Magnetic susceptibility of $YBa_2Cu_3O_{6+x}$: Effects of spin frustration and correlation

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(Received 1 July 1988; revised manuscript received 9 November 1988)

$YBa_2Cu_3O_{6+x}$ is known to undergo a transition from a magnetic semiconductor to a metallic high-temperature superconductor as the oxygen content is increased from the range $0.0 \leq x \leq 0.5$ to $0.5 \leq x \leq 1.0$. We report here detailed temperature-dependent magnetic-susceptibility studies for x in the composition range $0.0 \leq x \leq 1.0$. For $0.05 \leq x \leq 0.5$, the effective moment μ_{eff} decreases with decreasing temperature from 300–160 K, as expected for an antiferromagnet whose Néel temperature is above room temperature. Below 160 K, μ_{eff} increases, reaching a maximum at $\sim$40 K then decreases again. The magnitude of this low-temperature peak in μ_{eff} increases with x, reaches a maximum at $x=0.35$, then decreases toward zero. A Monte Carlo simulation method has been used to model the three-dimensional antiferromagnetic ordering of this system as a function of oxygen composition. The calculation reveals the presence of spin frustration as x increases from 0 through to 0.3 in accord with the increasing number of effective moments at low temperatures. Above $x=0.3$ a new long-range order (corresponding to a doubling of the magnetic unit cell perpendicular to the planes) is predicted to occur in agreement with the observed magnetic susceptibility and recent neutron-diffraction experiments of Kadowaki *et al.* [Phys. Rev. B **37**, 7932 (1988)] and Lynn *et al.* [Phys. Rev. Lett. **60**, 2781 (1988)]. Above $x=0.5$, relatively few localized moments are observed in the temperature-dependent susceptibility measurement. In the metallic regime the "Pauli susceptibility" is observed to increase approximately linearly with oxygen content. This is in accord with decreasing effects of antiferromagnetic correlation with increasing x.

I. INTRODUCTION

The discovery of superconductivity in layered cuprates has stimulated intensive experimental and theoretical study of these and related materials.[1,2] In the $YBa_2Cu_3O_{6+x}$ system there is an evolution from an antiferromagnetically ordered semiconductor for $x \leq 0.5$ to a superconducting nonmagnetically ordered system for $x \geq 0.5$.[3-7] For $YBa_2Cu_3O_{6+x}$ with $x \sim 0$ the magnetic structure consists of a simple antiparallel arrangement of Cu spins both within the Cu-O planes as well as along the tetragonal c axis, while the oxygen-deficient Cu planes possess no net moment.[4,6] In this system the three-dimensional ordering temperature is high, with $T_{N1} \sim 450$–500 K,[3-7] suggesting the presence of large exchange interaction energies. Because of the large separation and resulting anisotropic interactions between the two-dimensional planes containing the Cu spins, two-dimensional magnetic correlations should persist within these planes above T_{N1}. With increasing x, T_{N1} decreases until no magnetic ordering is observed for $x \sim 0.4$–0.5. Recent neutron-diffraction studies of $YBa_2Cu_3O_{6+x}$ by Kadowaki *et al.*[8(a)] show that for $x \approx 0.35$ there is a change in the antiferromagnetic sequencing along the c axis at $T_{N2} \sim 40$ K, while for $x \approx 0.2$ Sato *et al.*[8(b)] have not observed any change in the antiferromagnetic sequencing down to 5 K. Neutron diffraction studies of $NdBa_2Cu_3O_{6+x}$ show that changes in antiferromagnetic sequencing are more prominent in this system (perhaps due to greater interaction of the Nd $4f$ electrons with the surrounding lattice[9]). The magnetic orderings of the 1:2:3 systems are of particular interest because of suggestions that the magnetic interactions are responsible for the high-temperature superconducting pairing in these systems.[10-18]

We report here the results of an extensive study of the temperature (T) dependence of the susceptibility (χ) of $YBa_2Cu_3O_{6+x}$ for $0.0 \leq x \leq 1.0$. For $x \sim 0$, $\chi(T)$ is in agreement with simple antiferromagnetic sequencing of the spins with $T_{N1} \geq 320$ K, though there is a small increase in χ at low T. With increasing x this excess susceptibility is more pronounced, reaching a maximum for $x \sim 0.37$, and decreasing substantially as x approaches 0.5. The T-dependent effective moment μ_{eff} [$=p\mu_B$, where $p \equiv 2.83(\chi T)^{1/2}$ for χ in emu/mole $YBa_2Cu_3O_{6+x}$ and T in degrees Kelvin] increases with T at lower temperatures reaching a maximum at $\sim$40 K. The magnitude of μ_{eff} with increasing x to $\sim 0.8\mu_B$ for $x=0.37$ is in good agreement with the reported values of $0.7\mu_B$ and $T_{N2} \sim 40$ K obtained from neutron diffraction.[8]

We have performed Monte Carlo calculations of the effects of oxygen doping, which adds spins located at

formerly spinless Cu sites on the oxygen-deficient Cu planes. Frustration thereby introduced into the three-dimensional antiferromagnetic ordering leads to both excess μ_{eff} at low temperatures and a reordering of the three-dimensional magnetic lattice. The effective moment determined from the Monte Carlo calculations increases, then decreases with x similar to the experimental observations. Magnetic susceptibility measurements of samples in the metallic regime, $x \geq 0.5$, show only a modest increase in χ at low T. A composition-dependent Pauli susceptibility is observed, increasing approximately linearly with x, in contrast to early reports by Cava *et al.*[19] This increasing χ^{Pauli} is consistent with decreasing local antiferromagnetic correlations with increasing x.

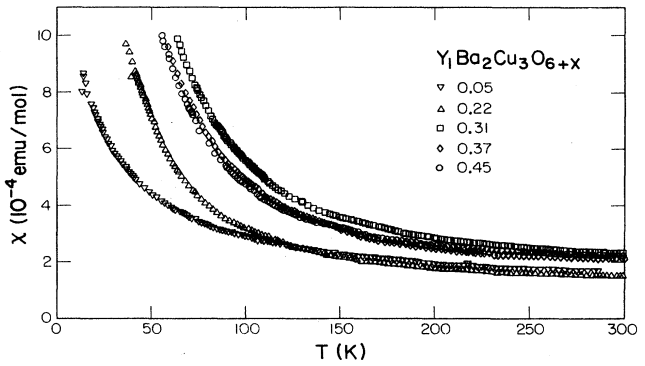

FIG. 1. Temperature-dependent magnetic susceptibility of $YBa_2Cu_3O_{6+x}$ for $0.0 \leq x \leq 0.5$. The data have been corrected for core diamagnetism.

II. EXPERIMENTAL TECHNIQUES

Powders of $YBa_2Cu_3O_{6+x}$ where x varies from 0 to 1 were prepared as described previously.[20] To summarize briefly, samples of variable oxygen content were prepared under conditions of both low-temperature vacuum annealing and rapid quenching. Unless otherwise indicated, the susceptibility data reported here are for the rapidly quenched samples. In this procedure, pressed but unsintered pellets of ~500 mg are equilibrated for 2 h in flowing air, nitrogen, or oxygen, at temperatures where the equilibrium oxygen content is known. These temperatures range from 900 °C for $x \leq 0.25$ to 450 °C for $x = 0.93$. Samples were then quenched by direct immersion in liquid N_2. Oxygen contents were subsequently measured by thermal gravimetric analysis and shown to correspond with the values expected for equilibrium at the temperature from which the sample was quenched. The samples were determined to be single phase by x-ray diffraction and neutron diffraction. In particular, no magnetic $BaCuO_2$ was evident from structural studies.

The magnetic susceptibility was measured on two previously described[21] Faraday susceptometers for temperatures of $2 \leq T \leq 320$ K and magnetic fields up to 75 kG. The magnetic susceptibility data presented here have been corrected for core diamagnetism using -12, -32, -15, and -12×10^{-6} emu per elemental mole of Y, Ba, Cu, and O, respectively.[22]

III. EXPERIMENTAL RESULTS

The magnetic susceptibility of $YBa_2Cu_3O_{6+x}$ as a function of temperature and oxygen content is summarized in Figs. 1 and 2 for oxygen content in the ranges of $0.05 \leq x \leq 0.5$, and $0.5 \leq x \leq 1.0$, respectively. Overall, the data are quite similar to the results of Johnston *et al.*[3] For samples of composition $x = 1.0$, the susceptibility is nearly temperature independent with the presence of a small increase at low temperatures. Analysis of the $YBa_2Cu_3O_7$ sample data in terms of

$$\chi = \chi_0 + C_0/(T - \Theta) \quad (1)$$

gives a very good fit with $\chi_0 = 2.84 \times 10^{-4}$ emu/mole Cu_3. We plot in the inset to Fig. 2 $(\chi - \chi_0)^{-1}$ vs T for this sample. The fit for $C_0 = 2.14 \times 10^{-2}$ emu K/mole and $\Theta = 19.1$ K suggests that the increase in the susceptibility at low temperature is due to the presence of 1.9×10^{-2} spin per Cu which may correspond to a magnetic impurity phase with a ferromagnetic $\Theta = 19$ K as has been suggested in other work.[23] For compositions of smaller x a similar analysis is no longer appropriate. Use of Eq. (1) yields Θ values other than 19 K for samples with $0.5 \leq x \leq 0.8$, and χ_0 terms no longer T independent. Hence, its application in this range of x is questionable, and the true behavior may be considerably more complex. For example, changing the annealing time at 625 °C from 2 to 12 h gave a sample with the same oxygen stoichiometry, $x = 0.65$, the same value of χ_0, but a Curie constant (C_0) smaller by a factor of two. It is unlikely that these samples could contain sufficiently different impurity concentrations to rationalize this observation. Both $YBa_2Cu_3O_{6.65}$ and $BaCuO_2$, the most likely impurity phase, should be stable and noninterconverting under these conditions.[23,24] In addition, nuclear quadrupole resonance (NQR) ^{63}Cu studies as a function of decreasing oxygen content beginning with $YBa_2Cu_3O_7$ suggest the presence of various Cu environments within the "metallic" sample.[25]

The semiconducting magnetic phase has a substantial increase in susceptibility as the temperature is decreased. Though it is tempting to attribute this rise as entirely due to impurities,[6] the systematic variation in the magnitude of the low-temperature susceptibility, combined with the absence of evidence for a magnetic impurity phase in the x-ray- and neutron-diffraction data supports the intrinsic nature of this phenomenon. The experimental susceptibility measured at 20 kG is presented as effective [$p^{expt} = 2.83(\chi T)^{1/2}$ for χ in emu/mol $YBa_2Cu_3O_{6+x}$] versus T in Fig. 3. The p^{expt} has a maximum value at $T \sim 40$ K. As oxygen content is increased $(\chi - \chi_0)$ from $x = 0$, p^{expt} at 40 K increases, reaches a maximum for $x \sim 3.5$, then decreases (Fig. 4).

It is instructive to examine the room temperature susceptibility as a function of composition (Fig. 5). Qualitatively, the susceptibility appears to increase linearly with x, though for $x > 0.5$ the susceptibility is nearly constant

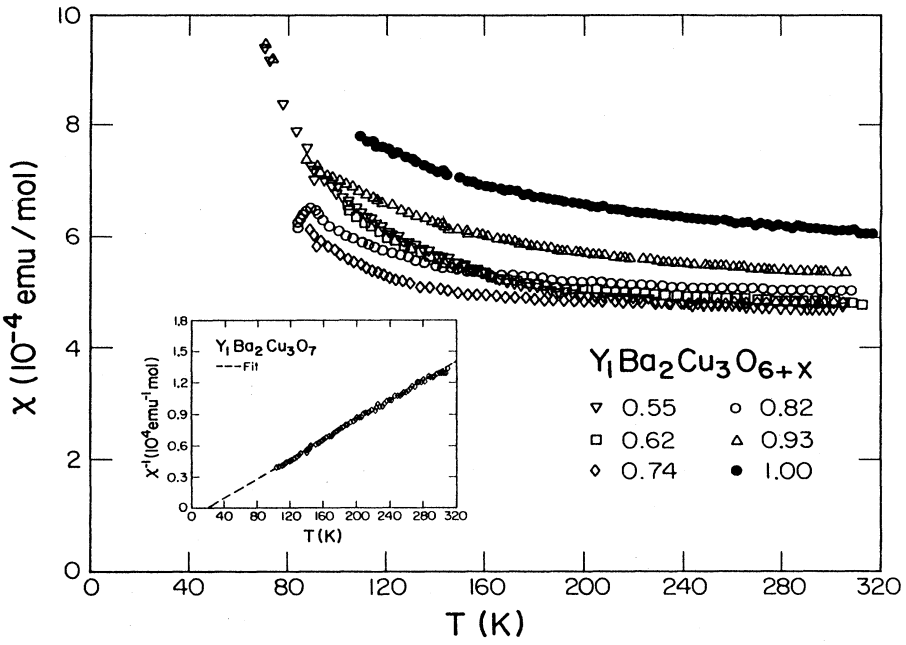

FIG. 2. Temperature-dependent magnetic susceptibility of $YBa_2Cu_3O_{6+x}$ for $0.5 \leq x \leq 1.00$. The data have been corrected for core diamagnetism. Inset: $(\chi - \chi_0)^{-1}$ vs T for $x = 1.0$ (see text).

until x exceeds 0.8 (Fig. 6). An nuclear magnetic resonance (NMR) ^{63}Cu study of the 300-K susceptibility as a function of composition for identically prepared samples confirm these results.[25]

IV. DISCUSSION

The magnetic properties of $YBa_2Cu_3O_{6+x}$ for $0 < x < 0.5$ can be understood by considering the spin frustration in the system. The unit cell consists of three layers of Cu sites, labeled in Fig. 7. For $x = 0.0$, neutron scattering experiments show that for the top (A,A') and bottom (C,C') layers all Cu sites are magnetic, while for the oxygen deficient central Cu (B,B') layer the Cu sites are nonmagnetic, consistent with no holes in the system for this value of x.[4] Within each magnetic layer (A,A',C,C'), magnetic Cu sites are coupled two dimensionally by strong antiferromagnetic superexchange J which is the origin of the strong two-dimensional (2D) correlation similar to that seen in La_2CuO_4.

The scattering experiments further indicate that along the c axis, the top layer of one unit cell (A'), and the bottom layer of the next unit cell (C) are coupled antiferromagnetically through the Y sites, presumably by a direct exchange J_1 between Cu^{2+}, since the O ions are

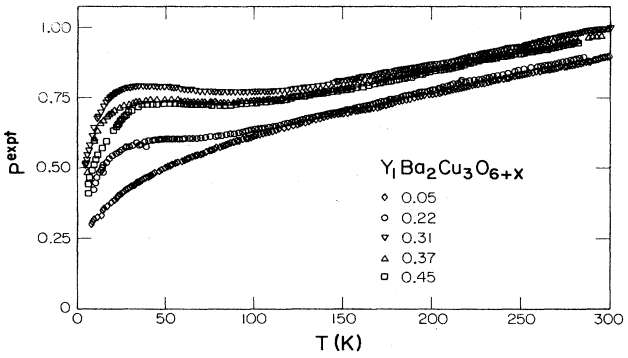

FIG. 3. Effective moment vs T for $YBa_2Cu_3O_{6+x}$ and $0.0 < x < 0.5$.

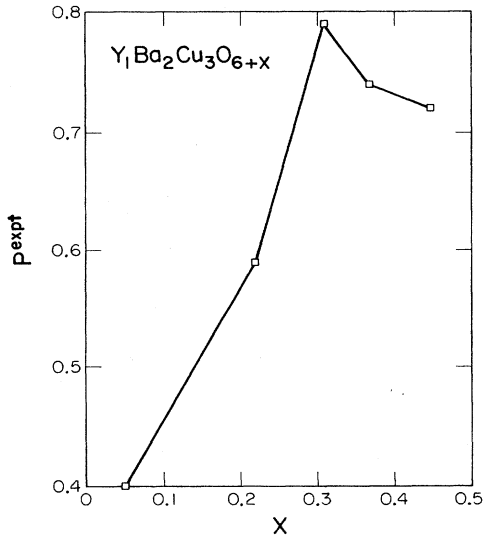

FIG. 4. Effective moment at 40 K vs x for $YBa_2Cu_3O_{6+x}$ and $0.0 < x < 0.5$.

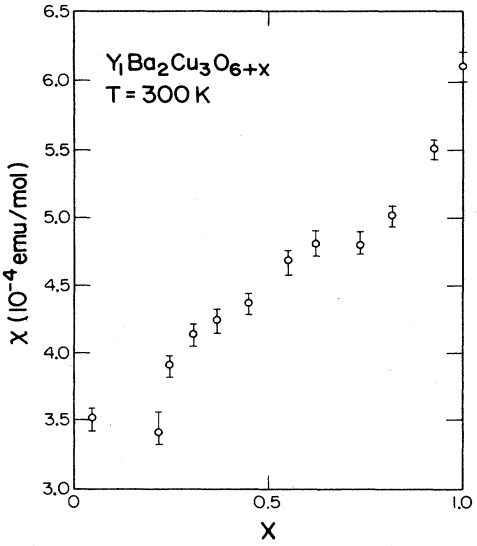

FIG. 5. Magnetic susceptibility at 300 K of $YBa_2Cu_3O_{6+x}$ vs x for $0.0 < x < 1.0$.

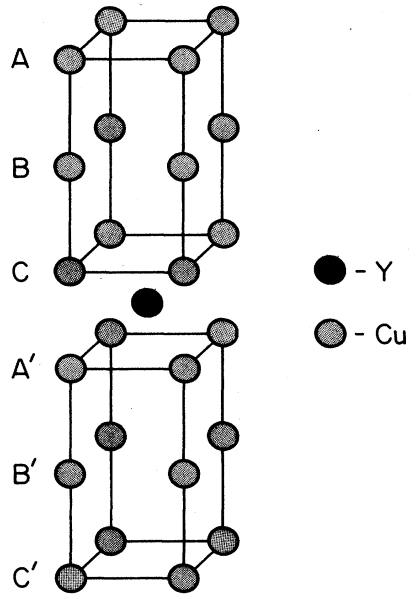

FIG. 7. Lattice structure of $YBa_2Cu_3O_{6+x}$ showing Cu and Y sites. The figure shows O locations (solid lines) for $x=0$. For finite x, O atoms fill in sites between Cu in B and B' planes.

missing around the Y sites. Within a unit cell, the top (A) and bottom (C) layers are coupled via the intervening O-deficient Cu layers (B). For $x=0.0$, when the Cu site on the central (B) plane is nonmagnetic, the A and C layers couple to each other antiferromagnetically (as indicated by the neutron scattering for $x=0.0$ sample) through a weak superexchange J_2 via O^{2-}, nonmagnetic Cu, and a second O^{2-}. This is type-I magnetic ordering below ordering temperature T_{N1}. However, when a Cu site on the B layer is magnetic, it couples to both the A and the C layers with a superexchange J_3 analogous to the one in the a-b plane, hence larger than the antiferromagnetic superexchange J_2 between the A and C layers just described. This is equivalent to coupling the A and C layers ferromagnetically. Thus whether the local coupling between the A and C layers within a unit cell is effective ferromagnetic (FM) or antiferromagnetic (AFM) is determined by whether the B layer Cu site is magnetic or not. This competing FM and AFM coupling due to the interactions J_2 and J_3 is the origin of frustration in the system. At $x=0$ the coupling of A and C is solely AFM (as long as no spins exist on the B layer), while as x increases the FM coupling increases producing frustration and a corresponding decrease in the Néel temperature.

There is not yet a consensus on how the oxidation states on the A, B, and C layers evolve with x.[26] Within our model, the spin concentration on each layer is determined by the number of holes produced by oxygen doping and their distribution among the A, B, and C layers.[27] Neutron-diffraction experiments indicate that there is an increase in the rate of addition of holes on the A and C layers per oxygen dopant as x increases beyond 0.4.[28] However, for simplicity we have used a linear variation of hole concentration on the A, B, and C layers with increasing x.

Monte Carlo simulations, based on this model of the couplings and oxygen valence evolution, have been carried out. The details are reported in Ref. 27. In the present case, we consider mainly the Ising model, since we have obtained qualitatively similar results in the x-y and Heisenberg versions of the model. The Ising model, plus the neglect of quantum fluctuations, overestimates the degree of 2D magnetic order within the A and C layers, and requires larger values of J_1, J_2, and J_3 ($=0.2$, 0.1, and 0.4 in units of J) than expected from exchange integrals and experiment, but does not change the nature of the frustration introduced by oxygen doping. The values of the J's were chosen so that, for hole concentrations of 40%, 20%, and 40% on the A, B, and C layers, respectively, T_N goes to zero near $x=0.5$ and the predominate stable phase for small x is type I rather than type II.[27] Here we will give the following interpretation of the measured magnetic sus-

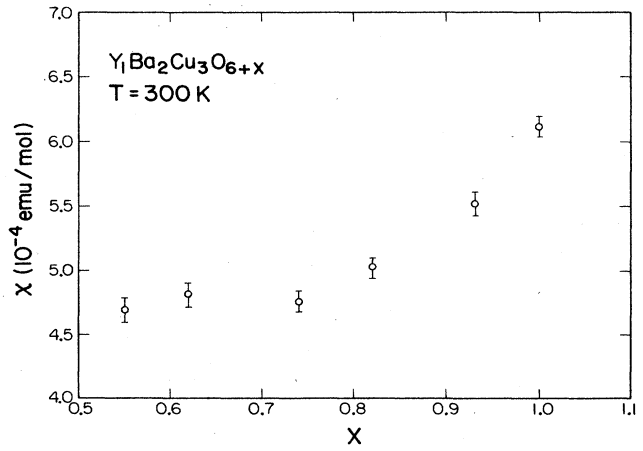

FIG. 6. Magnetic susceptibility at 300 K of $YBa_2Cu_3O_{6+x}$ vs x for $0.5 < x < 1.0$.

ceptibilities, using the results of simulations. For x close to 0.0, the A and C layers are strongly ordered within the a-b plane and are coupled to each other antiferromagnetically, because most of the Cu sites on the central B layer are Cu^{1+} and nonmagnetic. This ordering throughout the entire lattice gives the broad antiferromagnetic peak for the susceptibility of the $x \sim 0$ materials above 300 K.[3] At this point the small number of magnetic Cu^{2+} on the central B layers are totally frustrated and behave like free spins, resulting in a small increase in susceptibility at low temperature. As x increases, filling in O vacancies on the B layer, more Cu sites on the B layer have spin, introducing frustration into the system. A new magnetic phase (type II) develops below T_{N2}, in which a finite moment appears on the B layer, inducing parallel ordering of the A and C layer spins. This doubling of the antiferromagnetic unit cell competes with the type-I order and the resulting frustration lowers both T_{N1} and T_{N2}. As x approaches 0.4 to 0.5, large numbers of holes enter the Cu A and C planes, associated with the metal-insulator transition, reducing the magnetic ordering within the plane and rapidly driving T_{N1} and T_{N2} to zero.[6,29] Thus, as x increases from 0.0 to 0.5, the contribution to the susceptibility of the AFM-ordered A and C layers becomes weaker and finally disappears, while the number of "free spins" on the B layer increases up to $x \sim 0.3$, resulting in an initial increase in the low temperature χ. As x continues to increase beyond $x \sim 0.3$, the A- and C-layer antiferromagnetic order becomes weaker, and some spins on the B-layer order with the A and C layers, reducing the number of "free spins," and thus, the paramagnetic increase at low temperature.

Figure 8 presents the T-dependent susceptibility of the Ising model as a function of oxygen content. There is an initial drop of the Néel temperature with increasing oxygen content arising from frustration introduced by spins on the B-layer Cu sites. As x approaches 0.4, the second antiferromagnetic phase (type II) appears involving ordered spins on the chains. For $x=0.5$ the antiferromagnetic transitions have broadened and disappeared. The results for x-y Heisenberg models show a similar evolution

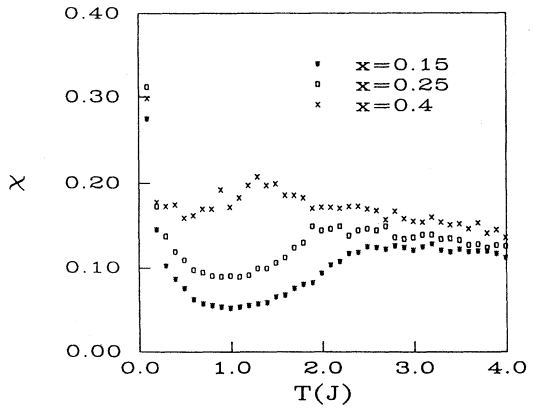

FIG. 8. Monte Carlo simulation of magnetic susceptibility per spin for Ising model representing $YBa_2Cu_3O_{6+x}$. The temperature is in units of the in plane AF exchange J and χ is in units of μ_B^2/J.

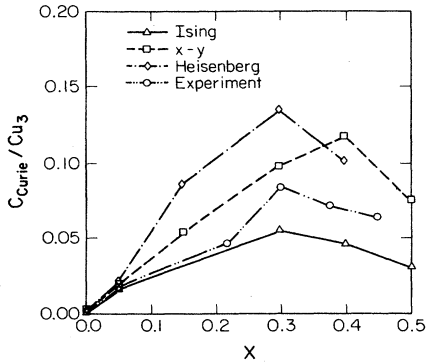

FIG. 9. Effective Curie constant obtained from Ising, x-y, and Heisenberg models for the frustrated spin lattice together with experimental Curie constant obtained at 40 K.

as a function of x with the disappearance of long-range order occurring at somewhat lower x.[27]

The low temperature effective Curie constant goes through a maximum in the vicinity of $x=0.3$ as x increases from 0.0 to 0.5. Figure 9 shows the results of the Monte Carlo calculations in the Ising x-y and Heisenberg limits together with comparison to experimental results obtained at 40 K.[27] The maximum value of p^{expt} at 40 K is also in agreement with the effective moment associated with new magnetic order occurring at 40 K as detected by neutron diffraction.[8]

The variation of the measured susceptibility χ(300 K) with x for $x > 0.5$ is in contrast with the earlier reported results of Cava *et al.*[19] [Note that χ(300 K) from Eq. (1), differs from χ_0 by only a small Curie contribution at $T=300$ K.] We have not observed the sharply increased χ at $0.8 \geq x \geq 0.6$ reported in Ref. 19 in either the quenched or vacuum-annealed samples. For example, two samples of $x=0.5$ prepared by quenching and annealing respectively show χ(300 K) values that differ by less than 5%. In light of the increasing metallic nature of the $YBa_2Cu_3O_{6+x}$ with increasing x, it is suggested that an increase in χ_0 for $x > 0.8$ may be related to a reduction in the antiferromagnetic correlations with increasing x. It is noted that a constant value of χ_0 for $0.55 \leq x \leq 0.74$ corresponds to a regime of constant $T_c \approx 55$ K, while the regime of increasing χ_0 ($x > 0.75$) corresponds to the transition to the stoichiometry range that gives the highest $T_c \approx 90$–95 K.

V. SUMMARY

The temperature-dependent magnetic susceptibility of $YBa_2Cu_3O_{6+x}$ varies smoothly with increasing x as the system varies from antiferromagnetic semiconductor to superconducting metal. For $x < 0.5$ the susceptibility shows a concentration-dependent maximum in the effective moment at 40 K. This phenomenon is associated with the role of spin frustration and the onset of a second antiferromagnetic ordering at 40 K. The variation of magnetic susceptibility with temperature and composition in the metallic phase is suggestive of a reduced role for spin correlation with increasing x and an increase in susceptibility for highest T_c.

ACKNOWLEDGMENTS

The authors acknowledge the assistance of Dr. S. Chittipeddi in obtaining neutron-diffraction data for samples used in this study, and Dr. R. K. Bordia in preparation of quenched samples. One of the authors (B.R.P.) would like to acknowledge support by the Air Force Office of Scientific Research and the Ohio Supercomputer Center.

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