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Magnetic transitions in the system $YBa_2Cu_{2.8}Co_{0.2}O_{6+y}$

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We have studied the oxygen dependence on the two magnetic transitions (antiferromagnetic ordering of chains and planes) in $YBa_2Cu_{2.8}Co_{0.2}O_{6+y}$ using neutron scattering. It is found that both transition temperatures increase with decreasing oxygen concentration. At $y \approx 0.37$ ($\equiv y_0$) the two transition temperatures are equal, so that chains and planes order at a single transition temperature for $y \leq y_0$. For $y = 1$ the compound is superconducting at 60 K. Therefore, this system qualitatively exhibits the magnetic and superconducting properties of pure $YBa_2Cu_3O_{6+y}$ while providing important insight on the oxygen dependence of chain site magnetic ordering. A discussion is presented which also includes results on Ni and Al substitutions.

Both $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{6+y}$ exhibit either superconductivity or antiferromagnetic order depending on the compositon. Spin fluctuations have been observed for the superconducting compositions, although no long-range magnetic order is present.[1,2] From an experimental viewpoint, a complete understanding of high-temperature superconductivity must include the interesting magnetic properties of the Cu-oxide-based superconductors, therefore, it is essential to investigate the magnetic behavior of these compounds.

The magnetic properties of La_2CuO_4 have been studied extensively by neutron scattering and this work was reviewed recently by Birgeneau and Shirane.[3] However, the magnetic properties of $YBa_2Cu_3O_{6+y}$ have received less attention due, in part, to the additional complication of Cu chain-site magnetic ordering[4] and to the difficulty in obtaining large single crystals. It is important, nevertheless, to understand the magnetic behavior of this superconducting system as a T_c of 90 K is probably well outside the range of conventional phonon mechanisms for superconductivity. In this paper, we present a neutron scattering study where we have determined the oxygen dependence of the two antiferromagnetic transitions[5] in $YBa_2Cu_{2.8}Co_{0.2}O_{6+y}$, corresponding to plane- and chain-site magnetic ordering. It is observed that at the lowest oxygen contents, chains and planes order at a single transition temperature. These results illustrate the general behavior of the competing magnetic interactions in this system.

In the first reports[6-8] of long-range magnetic order in $YBa_2Cu_3O_{6+y}$ it was found that magnetic moments on the Cu plane sites are arranged on an antiferromagnetic square planar lattice with the spin direction in the plane. The magnetic ordering temperature T_N is sensitive to the oxygen concentration and vanishes for $y \gtrsim 0.4$, whereupon the compound becomes superconducting.[9,10]

Although the early work did not report magnetic ordering on the Cu chain sites, such ordering was subsequently observed in single crystals.[4,11,12] This is a surprising result as (for $y = 0$) the Cu on the chain site is expected to be monovalent.[13] It was speculated[4] that chain-site magnetic ordering occurs only for $y > 0$ as the amount of divalent Cu increases, but there is some disagreement about this point in the literature.[11] Furthermore, some of these studies indicate a different magnetic ordering for the same reported[11,12] compositions, which could be due to the difficulty of determining composition in the single crystals, inhomogeneity, or substitutional defects as discussed below. Thus, the origin and nature of chain-site magnetic ordering is still not clear.

Previous work[5] has shown that the substitution of Co in nominally oxygen-deficient "1:2:3" enhances chain-site magnetic ordering. For low-Co concentration, there are two antiferromagnetic transitions: AF1, associated with Cu plane-site magnetic ordering (at a temperature T_{N_1}), and AF2, associated with Cu chain-site ordering (at a lower temperature T_{N_2}) in addition to the order on the planes. With only plane-site magnetic ordering in AF1, the antiferromagnetic coupling between nearest and next-nearest planes gives a magnetic cell that has a c-axis period equal to that of the chemical cell, producing magnetic Bragg reflections of the type (HKL) with H and K half-integral and L integral. However, when magnetic ordering occurs on both the chain and plane sites (AF2), the period along c becomes twice that of the chemical cell, giving half-integral L magnetic reflections.

The enhancement of chain-site magnetic ordering with Co substitution evidently arises because this magnetic ion substitutes[14] at the Cu chain site. However, for low-Co concentrations this system exhibits all of the essential magnetic and superconducting features which are present in pure $YBa_2Cu_3O_{6+y}$. Because we would like to investigate the oxygen dependence of the AF2 magnetic transition, dilute Co substitutions offer advantages over pure $YBa_2Cu_3O_{6+y}$. First, T_{N_2} was found[5] to be more than twice that in $YBa_2Cu_3O_{6+y}$, which may provide more control and reproducibility in the experiments. Second, because the Co substitutions produce a tetragonal[14,15] crystal symmetry, we do not need to be concerned about the effects of orthorhombic-to-tetragonal transitions or oxygen superlattices[16] as the oxygen concentration is varied. It is emphasized that although we refer to "chain sites," there are no long-range-ordered chains in these tetragonal compounds.

Experiments to determine the oxygen dependence of the two antiferromagnetic transition temperatures were performed on six powder samples (~10 g apiece), each containing different oxygen concentrations. The ceramics were prepared by standard[15] solid-state reaction techniques and oxygen was removed by Zr gettering, except for the sample with $y=0.5$, which was annealed in Ar. While it is known[17] that the microscopic oxygen configuration can depend on how the oxygen is removed, the tetragonal symmetry of the Co substitutions eliminates this consideration. This is further substantiated by the mutual consistency of the results below. It should be noted that this work was carried out on ceramic powders, which ensures better oxygen and compositional homogeneity over that of single crystals.

The oxygen concentrations were accurately (± 0.02) determined using the high-resolution neutron powder diffractometer and subsequent Rietveld analysis at the Neutron-Beam Split-Core Reactor (NBSR) at the National Institute of Standards and Technology in Gaithersburg, Maryland. In separate experiments, T_{N_1} and T_{N_2} were obtained from the temperature dependence of the whole and half-integral L magnetic Bragg reflections, respectively. These were performed on the triple-axis spectrometers at NBSR which were set for zero-energy transfer with either 14.8-meV or 13.5-meV incident energy. (002) highly oriented pyrolytic graphite was used for both monochromator and analyzer with collimators set at 40′-20′-20′-40′. Higher-order harmonics were eliminated using a pyrolytic graphite filter. Low-temperature measurements used either a variable temperature He gas-flow cryostat or a He closed-cycle refrigerator while measurements above room temperature used a vacuum ($<10^{-5}$ Torr) furnace.

Figure 1 shows the Néel temperatures of the two antiferromagnetic transitions as a function of oxygen concentration. Both transition temperatures decrease with increasing oxygen content, although their curvatures are opposite. No magnetic ordering was observed at $y=1$. For $y=0.32$, $\frac{1}{2}$ integral L reflections exhibit their highest transition temperature while whole integral L reflections were not observed. Therefore, when T_{N_2} equals T_{N_1} at low y, both chains and planes order at the same temperature and there is only one transition, AF2.

The ac magnetic susceptibility of the same samples have been measured in order to check for superconductivity. Only the fully oxygenated sample was superconducting with $T_c=60$ K, as expected[14,15] for this Co concentration. The absence of superconductivity in the other samples is consistent with the notion that long-range magnetic order and superconductivity are mutually exclusive. Questions regarding the coexistence of superconductivity and magnetic order would have to be addressed in a narrow ($\Delta y<0.1$) oxygen concentration range on unambiguously homogeneous samples, which would be difficult experimentally.

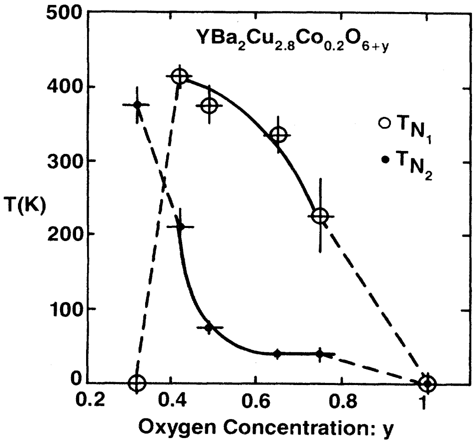

FIG. 1. Oxygen dependence of the two magnetic transition temperatures T_{N_1} and T_{N_2}, which were obtained from the temperature dependence of the whole- and half-integer L magnetic reflections, respectively. The solid and dashed lines serve as guides that connect transition temperatures of the same type; however, the dashed lines are not intended for interpolation. Both transitions increase with decreasing oxygen concentration until $y=0.32$ where both chains and planes order at a single transition with no whole integral L reflections observed. At $y=1$, no magnetic ordering is found.

To facilitate discussion, the salient features of our results are presented schematically in Fig. 2. For $y \gtrsim 0.82$, long-range magnetic order is absent and the compound is superconducting (SC) below T_c. Therefore, the general behavior of T_{N_1} with oxygen content is consistent with previous work (Refs. 9 and 10) on $YBa_2Cu_3O_{6+y}$, but our results indicate that Co shifts the transition temperature

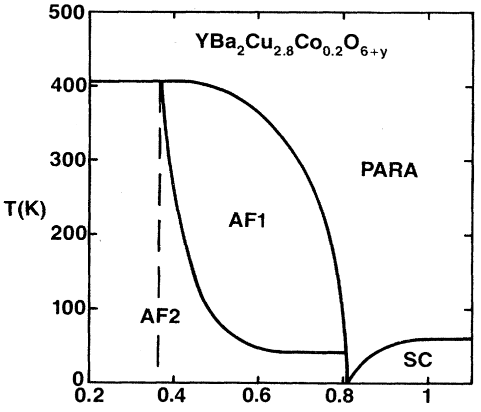

FIG. 2. Schematic diagram summarizing our results for $YBa_2Cu_{2.8}Co_{0.2}O_{6+y}$ shows paramagnetic (PARA), superconducting (SC), and antiferromagnetic behavior. AF1 indicates long-range antiferromagnetic order on the Cu plane sites, whereas AF2 indicates antiferromagnetic order on both plane and chain sites. At $y_0 \approx 0.37$, $T_{N_2}=T_{N_1}$ such that only one transition is observed for $y \lesssim y_0$. The dashed line (also drawn at y_0) indicates that qualitatively different types of magnetic ordering occur within AF2, as discussed in the text.

to a higher oxygen concentration. This shift reflects the fact that Co attracts additional oxygen[14,15] into the structure as a consequence of its 3+ valence.

Two important experimental observations at low y are depicted in Fig. 2. First, $T_{N_2}=T_{N_1}$ at an oxygen concentration of $y_0 \approx 0.37$ and a single transition temperature is found for $y \leq y_0$, corresponding to the simultaneous magnetic ordering of chains and planes. Second, the abrupt disappearance (see Fig. 1) of whole integral L reflections for $y<y_0$ is denoted by a vertical dashed line in Fig. 2. This line is placed at y_0, although a slight displacement from y_0 cannot be ruled out. The regions above and below y_0 are both referred to as AF2 since long-range magnetic order is observed on the chain sites in each case.

When $y>y_0$ and $T<T_{N_2}$, both whole- and half-integral L reflections are observed and the temperature dependence of the intensities for the whole-integral reflections deviate from a simple order parameter shape.[5] This behavior can arise from two successive magnetic transitions (at T_{N_1} and T_{N_2}) with a temperature-dependent rotation angle between chain and plane spins below T_{N_2}. The presence of only half-integral reflections for $y<y_0$ suggests that the spins then evolve into a structure which is completely antisymmetric along the c axis. Such a rotation could come from the competition between chain-plane and next-nearest-neighbor plane-plane interactions.[4] Alternatively, the observed mixture of half- and whole-integral L reflections could also come from *magnetic* phase separation where two antiferromagnetic phases coexist for $y>y_0$ and $T<T_{N_2}$. The two situations are difficult to distinguish experimentally.

We have performed similar experiments[18] for a higher ($x=0.8$) Co concentration. Antiferromagnetic order of the type AF2, exhibiting only half-integral L magnetic reflections, is found for all oxygen concentrations (with a relatively constant T_N) and the system is never superconducting. Therefore, the effect of adding Co is to raise the chain-site-ordering temperature T_{N_2} until $T_{N_2}=T_{N_1}$ whereupon there is just one transition.

Although it cannot be predicted how much T_{N_2} is lowered for $x=0$ (no Co), we can reflect on the available literature. For $NdBa_2Cu_3O_{6.1}$ single crystals, Lynn *et al.*[11] observe both half- and whole-integral L reflections while Moudden *et al.*[12] find only half-integral L reflections. This apparent discrepancy is resolved if the oxygen concentrations were actually slightly different than reported, such that $y<y_0$ in Ref. 12 and $y>y_0$ in Ref. 11, with y_0 having a value close to 0.1 for these compounds. Thus, the $NdBa_2Cu_3O_{6+y}$ system is in qualitative agreement with Fig. 2, aside from the shift to lower y. It is not clear what effect Nd has on the results.

Other experiments[18] on nominally oxygen-deficient compounds containing low concentrations ($x=0.1$) of Ni and Al exhibit contrasting magnetic behavior. Divalent Ni substitutes at both Cu sites whereas trivalent Al substitutes only in the Cu chain site.[15,19] The Ni substituted material exhibits an AF2-type magnetic ordering consistent with $y<y_0$, in Fig. 2. However, the Al-substituted compound exhibits only an AF1-type order, indicating that even very low concentrations of a nonmagnetic substitution on the chains suppresses chain-site magnetic ordering.

Because of the high sensitivity to low-substitution concentrations on the chain site, the question arises whether chain-site magnetic ordering is intrinsic to *pure* $YBa_2Cu_3O_{6+y}$. It has been demonstrated[20] that a significant amount of impurities can be inadvertently introduced during sample preparation. Experimentally this needs to be addressed on carefully prepared powders, rather than single crystals so that compositional homogeneity can be better controlled.

Conversely, it seems unlikely that such dilute substitution concentrations can be solely responsible for long-range antiferromagnetic order on the chain sites. Therefore, pure $YBa_2Cu_3O_{6+y}$ must have at least some propensity for magnetic behavior regarding the chain sites, but whether or not this long-range order is intrinsic to pure $YBa_2Cu_3O_{6+y}$ remains to be proven. Even if it turns out that chain-site ordering is not intrinsic, it is useful to understand the magnetic behavior of the substitutions as we can then gain some additional insight on the fundamental interactions in these materials.

In summary, we have studied the magnetic behavior of the system $YBa_2Cu_{2.8}Co_{0.2}O_{6+y}$ where the two antiferromagnetic ordering temperatures for planes and chains T_{N_1} and T_{N_2} increase with decreasing oxygen content. $T_{N_2}=T_{N_1}$ at y_0 so that chains and planes order at a single transition temperature for $y \leq y_0$. These observed qualitative features should generally represent all of the isomorphous $YBa_2Cu_3O_{6+y}$ compounds and provide a direct test for theoretical models which make predictions about the electronic and magnetic interactions.

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