Antiferromagnetism in La_2CuO_{4-y}

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Powder neutron diffraction studies of undoped La_2CuO_{4-y} have revealed new superlattice peaks below $\simeq 220$ K. The absence of corresponding x-ray superlattice lines and an observed susceptibility anomaly near 220 K suggest the occurrence of antiferromagnetism. From the magnetic peak intensities we deduce a structure consisting of ferromagnetic sheets of Cu spins alternating along the [100] orthorhombic axis, with the spins aligned along the [001] orthorhombic axis. The low-temperature magnetic moment is approximately $0.5\mu_B$/Cu-atom. The tetragonal-orthorhombic transition at 505 K has also been studied.

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We report on a powder neutron and x-ray diffraction study of the compound La_2CuO_{4-y}, which is the parent compound for the doped high-T_c superconductors of the type $La_{2-x}B_xCuO_{4-y}$, where B = Ca, Sr, or Ba.[1-4] The behavior of the undoped material La_2CuO_{4-y} is of interest as the starting point for a discussion of the physics of the superconducting compounds, particularly with regard to an evaluation of unusual microscopic mechanisms for superconductivity. In fact La_2CuO_{4-y} may itself be superconducting.[5]

It is known[6-9] that pure La_2CuO_{4-y} is tetragonal at high temperatures and undergoes an orthorhombic distortion at lower temperatures. Neutron-diffraction studies on this compound have been carried out by Jorgensen *et al.*[7] and structural refinement has been done at several temperatures. The tetragonal-orthorhombic transition temperature T_0 is highly sensitive to the concentration of oxygen vacancies (y) in the material,[8,9] varying from 450 to 530 K, depending on y. Magnetic susceptibility anomalies also occur in the undoped samples of La_2CuO_{4-y}, indicative of possible antiferromagnetic transitions at lower temperatures. The temperature at which the susceptibility anomaly occurs is highly sensitive to the value of y, increasing from $T_N \approx 0$ for $y = 0$ to $T_N \approx 295$ K for $y \approx 0.03$.[8] The anomaly disappears for $La_{2-x}Sr_xCuO_{4-y}$ samples doped with Sr concentrations $x \gtrsim 0.1$.

The La_2CuO_{4-y} sample studied here was prepared in air at 950 °C and oven-cooled in air with use of the normal ceramic-preparation techniques described in the literature.[8,9] The susceptibility and ESR data for this sample are given in Ref. 8. The sample was determined gravimetrically to have an oxygen-vacancy concentration corresponding to the formula La_2CuO_{4-y}, where $y \approx 0.015$.[8] The sample was sealed in a low-pressure helium atmosphere and mounted in either a Displex refrigerator or an oven on the neutron spectrometers *H*-4*S* and *H*-4*M* at the Brookhaven National Laboratory High Flux Beam Reactor. A neutron wavelength of $\lambda = 2.37$ 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. Powder neutron diffraction studies at room temperature revealed no detectable impurity-phase lines at an intensity level of 1% of a typical La_2CuO_{4-y} line, i.e., the (200) line. At room temperature, a profile-refinement analysis showed the powder diffraction pattern to be consistent with the orthorhombic structure parameters found by other workers.[6,7] The space group is *Cmca*; the a and c axes lie in the basal plane parallel to the Cu-O layers, and the b axis is along the high-temperature tetragonal c axis.

Figure 1 shows the measured order parameter η of the orthorhombic distortion, i.e., the quantity $2(c-a)/(c+a)$, as a function of reduced temperature T/T_0 (T_0 was found to be 505 K), along with the values of c and a. Also shown is the neutron diffraction intensity I of a typical orthorhombic peak, in this case the (041), which is forbidden in the tetragonal phase. Both data sets indicate a second-order phase transition, and are consistent with our x-ray diffraction results (300–900 K, not shown). From Fig. 1, I is not proportional to the square of the orthorhombic distortion. This behavior is consistent with the fact that there also occurs a rotation of the oxygen octahedra around each copper atom, causing a doubling of the unit cell.[7] It has been suggested that the orthorhombic distortion and oxygen-octahedron rotation may even occur at different temperatures.[10] Our data on the present sample indicate that these temperatures, if different, are within $\simeq 10$ K of each other. It can be shown that $I^{1/2}$ is proportional to the octahedral rotation order parameter δ for small δ. The fitted curves in Fig. 1(b) illustrate $(1-T/T_0)^{0.476}$ behavior for the (041) peak intensity and $(1-T/T_0)^{0.744}$ behavior for η. While the precision of the data does not warrant an interpretation of these exponents in terms of critical exponents, the fits to the data do reveal that $\delta^3 \propto \eta$ to within our measurement accuracy over the full range of temperatures measured.

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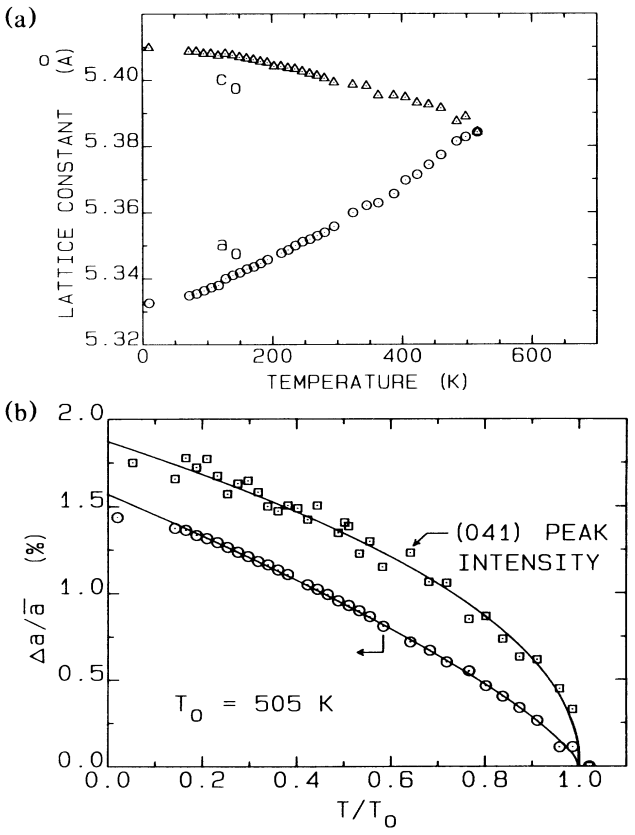

FIG. 1. (a) Orthorhombic lattice constants a and c vs temperature. (b) Orthorhombic distortion η and (041) nuclear reflection intensity (arbitrary units) vs reduced temperature (T_0=505 K); the solid curves are power-law fits with the data as discussed in the text.

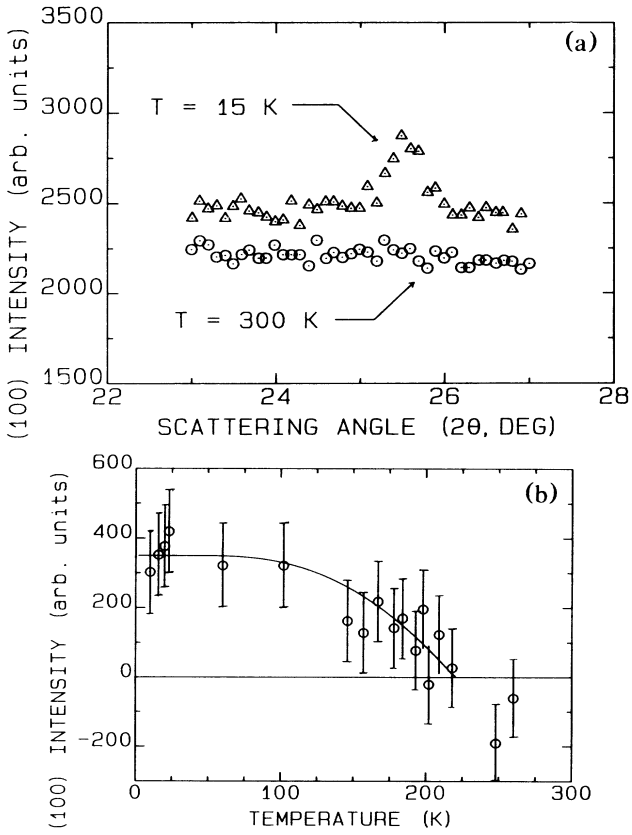

FIG. 2. (a) Intensity vs scattering angle 2θ for neutron powder scans of the (100) peak region at 15 K and at room temperature. (b) (100) peak intensity vs temperature. The line is a spin-$\frac{1}{2}$ magnetization curve for T_N=220 K, calculated from molecular-field theory.

As the sample was cooled below 200 K, an additional weak peak [0.5% of the (200) peak intensity] appeared at the (100) position of the orthorhombic structure. The instrumental resolution was sufficient to determine that it could not be a (001) peak. This peak at 15 K is shown in Fig. 2(a) and compared to the same scan carried out at room temperature. The (100) peak intensity (measured as peak height above background) is plotted versus temperature in Fig. 2(b) indicating an ordering temperature of $\simeq 220 \pm 10$ K. The symmetric line shape of the peak indicates three-dimensional ordering, in contrast to the asymmetric shape characteristic of two-dimensional ordering.[11] The peak width is resolution limited, indicating that the ordering is of long range. Additional low-temperature peaks were also found at the (011), (031), (120), and (300) positions, all of which are forbidden by the orthorhombic crystal structure. X-ray powder diffraction experiments carried out on a rotating-anode source did not reveal any (100) or (001) peaks to within 0.1% of the (002) nuclear peak intensity. It seemed possible that a model involving oxygen-vacancy ordering might explain these observed superlattice reflections.[9] However, preliminary calculations indicate that unrealistically high vacancy concentrations would be required to explain the observed intensities of these reflections, and the lack of corresponding x-ray peaks argues against such an interpretation. Similarly, a displacive structural phase transformation would yield superlattice peaks with intensities increasing roughly as $(\sin\theta/\lambda)^2$, contrary to observation. A recent neutron diffraction study of La_2CuO_{4-y} by Yamaguchi *et al.*[12] was interpreted as indicating antiferromagnetism modulated along the [001] axis, on the basis of an increasing intensity at the (021) peak position with decreasing temperature below 240 K. We doubt this interpretation since our (021) peak has no magnetic contribution.

We therefore conclude that the (100) and the other four peaks noted above are characteristic of an antiferromagnetic spin structure whose onset is associated with the susceptibility anomaly. From an analysis of the integrated intensities of the (100), (011), and (031) peaks, and assuming a magnetic moment on the copper sites only, we find that the spins are aligned along the [001] axis, while the antiferromagnetic modulation is along the

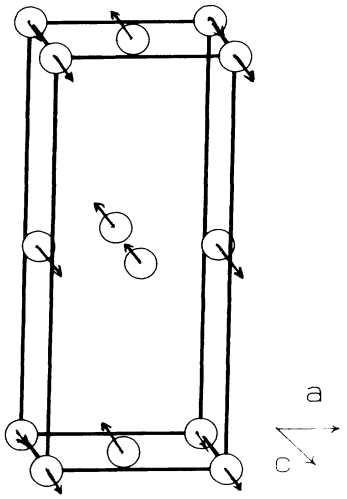

FIG. 3. Proposed spin structure of antiferromagnetic La_2CuO_{4-y}. Only copper sites in the orthorhombic unit cell are shown for clarity.

[100] axis. The corresponding spin structure is depicted in Fig. 3. This structure is similar to the well-known antiferromagnetic structure of the similar compound K_2NiF_4, which, however, has the undistorted tetragonal crystal structure and a slightly different ordered spin structure.[13]

From the assumed structure and the integrated magnetic nuclear peak intensities we may deduce μf for each magnetic reflection, where μ is the copper magnetic moment in Bohr magnetons (μ_B) and f is the copper magnetic form factor. The values of μf at 11 K deduced from the intensities of the (100), (011), (120), and (031) peaks are 0.35, 0.33, 0.374, and 0.384, respectively. The corresponding values of $\sin\theta/\lambda$ are 0.093, 0.10, 0.120, and 0.147. Measurements of the Cu magnetic form factor $f(Q)$ in the related compound[14] K_2CuF_4 indicate a shoulder at roughly the above $\sin\theta/\lambda$ values due to covalency effects. Thus the nondecreasing values of μf are consistent with such a form within experimental error. However, K_2CuF_4 is a ferromagnet and the shoulder on the form factor may arise from interference effects associated with an opposed F^--ion moment. It is not clear whether the oxygen ions in the present compounds would contribute in this way to the form factor. Single-crystal data are required to resolve better this question regarding the form factor. Note that the (120) peak sits on the shoulder of a nuclear (021) peak and its intensity estimate is subject to greater error. The (300) peak encompasses a total of four magnetic reflections [(300), (013), (071), and (251)] as well as the weak nuclear (152) peak and thus its intensity was not used in calculating μf.

With the assumption of a value[14] of $f(Q)\approx 0.75$ at the observed $\sin\theta/\lambda$ values, the Cu moment at 11 K is calculated to be $(0.48\pm 0.15)\mu_B$. On the other hand, the assumption of a pure Cu^{++} form factor (unlike that of K_2CuF_4) would yield a slightly smaller moment per Cu atom, i.e., $0.4\mu_B$, which is within the error limits just quoted. An assumption of Cu^{++} ions with spin $S=\frac{1}{2}$ and g factor[8b] $g=2.28$ would yield a moment of $\mu=gS\mu_B=1.14\mu_B$ per Cu ion. The observed lower value may arise from quantum zero-point fluctuations and/or covalency effects; alternatively, a subset of the copper ions may not carry a local magnetic moment, possibly because of inhomogeneous oxygen-vacancy concentrations. Figure 2(b) shows a spin-$\frac{1}{2}$ molecular-field calculation of the magnetization, assuming $T_N=220$ K. T_N as observed occurs somewhat below the peak of the susceptibility anomaly (230 K) observed by Johnston *et al.*[8a] for the same sample, suggesting possible antiferromagnetic fluctuation effects above T_N as might have been anticipated from the planar configuration of the Cu atoms within the structure.

As noted above, the existence of a small oxygen-vacancy concentration ($y>0$) appears to be crucial for promoting antiferromagnetism, as other La_2CuO_{4-y} samples with increasing oxygen concentrations closer to stoichiometry do not seem to exhibit magnetic ordering.[8] The fact that a magnetic instability occurs in pure La_2CuO_{4-y} has interesting implications for possible correlation-induced mechanisms of superconductivity in the corresponding doped compounds.[15-18] In principle, the occurrence of the Néel state means that the "resonating valence bond" or spin-liquid idea[15] for the ground state of pure La_2CuO_{4-y} may have to be modified (at least when oxygen vacancies are present), but it does mean that electron correlation effects are important in these materials. It is interesting that the ordering does not further double the orthorhombic unit cell, and in fact occurs at the wave vector which corresponds closely to the nesting–Fermi-surface instability in the tetragonal (undistorted) phase.[7,19,20] A crucial unanswered question in this context is whether the magnetic moment on the copper ions survives in the superconducting compositions. Further neutron scattering experiments may help to resolve this issue.

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