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Structural phase transitions and weak ferromagnetism in $La_{2-x}Nd_xCuO_{4+\delta}$

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When cooled, $La_{2-x}Nd_xCuO_{4+\delta}$ undergoes structural transformations involving tilts of the CuO_6 octahedra which can be controlled by varying x and δ. Using synchrotron x-ray and neutron powder diffraction we observe that the transformation from *Bmab* to *Pccn* space-group symmetry is accompanied by a 90° copper spin reorientation in the basal plane. Furthermore, a second magnetic transition at lower temperatures yields weak ferromagnetism. These observations may have important implications for the suppression of superconductivity in the $P4_2/ncm$ phase of $La_{1.875}Ba_{0.125}CuO_4$.

The correlation[1,2] of a drastic suppression of superconductivity in $La_{2-x}Ba_xCuO_4$ when $x\sim\frac{1}{8}$ with a structural phase transformation from orthorhombic *Bmab* to tetragonal $P4_2/ncm$ space-group symmetry has generated much interest. These structures are distinguished only by subtle differences in the tilting pattern of the CuO_6 octahedra in the copper oxygen sheets, and it is believed that important clues to the origin of high-temperature superconductivity may be obtained by unraveling the explanation for this phenomenon.

In La_2CuO_4-derived materials there are three observed structures[2,3] which involve rotations of the CuO_6 octahedra about the [110] and [1$\bar{1}$0] axes of the (undistorted) high-temperature tetragonal (HTT, *I4/mmm*) phase. The three (distorted) phases are the low-temperature orthorhombic 1 (LTO1, *Bmab*) phase, a lower symmetry low-temperature orthorhombic 2 (LTO2, *Pccn*) phase, and the low-temperature tetragonal (LTT, $P4_2/ncm$) phase. In the LTO1 phase the CuO_6 octahedra rotate about *either* the [110] or [1$\bar{1}$0] axes, whereas in the LTO2 and LTT structures rotations about *both* of these axes are simultaneously present. The absolute magnitudes of the two rotations are equal in the LTT structure, but unequal in the LTO2 structure. Thus the LTO2 structure can be viewed as intermediate between the LTO1 and LTT structures. The LTO2 and LTT structures arise from the condensation of the second of the degenerate CuO_6 octahedra tilting phonons at the Brillouin zone boundary of the HTT phase.[2,4] In fact, the LTO1 phase of La_2CuO_4 exhibits an incipient instability toward these transformations, as shown by the partial softening of the second zone boundary phonon with decreasing temperature observed by inelastic neutron scattering.[5]

In this paper we describe the results of structural and magnetic studies of the insulating materials $La_{2-x}Nd_xCuO_{4+\delta}$, where $\delta\sim0-0.03$. The substitution of Nd^{3+} for La^{3+} (ionic radii[6] of 1.163 Å and 1.216 Å, respectively) enhances incipient instability of La_2CuO_4, resulting in the appearance of low-temperature structural transformations similar to the LTO1$\rightarrow$LTT transformation[2] in $La_{1.875}Ba_{0.125}CuO_4$. We find these transformations to be very sensitive to the values of x and, in particular, δ. Furthermore, using neutron powder diffraction we observe two magnetic phase transitions in $La_{1.80}Nd_{0.20}CuO_{4.000(5)}$, one concurrent with the LTO1$\rightarrow$LTO2 structural transformation and the other at lower temperature in the LTO2 phase. Magnetic susceptibility and neutron diffraction data demonstrate that this low-temperature magnetic phase is a weak ferromagnet.

Samples of $La_{2-x}Nd_xCuO_{4+\delta}$ were prepared as described previously.[3] Oxygen contents were determined by iodometric titration. Thermogravimetry showed that the loss of excess oxygen proceeded rapidly at temperatures in excess of 425 °C and oxygen partial pressures below 10^{-5} Torr. The thermogravimetric data were in good agreement with the titration data, indicating δ values of 0.03–0.05 before N_2 reduction and $\delta<0.005$ after reduction. Samples were therefore annealed under these conditions to obtain materials which were nearly stoichiometric. Synchrotron x-ray powder diffraction measurements were performed at beamlines X-3A and X-7A at the National Synchrotron Light Source, Brookhaven National Laboratory. Neutron powder diffraction measurements were performed on a triple-axis spectrometer at beamline H-4S at the High Flux Beam Reactor, Brookhaven National Laboratory, using 20'-40'-40'-20' collimation, pyrolytic graphite (002) monochromator and analyzer, and a single pyrolytic graphite filter. The neutron wavelength was 2.373 Å and the resolution ($\Delta Q/Q$) was $\sim$0.03 $Å^{-1}$. Magnetic susceptibility measurements were made using a Quantum Design superconducting quantum interference device (SQUID) magnetometer.

As prepared in air, $La_{2-x}Nd_xCuO_{4+\delta}$, $\delta>0$, undergoes a LTO1$\rightarrow$LTO2 phase transformation,[3] the details of which depend upon the value of x. In Fig. 1 we show orthorhombicity versus temperature data for $La_{1.8}Nd_{0.2}CuO_{4.012(5)}$ and $La_{1.65}Nd_{0.35}CuO_{4.030(5)}$ determined by synchrotron x-ray powder diffraction. The LTO1$\rightarrow$LTO2 transition appears as a continuous decrease in the orthorhombicity at temperatures below 100 K. The LTO1 to LTO2 transition is second order (continuous), as allowed by the symmetries of the two structures.

When the oxygen content of these materials is reduced to a near stoichiometric value, the degree of orthorhombic distortion in the low-temperature structures significantly decreases. As shown in Fig. 1, stoichiometric $La_{1.8}Nd_{0.2}CuO_{4.000(5)}$ undergoes a nearly first-order transformation to LTO2 symmetry. The low-temperature orthorhombicity of the stoichiometric material is considerably smaller than that of the sample containing excess oxygen (Fig. 1). Furthermore, in $La_{1.65}Nd_{0.35}CuO_{3.996(2)}$ the orthorhombicity essentially disappears completely below 40 K, leading to the conclusion that the low-temperature phase in this material has the LTT structure. Thus the low-temperature structures of materials with controlled oxygen stoichiometries can be systematically changed from LTO1 (when $x=0$) to LTO2 to LTT by adjusting the Nd^{3+} content.

We now describe the results of measurements of the magnetic properties of these materials. In Fig. 2 we present neutron powder diffraction data for $La_{1.8}Nd_{0.2}CuO_{4.000(5)}$, which has LTO1 symmetry above 80 K but transforms to LTO2 symmetry below that temperature. We observe no magnetic reflections at 320 K, a temperature which is above the Néel temperature of 290 K determined from magnetic susceptibility measurements. At 80 K we observe the (100) and (011) magnetic reflections, which have an intensity ratio consistent with the La_2CuO_4-type magnetic structure,[7,8] that is, with the Cu^{2+} moments oriented in the [010] direction and an antiferromagnetic propagation vector parallel to the [100] direction. At 8 K the (100) reflection is no longer present, but instead we observe the (010) magnetic reflection, indicating that the Cu moments in the LTO2 phase are now oriented in the [100] direction with an antiferromagnetic propagation vector in the [010] direction.[8] Thus the 8 K neutron diffraction data demonstrate that the LTO1→LTO2 structural transformation is accompanied by a spin reorientation in which the moments rotate from alignment along the crystallographic b axis to alignment along the a axis. We have also obtained magnetic neutron diffraction data at 5.5 and 1.4 K (Fig. 2). At these temperatures we no longer observe the (010) magnetic reflection, but the (101) reflection is still present. These data therefore demonstrate that a second magnetic phase transition occurs in which the Cu spins adopt a magnetic structure similar to that of La_2NiO_4, that is, where the Cu moments and the antiferromagnetic propagation vector are both parallel to the [100] direction.[9] This magnetic structure is derived from the 8 K structure by rotating the spins in every other CuO_2 layer by 180°. In Fig. 3 we show schematically the three magnetic structures observed in $La_{1.80}Nd_{0.20}CuO_{4.000(5)}$. Finally, by comparing the intensities of the (100) magnetic reflection and the (200) nuclear reflection we estimate the ordered Cu^{2+} magnetic

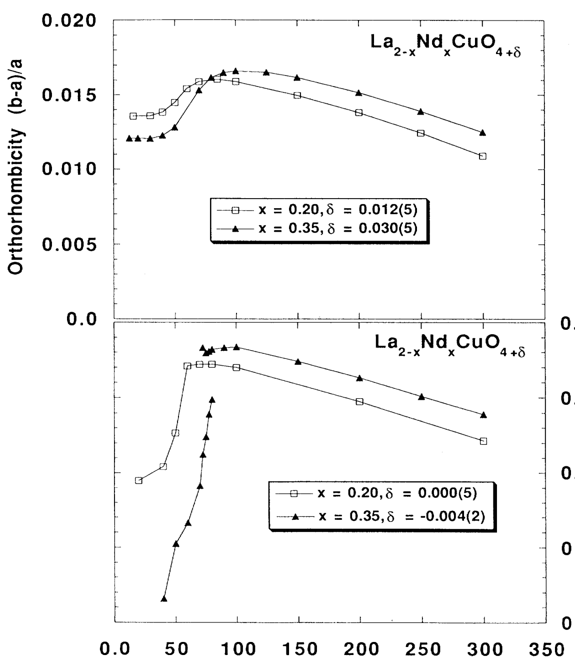

FIG. 1. Synchrotron x-ray powder diffraction measurements of orthorhombicity vs temperature for $La_{2-x}Nd_xCuO_{4+\delta}$ prepared in air (top) and after oxygen reduction (bottom). Note that the second-order (continuous) LTO1→LTO2 transformations in oxygen excess materials become nearly or completely first order (discontinuous) in the reduced materials.

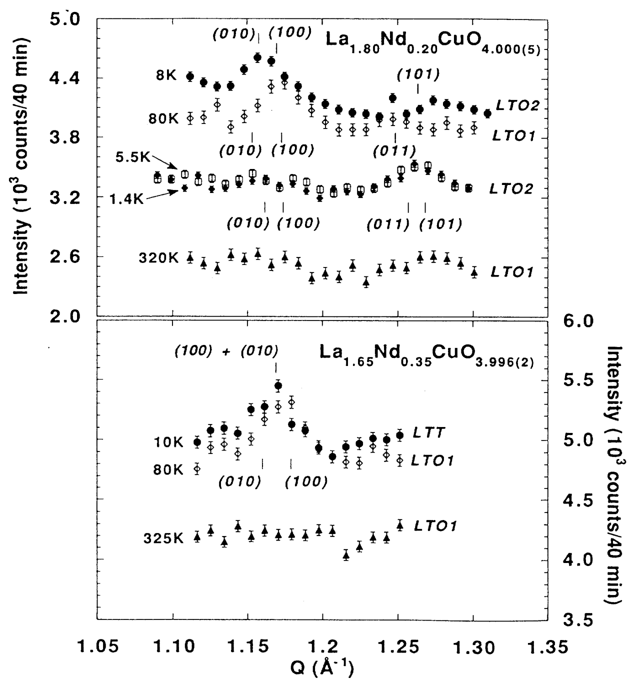

FIG. 2. Powder neutron diffraction measurements of antiferromagnetic Bragg reflections in $La_{1.8}Nd_{0.2}CuO_{4.000(5)}$ (top) and $La_{1.65}Nd_{0.35}CuO_{3.996(2)}$ (bottom) at several temperatures. Q is defined as $(4\pi\sin\theta/\lambda)$, where $\lambda=2.373$ Å and 2θ is the scattering angle. The labeled tick marks are the expected positions for the magnetic reflections as determined from measurements of nuclear Bragg reflections by neutron diffraction. The tick marks below the 5.5 and 1.4 K scans are based upon the 1.4 K nuclear Bragg positions. The lattice parameters (Å) determined by neutron diffraction are $La_{1.80}Nd_{0.20}CuO_{4.000(5)}$: (8 K, LTO2) a=5.373(1), b=5.428(1), c=13.124(2), (80 K, LTO1) a=5.357(1), b=5.448(1), c=13.126(2); $La_{1.65}Nd_{0.35}CuO_{3.996(2)}$: (10 K, LTT) a=b=5.374(4), c=13.033(8), (80 K, LTO1) a=5.329(2), b=5.417(2), c=13.034(4).

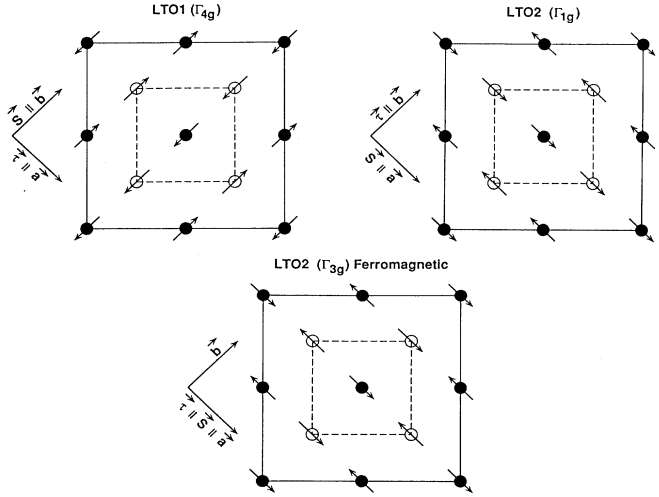

FIG. 3. Magnetic structures observed in $La_{1.80}Nd_{0.20}CuO_{4.999(5)}$ at 80 K (LTO1, Γ_{4g}), 8 K (LTO2, Γ_{1g}), and $T<6$ K (LTO2, Γ_{3g}, ferromagnetic). The perspective is looking down the c axis, and the solid and open circles represent Cu^{2+} ions in adjacent layers. The directions of the Cu^{2+} moments (**S**) and the antiferromagnetic propagation vectors (τ) are also shown.

moment to be $(0.6\pm0.2)\mu_B$.

In Fig. 2 we also show magnetic neutron diffraction data for reduced $La_{1.65}Nd_{0.35}CuO_{3.996(2)}$. There are no magnetic reflections present in the LTO1 phase at 325 K, which is above the Néel temperature of 318 K determined from magnetic susceptibility measurements. At 80 K the (100) reflection is present, but at 10 K we cannot distinguish whether the observed peak at 1.17 $Å^{-1}$ is the (100) or (010) magnetic reflection, which will appear at the same position in this tetragonal structure. From the observed magnetic scattering intensity we estimate the ordered moment to be $(0.6\pm0.2)\mu_B$, the same within error as the values found in $La_{1.80}Nd_{0.20}CuO_{4.000(5)}$ and La_2CuO_4.[7,8]

It is known[10] that the LTO1 phase of La_2CuO_4 is metamagnetic. This is due to a small net *ferromagnetic* moment, oriented parallel to the c axis, which is a result of the out-of-plane canting of the Cu moments. This canting is produced by the tilting of the CuO_6 octahedra through the Dzyaloshinsky-Moriya interaction,[10,11] that is, through the antisymmetric contribution to the in-plane superexchange. The ferromagnetic moment in each Cu-O plane is weakly antiferromagnetically coupled to the ferromagnetic moments in the adjacent layers, which permits a ferromagnetic interlayer arrangement to be stabilized if a sufficiently large magnetic field is applied parallel to the c axis.[10] This first-order, field-driven transformation is easily visible in magnetic susceptibility measurements and in neutron diffraction measurements where *the (100) reflection vanishes in the high field ferromagnetic phase.*[10]

As Nd^{3+} is partially substituted for La^{3+}, however, we observe the metamagnetic transition to shift to lower fields both with decreasing temperature and increasing Nd^{3+} concentration. Furthermore, at low temperatures a number of these materials exhibit a spontaneous magnetization, that is, *they are weak ferromagnets.* This is demonstrated in Fig. 4 where we show magnetic hysteresis loops for $La_{1.8}Nd_{0.2}CuO_{4.000(5)}$ and $La_{1.65}Nd_{0.35}CuO_{3.996(2)}$ at 2 K. The neutron diffraction measurements described above demonstrate that the magnetic order in the LTO1 phases of these materials is consistent with a Γ_{4g} magnetic mode, whereas in the LTO2 and LTT structures the magnetic structures correspond to a Γ_{1g} magnetic mode at high temperatures and a Γ_{3g} magnetic mode ($Pc'c'n$ or $P4_2/nc'm'$ magnetic symmetry) at low temperatures.[12] The Γ_{3g} mode, *for which the (100) and (010) reflections are not allowed,* permits a ferromagnetic polarization parallel to the c axis.[12] Thus the presence of the ferromagnetic Γ_{3g} mode at low temperature offers a consistent explanation for both the presence of hysteresis in the magnetization data of Fig. 4 and the disappearance of the (010) magnetic neutron diffraction peak at 5.5 and 1.4 K in $La_{1.80}Nd_{0.20}CuO_{4.000(5)}$ (Fig. 2). The magnetization and neutron diffraction data also indicate a coexistence of the Γ_{1g} and Γ_{3g} magnetic modes at intermediate temperatures, similar to the coexistence observed in Pr_2NiO_4.[12] This coexistence is most pronounced in the $La_{1.65}Nd_{0.35}CuO_{3.996(2)}$ sample. Whether these two modes are coherently superimposed or simply exist in different regions of the sample cannot be determined from our data.

In samples of $La_{2-x}Nd_xCuO_{4+\delta}$, where δ is close to zero, weak ferromagnetism is first observed at 2 K when x is as small as 0.05. As x increases, the onset temperatures for weak ferromagnetism increase until, at $x\sim0.35$, the weak ferromagnetism persists to a temperature of about 30 K, above which the material is metamagnetic.

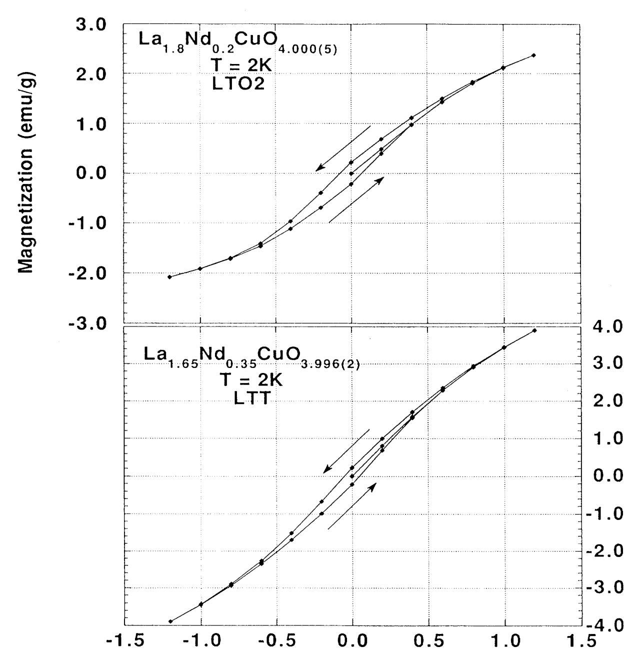

FIG. 4. Magnetic hysteresis curves at 2 K for (top) $La_{1.8}Nd_{0.2}CuO_{4.000(5)}$ and (bottom) $La_{1.65}Nd_{0.35}CuO_{3.996(2)}$. The arrows indicate the direction in which the magnetic field was changed during data collection.

(The Nd^{3+} solubility is limited to $x \sim 0.35-0.40$ by the T/T' phase boundary under our preparation conditions.) The introduction of Nd^{3+} simultaneously stabilizes the additional tilt of the CuO_6 octahedra leading to the LTO2 and LTT structures, with the LTT structure appearing only at the highest Nd^{3+} concentrations possible. Introducing excess oxygen suppresses the structural transformations and depresses the temperature of the magnetic transition to the weakly ferromagnetic state. For example, the samples shown in the top frame of Fig. 1 exhibit weak ferromagnetism at 2 K, but have reverted to metamagnetic behavior (that is, the Γ_{3g} magnetic mode has transformed to the Γ_{1g} mode) at temperatures of only 5–10 K, in comparison with 10–30 K for the stoichiometric materials. The spontaneous moments at 2 K estimated from the powder magnetic susceptibility data for the compositions in Fig. 1 are 0.06 Bohr magnetons (μ_B) for $x=0.20$ and $\delta=0.000(5)$, $0.04\mu_B$ for $x=0.20$ and $\delta=0.012(5)$, $0.05\mu_B$ for $x=0.35$ and $\delta=-0.004(2)$, and $0.04\mu_B$ for $x=0.35$ and $\delta=0.030(5)$. More detailed characterization of samples with excess oxygen is in progress and the results will be described elsewhere.

Finally, we discuss possible implications of these observations for the $La_{2-x}Ba_xCuO_4$ system, where a dramatic suppression of superconductivity has been reported in the LTT phase when $x=\frac{1}{8}$. It has recently been discovered[13] using muon spin resonance that $La_{1.875}Ba_{0.125}CuO_4$ magnetically orders at temperatures near 35 K. The type of magnetic order is not known, although the muon data are similar to those obtained in La_2CuO_4 below its Néel temperature, which suggests that the Cu moments order antiferromagnetically. Our results, however, show that antiferromagnetic order in the LTT phase could be accompanied by ferromagnetic alignment of the out-of-plane canted component of the Cu moments. Some early evidence for this may be the weak upturn of the magnetic susceptibility reported[14] for $La_{1.875}Ba_{0.125}CuO_4$ at temperatures below 50 K in the LTT phase. This susceptibility upturn is difficult to reconcile with a decrease in the density of states due to the structural transformation,[14] which was postulated to explain both the resistive upturn and suppressed T_c in this material. Weak ferromagnetism, however, would be expected to produce such an increase in the magnetic susceptibility.

A number of explanations have been advanced for the suppression of T_c in the LTT phase, including a decreased density of states at the Fermi level due to band splitting associated with the LTO→LTT structural transformation,[15] a charge density wave,[16] formation of localized bipolarons,[17] and commensurate antiferromagnetism due to spin-orbit coupling of Cu moments and itinerant holes.[18] At present there is no consensus on which of these, if any, is the correct explanation. In this paper we have presented evidence for the existence of weak ferromagnetism in insulating phases with the LTT and LTO2 structures, which indicates that the effective interlayer magnetic coupling may change sign as a consequence of the change from LTO1 to LTO2 or LTT symmetry. The suppression of T_c in the hole-doped LTT phases should be reconsidered in light of these findings. It has long been realized[19] that ferromagnetism and superconductivity are generally incompatible, making it plausible that pair breaking by the ferromagnetically aligned canted Cu moments contributes to the suppression of T_c in the LTT phases. If, in addition, spin-orbit coupling favors commensurate antiferromagnetic order[18] only near $x=\frac{1}{8}$, accompanying weak ferromagnetism may account for the drastic T_c suppression observed at this hole concentration.[2] Since the interlayer transport properties are also affected by the form of interlayer magnetic order,[10] it is not difficult to believe that a spin reorientation in the LTT phase could strongly influence superconductivity.

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