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Antiferromagnetic order in $YBa_2Cu_{3-x}Co_xO_{6+y}$

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We present a neutron scattering study of oxygen-deficient $YBa_2Cu_{3-x}Co_xO_{6+y}$ where, with increasing Co concentration, long-range antiferromagnetic order develops on the chain sites. For $x=0.2$, two magnetic transitions are found: Below $T_{N_2}=211$ K, there is an ordered moment on both Cu sites, while for $T_{N_2}<T<T_{N_1}=415$ K only a "plane" moment is present. For $x=0.8$, an ordered moment appears on both Cu sites with a single transition at 435 K. Evidence for magnetic ordering was also found by magnetic susceptibility measurements. These results imply that Co substitution enhances antiferromagnetic coupling between the "plane" and "chain" sites.

While the mechanism responsible for superconductivity in the new high-temperature superconducting oxides is still not understood, current theories suggest that electron pairing may arise from antiferromagnetic (AF) correlations.[1] Experimentally, it is found that long-range antiferromagnetic order exists in the nonsuperconducting parent compounds, La_2CuO_{4-y} (Ref. 2) and $YBa_2Cu_3O_{6+y}$ (Ref. 3), which leaves open the possibility that AF correlations may be important for superconductivity.

In order to understand the role of structure and chemistry in high-temperature superconductivity, isomorphous substitutions for Cu have been studied.[4-7] The observed depression of T_c appears not to follow from the magnetic character of the substitution alone, but rather, a recent neutron-powder-diffraction study[8] shows a correlation to bond lengths. Changes in bond lengths are related to local valence changes and charge transfer, which can affect the magnetic interactions that may be important for high T_c. Therefore, it is of interest to understand how substitutions for Cu, especially magnetic ions such as Co, behave in the antiferromagnetic, nonsuperconducting parent compound.

In this paper, we present a neutron scattering study of magnetic order in oxygen deficient $YBa_2Cu_{3-x}Co_xO_{6+y}$, for two powder samples, ($x=0.2$, $y=0.45$) and ($x=0.8$, $y=0.91$), where an evolution of "chain" site AF ordering is found with increasing x. The structural properties of these samples have been previously[8] characterized by neutron powder diffraction where the x and y values were accurately (± 0.02) determined. The samples are single phase and homogeneous. Of the two crystallographically distinct Cu sites (one "chain" site and two "plane" sites per chemical unit cell), it was found that Co resides on the chain site. Also, Co is trivalent in this compound, thus, attracting additional oxygen so that the y values for these argon annealed samples are significantly greater than zero. Although we shall refer to "chain" sites, there are no long-range-ordered chains in the Co substitutions, which are tetragonal. The details of sample preparation have been reported elsewhere.[7]

The neutron scattering experiments were performed on 10 g of powder sample using the BT-9 spectrometer at the National Bureau of Standards Reactor in Gaithersburg, Maryland. The spectrometer was used in the triple-axis mode, set for zero-energy transfer with 14.8 meV incident energy monochromated from (002) highly oriented pyrolytic graphite (HOPG), which was also used for the analyzer. The collimation was 40′-20′-20′ before and after the monochromator and after the sample, respectively. A pyrolytic graphite (PG) filter was employed to eliminate higher-order harmonics. Low-temperature measurements were performed with a variable-temperature He gas-flow cryostat while measurements above room temperature were performed with a vacuum ($<10^{-5}$ Torr) furnace.

Figure 1(a) shows a scan of the $x=0.2$ sample at 5 K where $(\frac{1}{2}\,\frac{1}{2}\,L)$ magnetic reflections are present for L equal to *both* half and whole integers. At 300 K [Fig. 1(b)], however, the half-integral reflections have disappeared while the whole integral reflections remain. Their temperature dependence, shown in Fig. 2, displays two magnetic transitions: a lower transition at $T_{N_2}=211\pm 6$ K, where the half integral reflections vanish and an upper transition at $T_{N_1}=415\pm 7$ K where the whole integral reflections vanish. A least-squares fit of the integrated intensities to the function, $(T_N-T)^{2\beta}$, yields $\beta=0.22\pm 0.03$ for the $(\frac{1}{2}\,\frac{1}{2}\,\frac{3}{2})$ while the $(\frac{1}{2}\,\frac{1}{2}\,1)$ gives $\beta=0.35\pm 0.05$ for $T>T_{N_2}$. It is seen that the onset of ordering below T_{N_2} introduces significant deviation from power-law behavior for the $(\frac{1}{2}\,\frac{1}{2}\,1)$.

A substantially different magnetic structure is found for $x=0.8$, where only half integral reflections appear [Fig. 3(a)]. Besides the absence of $(\frac{1}{2}\,\frac{1}{2}\,1)$, a careful search for the $(\frac{1}{2}\,\frac{1}{2}\,2)$ and $(\frac{1}{2}\,\frac{1}{2}\,4)$ did not reveal their presence. The temperature dependence of the $(\frac{1}{2}\,\frac{1}{2}\,\frac{3}{2})$ intensity is shown in Fig. 3(b) where a single transition is observed at $T_N=435\pm 5$ K with $\beta=0.31\pm 0.02$. Above the transi-

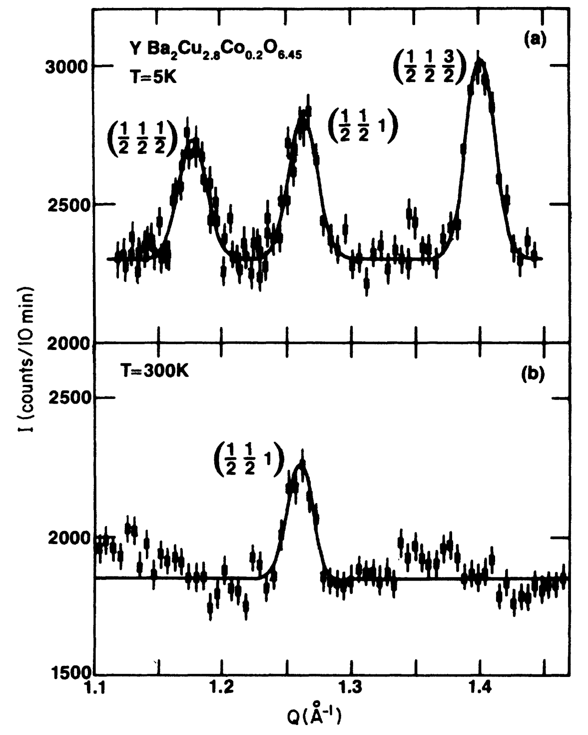

FIG. 1. Magnetic reflections for $x=0.2$. At (a) 5 K, both half and whole integer L reflections are found, while at (b) 300 K, only whole integer reflections are present.

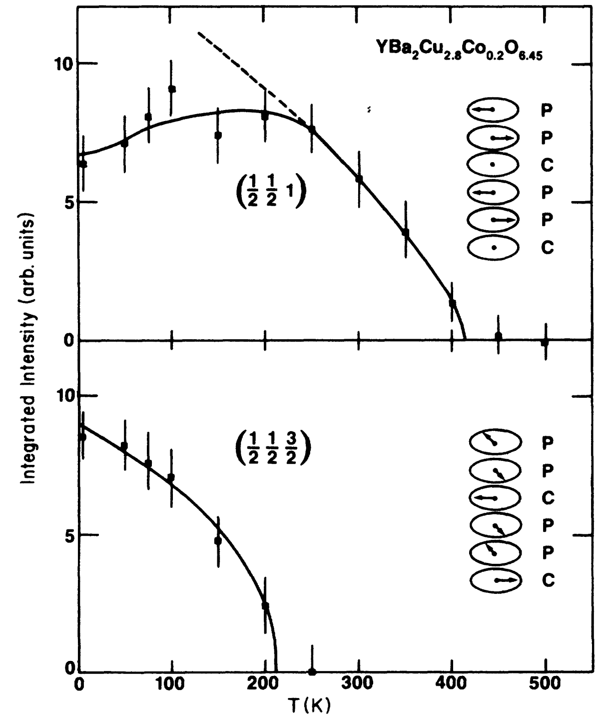

FIG. 2. Temperature dependence of the integrated intensities for $x=0.2$ show two magnetic transitions, at 211 and 415 K. As indicated by the dashed line, there is substantial deviation from power-law behavior below 211 K. Insets show the orientation of the chain "c" and plane "p" spins at 5 K for the (a) symmetric and (b) antisymmetic contributions to the spin structure.

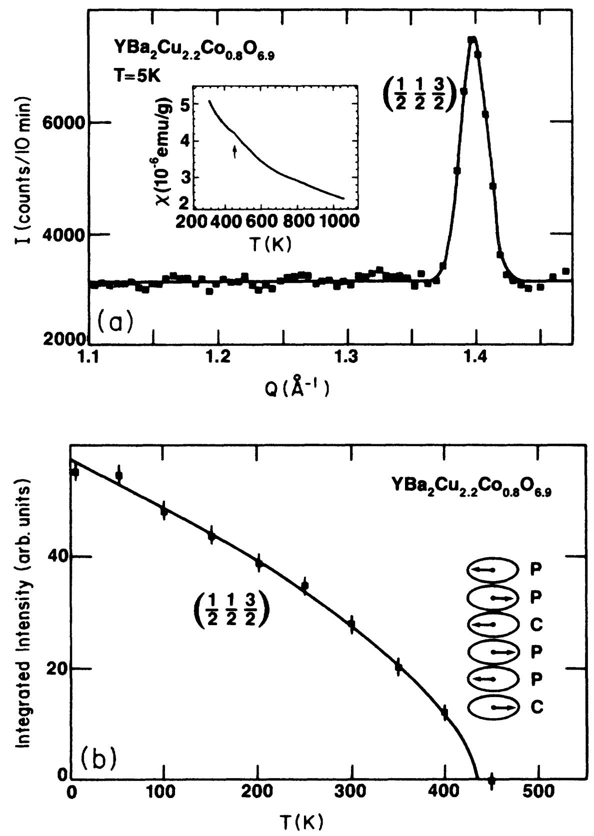

FIG. 3. (a) For $x=0.8$, only half-integral L magnetic reflections are observed at 5 K. Inset: magnetic susceptibility showing the anomaly at T_N. (b) Temperature dependence of the $(\frac{1}{2}\ \frac{1}{2}\ \frac{3}{2})$ integrated intensity. Inset: orientation of the chain and plane spins.

tion, there was still no evidence for the $(\frac{1}{2}\ \frac{1}{2}\ 1)$.

To determine the magnetic structure, integrated intensity data from various reflections (at 5 K) were compared to those calculated from several spin models. We have used the magnetic form factor measured by Freltoft *et al.*[9] in our calculations. The appearance of $(\frac{1}{2}\ \frac{1}{2}\ L)$ peaks indicate a structure consisting of antiferromagnetic sheets with ordering wave vector along [110]. Thus, the remaining problem is to determine the stacking sequence of the six Cu sites, located along the doubled c axis. It is useful to recognize that the sets of half and whole integral reflections can be analyzed independently, where the whole integral set represents a symmetric structure across the double cell along c, while the half-integral set represents an antisymmetric structure across the double cell. The resultant spin structure is obtained from the vector sum of the independently determined structures.

We now discuss the magnetic structure of the $x=0.2$ sample. The absence of a $(\frac{1}{2}\ \frac{1}{2}\ 0)$ peak indicates stacking which is antiferromagnetic along c, thus, a symmetrical cell doubling, corresponding to the whole integral peaks, can be achieved only if the chain moment is zero. The best agreement (Table I) for the symmetric structure has spins lying perpendicular to c and a colinear stacking of antiferromagnetic sheets on the order of "0+ −0+ −"

TABLE I. Experimental and calculated intensities for $x = 0.2$.

Integral peaks	Measured	Calc.	
$(\frac{1}{2}\,\frac{1}{2}\,0)$	0.00 ± 0.13	0.00	
$(\frac{1}{2}\,\frac{1}{2}\,1)$	0.79 ± 0.08	0.79	
$(\frac{1}{2}\,\frac{1}{2}\,2)$	1.00 ± 0.10	1.00	
$(\frac{1}{2}\,\frac{1}{2}\,4)$	0.00 ± 0.08	0.05	
$\frac{1}{2}$-integral peaks	Measured	Calc.[a]	Calc.[b]
$(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$	0.60 ± 0.13	0.59	0.55
$(\frac{1}{2}\,\frac{1}{2}\,\frac{3}{2})$	1.00 ± 0.08	1.00	1.00
$(\frac{1}{2}\,\frac{1}{2}\,\frac{5}{2})$	0.36 ± 0.13	0.36	0.33

[a] Calculated for spins in the plane.
[b] Calculated for spins out of the plane.

TABLE II. Experimental and calculated intensities for $x = 0.8$.

	Measured	Calc.[a]	Calc.[b]
$(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$	0.0 ± 0.04	0.01	0.00
$(\frac{1}{2}\,\frac{1}{2}\,\frac{3}{2})$	1.00 ± 0.04	1.00	1.00
$(\frac{1}{2}\,\frac{1}{2}\,\frac{5}{2})$	0.06 ± 0.04	0.04	0.03
$(\frac{1}{2}\,\frac{1}{2}\,\frac{7}{2})$	0.10 ± 0.04	0.08	0.07

[a] 168° angle between chain and plane spin directions.
[b] 180° angle between chain and plane spin directions.

[inset Fig. 2(a)], with a magnetic moment ($g\mu_B S$) of $(0.41 \pm 0.06)\mu_B$.

To model the half integral reflections, a nonzero chain site moment was allowed, with the antiferromagnetic sheets stacked colinearly. Although this configuration was previously found in the undoped compounds,[10,11] we were unable to obtain reasonable agreement with the observed intensities, regardless of the choice of magnitude and sign of the chain site moment. Instead, significantly better agreement was obtained if an arbitrary angle was allowed between the chain and plane site spins [inset Fig. 2(b)]. A least-squares fit yields an angle of 110° ± 20° with moments of $(0.62 \pm 0.06)\mu_B$ and $(0.18 \pm 0.02)\mu_B$ for the chain and plane sites, respectively (Table I, Calc.[a]). The resultant moments, obtained by vectorially adding the whole and half-integral structures, are $(0.62 \pm 0.06)\mu_B$ and $(0.45 \pm 0.05)\mu_B$ for the chain and plane sites, respectively. Due to the limited number of unobscured magnetic reflections collected, the half-integral peaks could also fit another structure: spins pointing along the c axis, stacked antiferromagntically with moment, $(0.044 \pm 0.005)\mu_B$ and $(0.44 \pm 0.04)\mu_B$, for the chain and plane sites, respectively (Table I, Calc.[b]). Since all previously reported spin structures[2,3,10–12] for these materials, as well as the whole integral spin contribution for this sample, exhibit spins perpendicular to c, we assume that the half integral spin contribution is also perpendicular to the c axis for $x = 0.2$.

Aside from exhibiting only half-intergal reflections, the $x = 0.8$ sample did not have a $(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$ peak, indicating that the chain and plane site moments are similar. The best agreement with the data gives equal moments of $(0.68 \pm 0.06)\mu_B$ and an angle of 170° ± 20° between the chain and plane site spins. To within uncertainty limits, this angle is sufficiently close to 180° that it suggests a simple "$+-+-+-$" stacking of antiferromagnetic sheets, as shown in the inset of Fig. 3(b) and Table II.

Recent work on $YBa_2Cu_3O_{6+y}$ (Ref. 10) and $NdBa_2Cu_3O_{6+y}$ (Ref. 11) single crystals has also shown a mixture of both half and whole integral reflections with different transition temperatures. However, the transition temperature of $T_{N_2} = 211$ K for the $x = 0.2$ sample is considerably higher than the highest previously reported value of 80 K.[11] These results suggest that the presence of Co encourages ordering on the chain sites, since T_{N_2} is low with no Co, higher for $x = 0.2$, while for $x = 0.8$, the chain moments order up to 435 K. The effect of Co substitution may be to enhance the AF exchange interaction among the chain sites as well as between chains and planes.

Half-integral-only-type ordering has recently been observed in a $NdBa_2Cu_3O_{6.1}$ single crystal;[12] however, the size of the chain site moment is considerably smaller than in the Co substitution with $x = 0.8$. Even in the Co-free compounds, the role of oxygen and the origin of the chain site moment is not well understood.[11] In the Co substitutions, the additional oxygen accommodates the trivalency of Co; therefore, this oxygen behaves chemically different. The higher oxygen concentration, however, might enhance the AF exchange interaction among the chain sites.

Magnetic susceptibility measurements have been performed on the same samples over the temperature range 4.2–900 K using the Faraday method. The samples were maintained under helium flow during the measurements to prevent incorporation of oxygen. For $x = 0.8$, a small anomaly appears in the temperature dependence of the susceptibility [inset Fig. 3(a)] at T_N, which is consistent with AF ordering found from neutron scattering. This anomaly is not observed for the $x = 0.2$ sample nor has it been reported previously. It is presumably seen here as a consequence of all six sites participating in the transition at T_N.

Both samples exhibit a Curie-Weiss temperature dependence which extends over the entire temperature range (except near the anomaly for $x = 0.8$), giving an effective *paramagnetic* moment of $3.5\mu_B$ ($\equiv g\sqrt{S(S+1)}\mu_B$) per Co ion. The size of the paramagnetic moment is substantial, corresponding to a spin contribution of 2–3 electrons (assuming $g = 2$), however, this is less than the 4 unpaired electrons expected for trivalent[8] Co. The paramagnetic moment is found to be independent of oxygen concentration;[7] therefore, the moment due to Co is not associated with oxygen disorder. A large, temperature-dependent background was also observed in the neutron scattering, which is indicative of magnetic disorder scattering arising from paramagnetic moments.

The observation of a large paramagnetic moment upon Co substitution would suggest that the Co ions do not contribute to the long-range magnetic order. However, this restriction draws attention to the magnitude of the chain site moment for the $x=0.8$ sample, since Co predominantly occupies this site. If the *ordered* moment appearing on the chain site was due to just the Cu ions, it would imply $2.3\mu_B$ per Cu, which is much larger than expected for divalent Cu and is more than twice as large as the largest Cu moments reported in the "superconducting" oxides (typically $< 1\mu_B$). Furthermore, at such large dilutions of Cu on the chain site, it would be difficult to develop long-range AF order on these sites if the ordering was due only to the Cu ions, although we cannot rule out the possibility that ordering on the chain site arises parasitically.

A comparison of the neutron scattering and magnetic measurements for $x=0.8$ leaves several possible conclusions which cannot be distinguished. It appears that the addition of Co induces an anomalously large moment on the remaining Cu ions at the chain sites; however, an interesting possibility is if the chain moment arises from the oxygens, which could then account for the size of the moment. Alternatively, Co might contribute to both a paramagnetic and ordered moment, although we recognize that this would be inconsistent with conventional localized ionic moments and would require a band model where the two moments could have no mutual interaction. Finally, another possibility is if Co paramagnetic moments experience an internal, staggered magnetization field which would then provide additional Bragg intensity at the half-integral AF reflections, thereby yielding an effectively larger ordered chain moment.

In summary, the substitution of Co alters the AF ordering in oxygen-deficient $YBa_2Cu_{3-x}Co_xO_{6+y}$. At low x, two transitions are observed, which evolve into a single transition at high x, with an ordered moment on the Cu chain site. Co substitution enhances the AF coupling between chain and plane sites; however, the nature of this coupling will be of interest for future experiments.

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[1] P. W. Andrson, G. Baskaran, Z. Zou and T. Hsu, Phys. Rev. Lett. **58**, 2790 (1987); V. J. Emery, *ibid.* **58**, 2794 (1987); J. E. Hirsch, *ibid.* **59**, 228 (1987).

[2] D. Vaknin, S. K. Sinha, D. E. Moncton, D. C. Johnston, J. M. Newsam, C. R. Safinya, and H. E. King, Phys. Rev. Lett. **58**, 2802 (1987).

[3] J. M. Tranquada, D. E. Cox, W. Kunnmann, H. Moudden, G. Shirane, M. Suenaga, P. Zolliker, D. Vaknin, S. K. Sinha, M. S. Alvarez, A. J. Jacobson, and D. C. Johnston, Phys. Rev. Lett. **60**, 156 (1988).

[4] G. Xiao, F. H. Streitz, A. Gavrin, Y. W. Du, and C. L. Chien, Phys. Rev. B **35**, 8782 (1987).

[5] Y. Maeno, T. Tomita, M. Kyogoku, S. Awaji, Y. A. Oli, K. Hoshino, A. A. Miniami, and T. Fujita, Nature (London) **328**, 512 (1987).

[6] J. M. Tarascon, L. H. Greene, B. G. Bagley, W. R. McKinnon, P. Barboux, and G. W. Hull, in *Novel Superconductivity,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 705.

[7] J. M. Tarascon, P. Barboux, P. F. Miceli, L. H. Greene, G. W. Hull, M. Eibschutz, and S. A. Sunshine, Phys. Rev. B **37**, 7458 (1988).

[8] P. F. Miceli, J. M. Tarascon, L. H. Greene, P. Barboux, F. J. Rotella, and J. D. Jorgensen, Phys. Rev. B **37**, 5932 (1988).

[9] T. Freltoft, G. Shirane, S. Mitsuda, J. Remeika and A. S. Cooper, Phys. Rev. B **137** (1988).

[10] H. Kadowaki, M. Nishi, Y. Yamada, H. Takeya, H. Takei, S. M. Shapiro, and G. Shirane, Phys. Rev. B **37**, 7932 (1988).

[11] J. W. Lynn, W.-H. Li, H. A. Mook, B. C. Sales, and Z. Fisk, Phys. Rev. Lett. **60**, 2781 (1988).

[12] A. H. Moudden, G. Shirane, J. M. Tranquada, R. J. Birgeneau, Y. Endoh, K. Yamada, Y. Hidaka, and T. Murakami, this issue, Phys. Rev. B **38**, 8720 (1988).