_{x-0.5}$), neither sample is superconducting. Two muon signals are observed in the $x \approx 6$ sample, as in $YBa_2Cu_3O_6$, but only one (the weaker) has the same local magnetic field as in $YBa_2Cu_3O_6$. In the $x \approx 7$ sample, only one site is observed; its local field is reduced with respect to that of the primary site in $YBa_2Cu_3O_6$ by a factor roughly consistent with the carrier-density dependence of the Cu ion moment in antiferromagnetic $YBa_2Cu_3O_x$.

The (Pr,Y) position in the $(RE)Ba_2Cu_3O_x$ perovskite structure is adjacent to planes of CuO_2 and distant from the CuO chains. Analysis of T_c as measured by resistivity in series of $(Y_{1-x-y}Ca_y)Pr_xBa_2Cu_3O_7$ ([1], [2] and references therein) indicate that the Pr has a valence of nearly +4 (compared to +3 for Y). There is significant hybridization between the Pr 4f electronic levels and the surrounding 2p orbitals of the "plane" oxygens – i.e., each Pr contributes an electron to the CuO_2 planes but not to the more distant chains.

There are two reasons why superconductivity is not seen in $PrBa_2Cu_3O_x$. First of all, since oxygen has a valence of −2, the substitution of Pr for Y nominally reduces the hole carrier density by the same amount as does a reduction of the oxygen content by $\delta x = -0.5$; thus, since $YBa_2Cu_3O_x$ is superconducting only for $x \gtrsim 6.5$, one would naively expect that $x \gtrsim 7$ would be needed to restore sufficient carrier concentration for superconductivity in $PrBa_2Cu_3O_x$. In addition, the hybridization between Pr and O electrons in the planes could produce a significant exchange interaction between the Pr magnetic moments and the spins of the carrier holes in the CuO_2 planes, resulting in a reduction of T_c – which is in fact observed [1] in $(Y_{1-x-y}Ca_y)Pr_xBa_2Cu_3O_7$.

Therefore, the interesting question arises: In zero field μ^+SR experiments, is antiferromagnetic $PrBa_2Cu_3O_x$ just like $YBa_2Cu_3O_{x-0.5}$ or not?

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A sample of $PrBa_2Cu_3O_x$ with $x \approx 7$ shows magnetic ordering below about 275 K; the order is at least locally antiferromagnetic – i.e., we see a long-lived oscillation in ZF-μ^+SR much as in $YBa_2Cu_3O_6$. The antiferromagnetism is presumed to be from ordering of the copper moments on the CuO_2 planes. (We rule out ferromagnetic order only because it would presumably have been seen easily in susceptibility studies.) The amplitude of the oscillating signal is $\approx 29\%$ of the total signal. Below 17 K the relaxation rate increases and the local field decreases dramatically due to ordering of the Pr moments ($J_{Pr} = 5/2$).

In a study of the muon precession frequency in antiferromagnetic $YBa_2Cu_3O_x$ as a function of x below 90 mK, Kiefl et al. [3] found that the local field at the primary "4 MHz site" (site 1) fell gradually from ≈ 300 G for $6.0 < x < 6.25$ to 20 G for $x = 6.44$ and then plunged to 0 G by $x = 6.5$; the decrease in the average field is due either to random dilution or reduction of the copper moments. The local field's rms deviation (seen as a relaxation rate in the muon spin polarization) increased sharply and the magnetic ordering temperature T_N dropped abruptly just below the insulating-superconducting transition. The local field (2.27 MHz $\Rightarrow$ 170 G) observed at $T \sim T_N/2$ in our $PrBa_2Cu_3O_7$ sample (which should have a nominal hole carrier concentration similar to that of $YBa_2Cu_3O_{\sim 6.5}$) corresponds roughly to the field at site 1 in $YBa_2Cu_3O_{6.44}$ for $T \sim T_N/2$, although T_N is much lower in the latter (see below). This suggests that the observed muon site in $PrBa_2Cu_3O_7$ may be the same as site 1 in $YBa_2Cu_3O_{6.0-6.5}$, although this is by no means certain.

The enticing thesis that the muon site is the same may or may not contradict the observation that the relaxation rate in $PrBa_2Cu_3O_7$ is much smaller than that seen in $YBa_2Cu_3O_{6.44}$, even though the different temperatures at which the data were taken (50 K vs. 20 mK), would be expected to produce the opposite effect. The high Néel temperature of $PrBa_2Cu_3O_7$ is also remarkably different from those of $YBa_2Cu_3O_x$ samples with $6.0 \leq x \leq 6.5$, for which T_N drops rapidly with increasing x to ~ 10 K at $x \sim 6.4$ [4]. This suggests that the proposed exchange interaction between the Pr magnetic moments and the spins of the carrier holes in the CuO_2 planes (which causes a reduction of T_c) also has the effect of preserving the ordering of plane Cu moments over much larger temperature ranges.

An alternate explanation is, of course, that the primary muon site in $PrBa_2Cu_3O_7$ is different from that in $YBa_2Cu_3O_6$ and that the similarity of the local field at the $PrBa_2Cu_3O_7$ site to that at the $YBa_2Cu_3O_{6.44}$ site is merely a coincidence.

In the second sample of $PrBa_2Cu_3O_x$ with $x \approx 6$, T_N is well above room temperature, as expected. Muon diffusion spoils our measurements of local fields above about 270 K, so the data shown in fig. 1 extend only to that temperature.

Analysis of the ZF data for $PrBa_2Cu_3O_6$ was much more difficult than for $PrBa_2Cu_3O_7$ due in part to the presence of two oscillatory signals, one of which was quite weak. The weaker signal is somewhat perversely labelled "site 1" in fig. 1 because the temperature dependence of its frequency almost perfectly

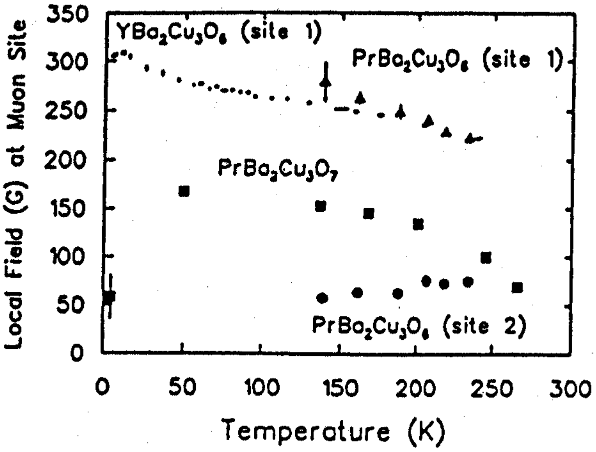

Fig. 1. Local magnetic field at μ^+ sites in $PrBa_2Cu_3O_7$ (squares) and $PrBa_2Cu_3O_6$ (site 1: triangles; site 2: circles) determined by ZF-μ^+SR as a function of temperature. Also shown (without symbols) are data for site 1 in $YBa_2Cu_3O_6$. Not shown is the site 2 field in $YBa_2Cu_3O_6$, which is ≈ 1300 G.

matches that of the site 1 ("4 MHz") signal in $YBa_2Cu_3O_6$ in the temperature range where it is observable. The amplitude of this signal changes from $\approx 1.2\%$ of the total signal at 284 K to 3.7% at 161 K and appears to keep the same amplitude below 135 K but with very much higher relaxation rates (too fast to allow meaningful frequency determinations).

In antiferromagnetic $YBa_2Cu_3O_x$ for $6.0 \leq x \leq 6.24$ there is also a second muon site (site 2 or "18 MHz site") [4], at which the local field (18 MHz $\Rightarrow$ 1300 G at $T \approx 20$ K for $x = 6.0$) is approximately parallel to the $\hat{c}$ axis; in a randomly oriented $YBa_2Cu_3O_x$ powder, the oscillatory signal from site 2 has roughly 1/4 the amplitude of the site 1 signal for $6.0 \lesssim x \lesssim 6.2$ and becomes unmeasurable for $x \gtrsim 6.24$. However, no high-field (~ 18 MHz) signal is observed in $PrBa_2Cu_3O_x$ for any x; instead, we see a *lower* local field (1 MHz $\Rightarrow$ 70 G) at site 2 in $PrBa_2Cu_3O_6$. Moreover, the signal from this site is *stronger* than that from the "4 MHz" site (site 1): the site 2 signal amplitude gradually increases with T from nearly zero below 125 K to 13.8% of the total signal at 161 K to a maximum of about 44% at 284 K. Since the site 1 signal amplitude has the opposite T-dependence (see above) this suggests that the "4 MHz" site is being depopulated in favour of the "1 MHz" site as the temperature increases.

Another possible interpretation of this behaviour is that there is a very pronounced inhomogeneity of the oxygen distribution in $PrBa_2Cu_3O_6$, 10% of the sample having $x = 6.5$ [resembling $YBa_2Cu_3O_{6.0}$] and the rest having $x = 5.95$ [resembling $YBa_2Cu_3O_{5.45}$]; this is regarded as unlikely. Yet another possibility is that 10% of the Pr ions have valence +3 (like Y) and the remaining 90% have +4; the muon site preference could be influenced by the effective charges of its nearest Pr neighbours, especially if the extra electron due to the difference in valence were localized on the oxygen ions in the CuO_2 planes. This would explain the odd temperature dependence in terms of a decrease of the Pr^{+3} concentration with increasing temperature. Without data involving more samples of $PrBa_2Cu_3O_{6.0-6.5}$ as well as $YBa_2Cu_3O_{x<6}$, it is difficult to choose between these models.

In this sample the relaxation rates of the antiferromagnetic signals increase dramatically below about 150 K, so that no reliable frequency information can be extracted from the relaxation data below about 135 K. This effect may be due to the Pr moments starting to order; if so, it is curious that the Pr moments destroy the oscillatory signal over a much larger temperature range in $PrBa_2Cu_3O_6$ than in $PrBa_2Cu_3O_7$.

The $PrBa_2Cu_3O_6$ sample has a hole carrier concentration similar to that of $YBa_2Cu_3O_{\sim 5.5}$, if the valence arguments are still valid for $x < 6.0$ in $YBa_2Cu_3O_x$. We have observed spin glass behavior and a high ordering temperature in $YBa_2Cu_3O_{5.98}$, which implies that long range order of the Cu moments is frustrated [3]. In contrast, $PrBa_2Cu_3O_6$ clearly shows two antiferromagnetic signals, the stronger of which ("site 2") is peculiar in that its frequency *decreases* with decreasing temperature (see Fig. 1).

In conclusion, we have measured the local magnetic fields at several μ^+ sites in $PrBa_2Cu_3O_{6\ \mathrm{and}\ 7}$ and have found evidence that the μ^+ site preference and/or the fields at the different sites depend on both temperature and oxygen deficiency. The local field observed in $PrBa_2Cu_3O_7$ is consistent with that at the primary μ^+ site in $YBa_2Cu_3O_{6.44}$ if we assume that a Pr valence of nearly +4 reduces the effective Cu moments by the same amount as an oxygen deficiency of −0.56. Two sites are observed in $PrBa_2Cu_3O_6$, one of which has the same local field as the primary site in $YBa_2Cu_3O_6$; the other (which dominates) is quite different from the second site in $YBa_2Cu_3O_6$ and has a peculiar temperature dependence. Ultimately we would like to come to an understanding of the relationships between the muon sites, the valence(s) of Pr ions, the ordering of local spins and all the other effects of substituting Pr for Y in $(Y,Pr)Ba_2Cu_3O_x$.

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