Antiferromagnetism in $(Ca_{0.85}Sr_{0.15})CuO_2$, the parent of the cuprate family of superconducting compounds

D. Vaknin,* E. Caignol,† P. K. Davies,† and J. E. Fischer†
Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

D. C. Johnston
Ames Laboratory-United States Department of Energy, Iowa State University, Ames, Iowa 50011 and Department of Physics, Iowa State University, Ames, Iowa 50011

D. P. Goshorn
Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801
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A three-dimensional (3D) antiferromagnetic structure is identified in $(Ca_{0.85}Sr_{0.15})CuO_2$, a prototypical parent compound of all high-T_c superconductors. Magnetic neutron scattering and a weak susceptibility anomaly give $T_N = 537 \pm 5$ K while $\chi(T)$ suggests magnetic fluctuations above T_N in common with $La_{2-x}Sr_xCuO_{4-y}$ and $YBa_2Cu_3O_{7-\delta}$. Both experiments are consistent with a crossover from large intraplanar spin-spin correlations at high T to a 3D ground state driven by very weak out-of-plane couplings between Cu^{2+} ions.

There are now three closely related families of cuprate compounds that exhibit high-temperature superconductivity: $La_{2-x}A_xCuO_{4-y}$ (A=Ba,Sr,Ca,Na),[1] $RBa_2Cu_3O_{7-\delta}$ (R is a rare-earth element),[2] and the novel group $(AO)_y(B_2Ca_{n-1}Cu_nO_{2n+2})$ [A=Bi(y=2),Tl(y=1,2); B=Sr,Ba] of compounds.[3] These are all constructed from intergrowths of perovskite and rocksalt elements and contain CuO_2 sheets with Cu in essentially a square-planar coordination. An important feature in the phase diagram of the first two families is the existence of an antiferromagnetic (AF) insulating phase.[4] In the first family, the parent La_2CuO_4 is an antiferromagnet below 300 K, with a Néel temperature (T_N) that is strongly dependent upon dopant concentration and oxygen deficiency.[5,6] Actually, above T_N this system is a two-dimensional (2D) spin-$\frac{1}{2}$ Heisenberg AF with very strong exchange couplings among the intralayer Cu^{2+}, which give rise to large magnetic correlation lengths within the planes.[7] Thus, extremely weak interplanar couplings are sufficient to induce the 3D Néel state.[6-9] Furthermore, for doped $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{6+x}$ materials, the Néel state is destroyed, yet spin-spin correlations persist even in the superconducting phase.[6,9] The second family with a typical parent material $YBa_2Cu_3O_{6+x}$ ($x<0.4$), also displays 3D AF with T_N as high as 500 K for $x=0$;[10] similarly strong 2D spin-spin correlations in a single crystal with $x=0.2$ have also been reported recently.[11] Recent muon-spin rotation measurements have indicated that strong magnetic fluctuations also occur in selected members of the third family of superconductors.[12] For example, static magnetic order has been detected in insulating $Bi_2Sr_2YCu_2O_x$ below 200 K. Whether magnetic interactions prove to be pivotal in triggering superconductivity is yet to be determined; nevertheless, a global model must certainly take such magnetic properties into account.[4]

We have undertaken the present investigation to characterize the magnetic properties of the parent material of the $(AO)_y(B_2Ca_{n-1}Cu_nO_{2n+2})$ family of superconductors. For at least $n \leq 3$, the superconducting transition temperature increases with the number of CuO_2 layers.[13] For large n the stoichiometry of these compounds approaches $CaCuO_2$, i.e., a layered, defect perovskite structure free of intergrowths of other structural elements, with CuO_2 planes separated only by Ca atoms. Substitution of small amounts of Sr for Ca can stabilize this hypothetical tetragonal structure.[14] A single-crystal study by Siegrist *et al.*[15] confirmed that crystals of composition $(Ca_{0.86}Sr_{0.14})CuO_2$ contain $[CuO_2]_\infty$ layers with the Ca and Sr ions apparently occupying the interlayer, eightfold coordinate sites. Therefore, this compound (which was identified as the parent material of the Tl and Bi superconductors[15] and which also can be viewed as the end-member of all the superconducting cuprate perovskites) represents an ideal model system for the study and analysis of magnetic interactions and electronic structure in the layered cuprates. In this paper we report the results of powder-neutron diffraction and magnetic susceptibility $\chi(T)$ of this novel 2D solid.

Phase equilibria studies have shown that the tetragonal, defect-perovskite phase, $Ca_xSr_{1-x}CuO_2$ is stable over a very limited range of stoichiometry, approximately $0.83 \leq x \leq 0.87$. In this work powdered samples with $x=0.85$ were prepared by solid-state reaction in air from stoichiometric amounts of dried $CaCO_3$, $SrCO_3$, and CuO. The mixture was first heated for 6 h at 865 °C to eliminate CO_2, and successively ground and heated at temperatures ranging from 925 to 985 °C until the x-ray pattern was free of any peaks from impurity phases. All samples were air-cooled from the final synthesis temperature. Despite the limited range of composition, no evidence for long-range Ca-Sr order was found in either the x-ray or neutron-diffraction studies. Thermogravimetric analysis in air and oxygen indicated no detectable change in the oxygen stoichiometry up to the melting point

~985 °C; under a 30-Torr helium atmosphere no weight changes were observed until decomposition began at approximately 680 °C.

A 30-g sample was sealed in helium and mounted in either a Displex closed-cycle cooling system, or in a furnace on the H4S spectrometer at the Brookhaven National Laboratory High Flux Beam Reactor. A neutron wavelength of 2.37 Å was used along with a set of pyrolytic graphite filters capable of discriminating against the $\lambda/2$ component in the beam to better than 1 part in 10^4. At 298 K the lattice parameters are $a=3.86(1)$ Å and $c=3.20(1)$ Å, in good agreement with Ref. 15 (tetragonal $P4/mmm$ with one formula per unit cell). The R factor for four nuclear peaks compared with this structure is 0.03. We also observed Ca_2CuO_3 impurity peaks at the 1% level which were undetectable with x rays. Four additional peaks were indexed as $(\frac{1}{2}+h, \frac{1}{2}+k, \frac{1}{2}+l)$ suggestive of a 3D AF ordering; the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is the strongest, with 2.5% the integrated intensity of the (001) nuclear peak at 294 K. The $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ grows in intensity by 25% upon cooling to 10 K, and no additional peaks are seen at low T. Figure 1 shows that the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (294 K, solid circles) disappears at 557 K (open circles), indicating the loss of an ordered magnetic structure. Figure 2 shows the normalized intensity T dependence, which is characteristic of a continuous transition. The fitted curve is of the form $I \sim (1-T/T_N)^{2\beta}$ with $T_N=537\pm5$ K and $\beta=0.26\pm0.03$ (the fitted region is 290–550 K). The line shape is symmetric and resolution limited at all $T<T_N$ indicative of 3D long-range order. A careful search for x-ray scattering at the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ puts an upper bound of 0.3% of the (001) x-ray intensity for any nonmagnetic contribution. Polarized beam measurements on a single crystal show unequivocally that the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is magnetic in origin.

Therefore, we conclude that the peaks at the $(\frac{1}{2}+h, \frac{1}{2}+k, \frac{1}{2}+l)$ positions are characteristic of an AF spin structure. The magnetic structure depicted in Fig. 2 contains AF sheets similar to the in-plane ordering in

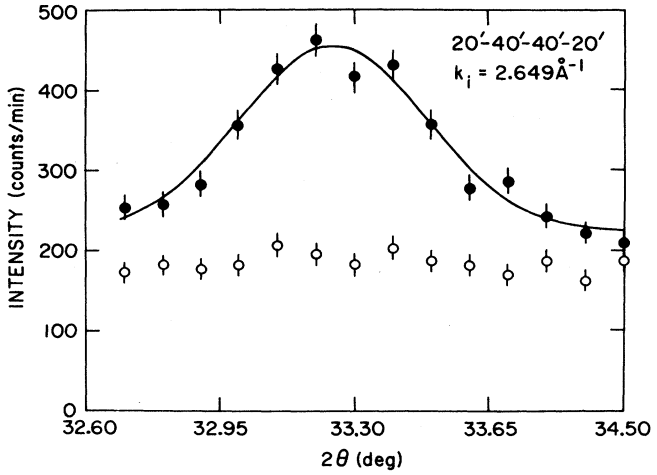

FIG. 1. Intensity vs Bragg angle 2θ for neutron-powder scans of the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ peak region at 557 K and at room temperature.

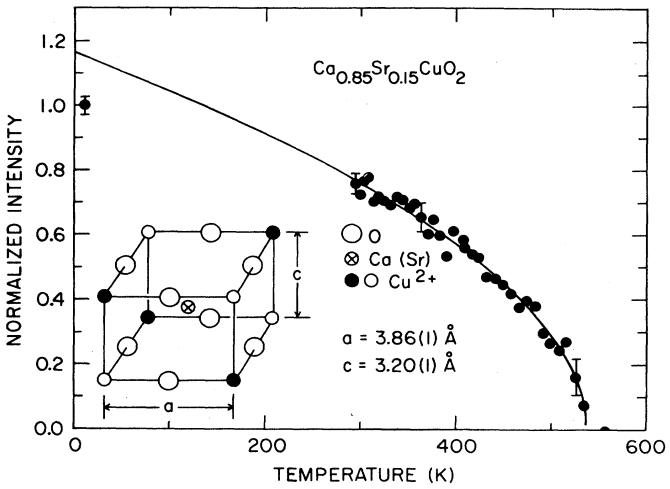

FIG. 2. The normalized integrated intensity (I) of the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ peak vs temperature. The full line is the fitted curve $I=C(1-T/T_N)^{2\beta}$, with $T_N=537\pm5$ K and $\beta=0.26\pm0.03$; the fit region was 290–550 K. Inset: Atomic positions and proposed magnetic spin structure of antiferromagnetic $(Ca_{0.85}Sr_{0.15})CuO_2$. Filled and open circles at Cu^{2+} sites indicate antiparallel spins.

La_2CuO_4 (Ref. 5) and $YBa_2Cu_3O_6$,[10] with AF stacking between adjacent layers similar to that observed in $YBa_2Cu_3O_6$.[10] The filled and open circles on the Cu^{2+} sites indicate antiparallel spins. We considered two models for the orientation of the magnetic moment: along the c axis ($\parallel$) and in the plane ($\perp$). It has been noted[16] that from a powder-diffraction pattern of a system with tetragonal symmetry, one can at most determine the spin direction with respect to the c axis but not within the plane. Table I compares the data on the magnetic peaks taken at 10 K with the two possible orientations of the magnetic moment. The values for the $(\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$ peak show that a model, in which the largest component of the magnetic moment is in the plane, is more likely. Using the form factor values of Ref. 17 we estimate the ordered magnetic moment to be $\langle\mu\rangle=0.51\pm0.05\mu_B$/Cu ion.

Magnetization data were obtained with a George Associates Faraday magnetometer in magnetic fields H up to 8 kG. The ferromagnetic impurity contribution to M was determined via $M(H)$ isotherms at four temperatures between 77 and 801 K; it was equivalent to the contribution of about 1.9 at. ppm of Fe metal impurities with respect to Cu, and is corrected for in the $\chi(T)$ data presented below.

TABLE I. The product of the ordered magnetic moment μ at 10 K and the form factor f determined from the magnetic reflections assuming the moment is along the c axis $(\mu f)_\parallel$ or lying in the a-b plane $(\mu f)_\perp$.

(hkl)	Q (Å^{-1})	$\sin(\theta)/\lambda$	$(\mu f)_\parallel$	$(\mu f)_\perp$
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	1.519	0.12	0.45(5)	0.41(5)
$(\frac{3}{2}, \frac{1}{2}, \frac{1}{2})$	2.680	0.22	0.29(6)	0.36(7)
$(\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$	3.174	0.25	0.78(10)	0.29(6)
$(\frac{3}{2}, \frac{3}{2}, \frac{1}{2})$	3.604	0.28	0.20(8)	0.23(8)

These data have also been corrected for a low-T Curie-Law contribution arising from $\simeq 0.19$ at.% of nearly isolated Cu^{2+} ($g=2$) defects and/or impurity phases.

The corrected $\chi(T)$ data between 4 and 700 K for $H=6.3$ kG are plotted in Fig. 3. The data above 400 K are very similar in form and magnitude to those for the related layered compounds $La_{2-x}Sr_xCuO_{4-y}$ and $YBa_2Cu_3O_{7-x}$.[6] We have included the corrected $\chi(T)$ data[6,18] for $YBa_2Cu_3O_{6.01}$ and $La_{1.95}Sr_{0.05}CuO_{4-y}$ in Fig. 3; these compounds were chosen for comparison because they both have Cu in a formal oxidation state close to +2 in CuO_2 layers and the Sr doping in the latter removes the anomalous ferromagnetic peak associated with long-range AF ordering in undoped La_2CuO_{4-y}.[5,6,8,9] From Fig. 3, the $\chi(T)$ data for the three compounds are remarkably similar. The data for all three compounds appear to be approaching high-temperature maxima as expected for 2D antiferromagnets. [In $La_{2-x}Sr_xCuO_{4-y}$ this postulated broad peak is brought into the temperature range of this measurement for Sr content $x \geq 0.1$ (Ref. 18).] This shows that the magnetic behavior of insulating members of the cuprate family is determined mainly by the CuO_2 sheets, with little influence from the other cations or out-of-plane oxygen ions. The broad maxima at $T \geq 800$ K are attributed[6,18] to the onset of short-range AF order within the CuO_2 layers upon cooling.[18] Below T_N, $\chi(T)$ is as expected; it is finite and nearly temperature independent below $T_N/2$, originating from the $\chi_\perp(T)$ contributions in the powder. Our results are consistent with the observation[7] of large spin-spin correlation lengths in the CuO_2 plane above T_N, so that the 3D ordering is induced by weak interplanar coupling between 2D AF entities, which are already well ordered but fluctuate in time. Therefore, from entropy considerations, only small effects are expected in the thermodynamic properties at T_N, consistent with the $\chi(T)$ data near T_N for $(Ca_{0.85}Sr_{0.15})CuO_2$ in Fig. 3. Closer inspection does reveal a small anomaly in $\chi(T)$ at T_N. In fact, the value of T_N (540 ± 10 K) extracted from the derivitive of $\chi(T)$ (see Fig. 4), is in excellent agreement with that obtained from the neutron scattering.

From simple electron counting considerations, $(Ca_{0.85}Sr_{0.15})CuO_2$ can be regarded as a Mott-Hubbard insulator if we think of the CuO_2 planes as being made of Cu^{2+} and O^{2-}, so that with the strong superexchange it should exhibit an AF ground state. The structure depicted in Fig. 2 shows copper in square planar coordination with oxygen bridging the nearest-neighbor Cu^{2+} and supplying the strong superexchange pathway between spins in the plane. The out-of-plane coupling between nearest-neighbor spins in adjacent layers originates either from direct exchange or dipole-dipole interaction, the latter energy being on the order of 0.02 K. In fact, a value for $J_\perp$ can be estimated using the simple argument[7,8] that the 3D AF transition occurs when $k_B T_N \sim J_\perp (\xi_{2D}/a)^2$, where ξ_{2D} and a are the correlation length and the in-plane lattice constant, respectively. Using the correlation length determined in Ref. 8, we get $J_\perp \sim 5$ K, implying that the coupling between planes originates from direct exchange between Cu ions in adjacent layers. At temperatures higher than T_N, the magnetic system is essentially 2D, so that we can estimate J_{2D} from the temperature $T_M = T(\chi^{max})$ of the maximum in $\chi(T)$,[19] $J_{2D} \sim T_M/S(S+1) \sim 1000$ K, which is of the same order as in the case of $La_{2-x}CuO_{4-y}$.[7]

We conclude by emphasizing the importance of $(Ca_{0.85}Sr_{0.15})CuO_2$ as an ideal model system for the study and analysis of the magnetic and electronic transport properties of the other 2D cuprate systems. The absence of any intergrowth layers of other structural elements should permit further detailed studies of the 2D and 3D spin correlations intrinsic to the CuO_2 sheets. However, the lack of intersheet intergrowths apparently severely hinders the synthesis of a doped metallic system. Our attempts to directly substitute the interlayer divalent cations with monovalent species and drive the system metallic have so far proved unsuccessful. However, further experiments using alternative substitution mechanisms and different synthetic techniques are still in progress.

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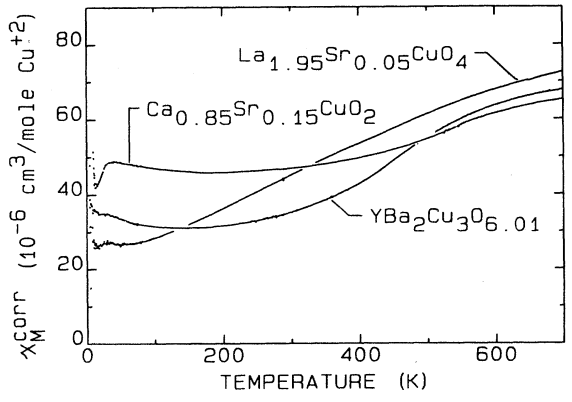

FIG. 3. Molar magnetic susceptibility corrected for the contribution of paramagnetic impurities/defects χ^{corr} vs temperature for $(Ca_{0.85}Sr_{0.15})CuO_2$, $La_{1.95}Sr_{0.05}CuO_{4-y}$ and $YBa_2Cu_3O_{6.01}$. The data for the latter two compounds are from Refs. 6 and 18.

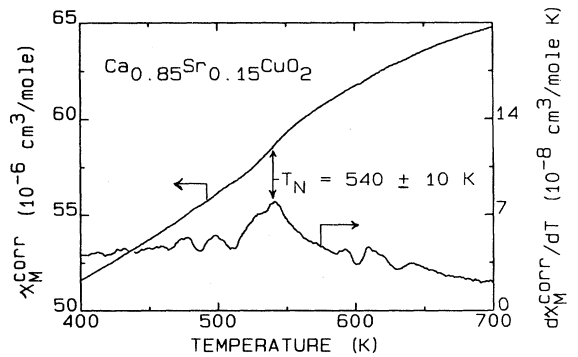

FIG. 4. Expanded plot of χ^{corr} vs temperature for $(Ca_{0.85}Sr_{0.15})CuO_2$, in the vicinity of T_N. Also shown is the temperature derivative of $\chi(T)$, clearly indicating the antiferromagnetic transition at 540 ± 10 K.

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*Also at Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, NJ 08801. Mailing address: Phys. Bldg. 510/B, Brookhaven National Laboratory, Upton, NY 11973.

†Also at Materials Science Department, University of Pennsylvania, Philadelphia, PA 19104.

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