Antiferromagnetism and Superconductivity in Oxygen-Deficient $YBa_2Cu_3O_x$

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Positive-muon spin-rotation and -relaxation measurements of the oxygen-deficient perovskite $YBa_2Cu_3O_x$ have revealed local antiferromagnetic order for $6.0 \lesssim x \lesssim 6.4$ with a Néel temperature T_N that *decreases* rapidly with increasing oxygen content x. For slowly annealed samples with $6.35 \lesssim x \lesssim 6.5$ the superconducting transition temperature T_c increases smoothly with x from 25 K at $x = 6.348$ to 60 K at $x = 6.507$. Two such samples with $x = 6.348$ and $x = 6.400$ appear to "switch" from superconductivity to antiferromagnetic order at lower temperatures.

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The recent discovery[1] of superconductivity at the anomalously high temperature of $T_c \approx 90$ K in the perovskite $YBa_2Cu_3O_x$ $(6.9 \lesssim x \lesssim 7.0)$ has stimulated theorists to explore new mechanisms for superconductivity. Several such theories[2] involve frustrated antiferromagnetic couplings between copper and/or oxygen ions in the CuO_2 planes that these materials have in common with the slightly lower-T_c perovskite $La_{1.85}Sr_{0.15}CuO_{4-\delta}$. It was therefore interesting to learn, both from neutron diffraction[3] and from positive-muon spin-rotation and -relaxation (μ^+SR) and susceptibility measurements,[4] that the (insulating) parent compound $La_2CuO_{4-\delta}$ exhibits antiferromagnetic (AFM) order below a Néel temperature T_N that depends critically upon the oxygen deficiency δ (T_N increases with increasing δ), lanthanum stoichiometry, and/or doping of Sr for La. For instance, we have found that replacing La_2 by $La_{1.98}Sr_{0.02}$ reduces T_N from around 250 K to less than 15 K. Similar AFM ordering was discovered in the oxygen-deficient YBa_2Cu_3-O_x materials (insulating for $x \lesssim 6.3$) with use of muon spin rotation.[5] Although it has been more difficult to detect the antiferromagnetism in this material by other techniques, recent neutron-diffraction measurements on an oriented powder have now confirmed the presence of long-range AFM order.[6]

In this Letter we report on the competition between AFM and superconductivity (SC) in $YBa_2Cu_3O_x$ as a function of x, using the technique of μ^+SR.[7,8] The positive muon serves as a microscopic probe of the local magnetic environment at interstitial sites and is sensitive to and can differentiate between AFM and SC in the bulk of the sample.

The samples used in these measurements were sintered powders of $YBa_2Cu_3O_x$ prepared by two rather different methods. In the "quench" method, samples were heated in controlled atmospheres of oxygen and/or argon and allowed to equilibrate to the oxygen content determined by thermogravimetric analysis on test samples, using as a reference neutron-diffraction results from Jorgensen *et al.*[9] which show that as the oxygen content x is decreased, oxygen atoms are selectively removed first from the CuO "chains," leaving the CuO_2 "planes" essentially intact down to $x = 6.0$ where the "chains" are fully deoxygenated. The samples were then dropped directly into liquid nitrogen and transported under argon to TRIUMF for μ^+SR experiments. In the "slow-anneal" method, a "mother batch" of $YBa_2Cu_3O_x$ powder was pressed into disks and annealed in pure O_2 at 450 °C for 24 h, a procedure which produces fully oxygenated samples with $x = 6.95 \pm 0.05$ (where the uncertainty is not in the

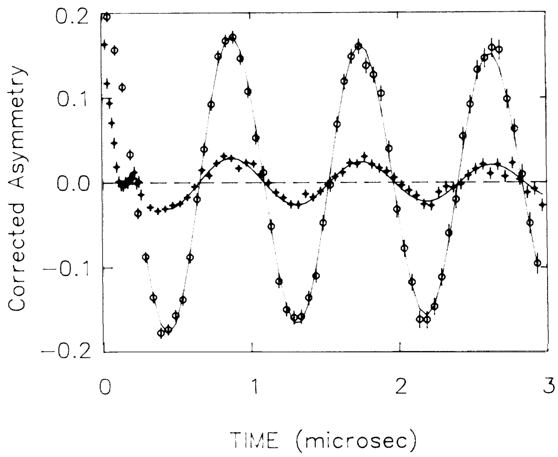

FIG. 1. TF-μ^+SR time spectra in $YBa_2Cu_3O_{6.298}$ (slow annealed) for $T=70$ K (circles) and $T=5$ K (crosses) showing the effect of AFM ordering on the precession signal. Note that in the 5-K data a faster oscillation is apparent at earlier times as a result of muons precessing in the local field of the ordered phase.

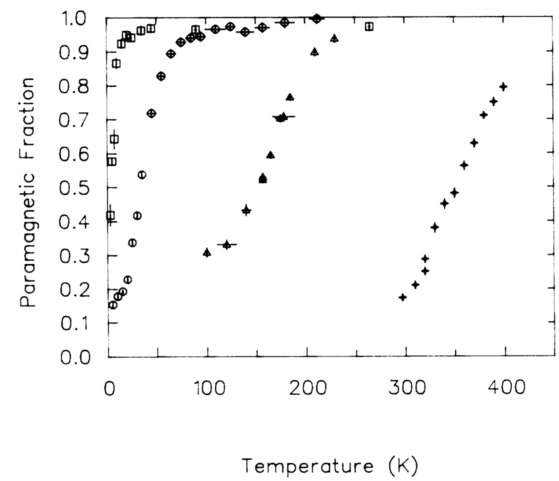

FIG. 2. Temperature dependence of the paramagnetic fraction in $YBa_2Cu_3O_x$ for a quenched $x=6.0$ sample (crosss) and for three slow-annealed samples: $x=6.262$ (triangles), $x=6.298$ (circles), and $x=6.348$ (squares).

reproducibility of the end point, but in its absolute value, which has been reported in the literature to have fixed values ranging between 6.9 and 7.0). The requisite amount of oxygen was then removed from each sample at temperatures between 420 and 460 °C with a helium-cooled wand in a closed system. Next, each sample was held at a constant temperature of ≈ 420 °C for 24 h in order to allow any gradients in x to be dissipated. Finally, the remaining O_2 was suddenly removed from the chamber and the sample cooled in a few seconds to room temperature. The resultant slow-annealed samples were intended to have a more homogeneous oxygen distribution than the quenched samples. It is important to note that, while the *absolute* x values are uncertain by as much as 0.05, the *relative* x values in such a series of samples are known to better than 0.01.

Magnetic ordering is readily detected by the application of a small external magnetic field ($B_{ext}=85$ G) transverse to the initial muon polarization direction (TF-μ^+SR).[4] Provided that B_{ext} is less than the spontaneous local field at the site of the muon (B_{loc}), the amplitude of the precession signal at the frequency corresponding to B_{ext} reflects *only* that fraction of the sample which has *not* ordered magnetically, i.e., the paramagnetic fraction. Any muon in an AFM region experiences B_{loc}, upon which B_{ext} is in effect a random perturbation. The TF-μ^+SR precession asymmetry is thus a quantitative and *normalizable* measure of the paramagnetic fraction. This is illustrated in Fig. 1, which shows TF-μ^+SR time spectra for $T > T_N$ (circles) and for $T < T_N$ (crosses). The paramagnetic fraction as a function of temperature is shown in Fig. 2 for various values of x. In Fig. 3 the mean T_N, which is taken as the temperature at which half the sample has ordered, is plotted as a function of x.

Superconductivity is easily distinguished from AFM in low TF. The onset of AFM order is accompanied by a small negative frequency shift (-1%) relative to that expected from B_{ext} and by a small increase in the T_2 relaxation rate (0.1–0.3 μs^{-1}) for the muons in the residual paramagnetic fraction of the sample. More pronounced muon relaxation rates and frequency shifts are observed in field-cooled SC samples, because of partial flux exclusion and the granularity of the sample.[8] In these cases a negative frequency shift of 5%–10% and a T_2 relaxation rate of 0.5–1.0 μs^{-1} are observed. In the

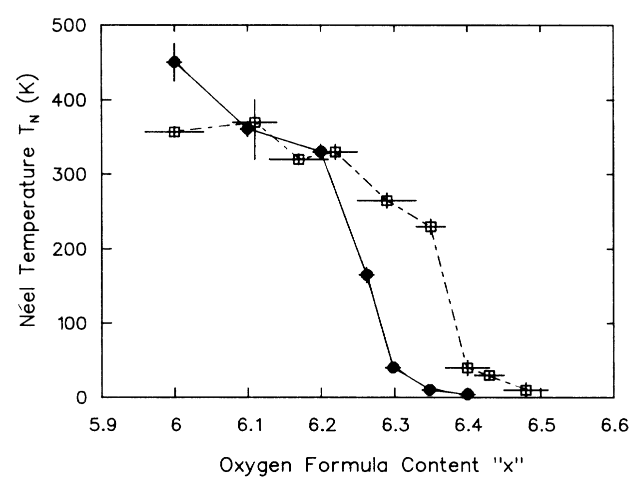

FIG. 3. Dependence of T_N upon the oxygen content x in $YBa_2Cu_3O_x$. Open squares denote quenched samples and filled circles denote slow-annealed samples. The slow-annealed samples with $x=6.348$ and $x=6.4000$ also have sharp superconducting transitions at $T_c=25$ K and $T_c=33$ K, respectively.

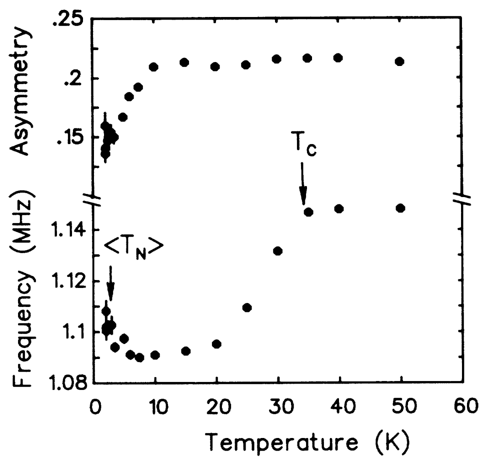

FIG. 4. Temperature dependence of the TF muon precession amplitude and frequency in $YBa_2Cu_3O_x$ with $x=6.40$. The sample is superconducting at T_c and has an average Néel temperature $<T_N>$.

very fine powders used in this experiment the field is never completely excluded from the grains so that there is no loss in the amplitude of the precessing component of the muon polarization. Finally, the SC transitions are quite sharp, as is the onset of their effects on frequency shifts and relaxation, in contrast to the gradual onset of smaller effects in the AFM transitions. This gradual onset of AFM ordering (see Fig. 2) has a simple explanation in terms of the inevitable inhomogeneity of x and the strong dependence of T_N upon x (see Fig. 3). Where dT_N/dx is largest, the transition tends to be the broadest.

It is clear from Fig. 3 that T_N increases dramatically as the oxygen content is reduced. For the slow-annealed samples with T_N greater than 100 K, it was possible to measure precession frequency of the muon in zero applied field in the limit $T/T_N \ll 1$. The resulting low-temperature limit for B_{loc} was measured to be about 300 G (in agreement with Ref. 5) and independent of x for $x<6.27$. This shows that the size of the moments which are ordering does not change appreciably over a range of x where T_N changes by more than a factor of 2. One possible explanation for the strong dependence of T_N on x is that the removal of oxygen from the CuO chains alters the interplane AFM coupling between the CuO planes, which is necessary to establish true long-range AFM order. It is interesting to note from Fig. 3 that the "quenched" samples show an onset of AFM order with x about 0.1 higher than the "annealed" samples. This is indication that the arrangement of the oxygens in the chains also affects T_N.

Another interesting feature of $T_N(x)$ is that the steep drop off around $x \approx 6.25$ is followed by a "tail" at higher x, where the samples are on the verge of becoming superconductors. In fact, the two annealed samples at $x=6.348$ and $x=6.400$ both showed sharp SC transitions at $T_c=25$ K and $T_c=33$ K, respectively, and then ordered magnetically below $T=10$ K and $T=5$ K, respectively. The onset of AFM order in the presence of SC in these two samples is accompanied by a *lessening* of the large negative SC frequency shift (see Fig. 4), which suggests that material which was SC relinquishes its superconductivity to become AFM.

The most interesting empirical question, of course, is whether these samples at the borderline between AFM and SC are merely heterogeneous, so that part of the sample can be SC while another part is AFM, or whether the same material can be simultaneously AFM and SC (as is the case for analogous materials containing magnetic rare earths,[10] but would be surprising for a system in which both AFM and SC are believed to be mediated by the same electrons) or whether, as we suspect, a region which is SC at 20 K "turns off" its superconductivity to become AFM below 5 K. Further experiments are required to resolve this question.

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