Order-Disorder Structural Phase Transition in $La_{2-x}Sr_xCuO_{4+\delta}$ at 150 K

J. Saylor and C. Hohenemser
Department of Physics, Clark University, Worcester, Massachusetts 01610
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Using perturbed $\gamma\gamma$ angular correlations of ^{111}In in the La site, we report a structurally disordered phase in oxygen stoichiometric $La_{2-x}Sr_xCuO_{4+\delta}$. So far this phase has been defined for $0 \leq x \leq 0.07$, involves a reversible order-disorder transition at $T_d = 150(20)$ K, and is observed by changes in the electric-field gradient (EFG). These changes involve a continuous *broadening* of the EFG distribution and *decrease* of the average EFG asymmetry parameter as $T \rightarrow 0$. The new disordered phase is associated with a loss of 3D magnetic order in the range $0.015 < x < 0.018$, and may be due to short-range disorder in the tilting of the CuO_6 octahedra as proposed by Egami *et al.*

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As one of the first high-temperature superconductors, $La_{2-x}Sr_xCuO_{4+\delta}$ has been the object of numerous studies since 1987.[1] Structural studies have shown that oxygen stoichiometric material ($\delta = 0$) has a tetragonal (T) and an orthorhombic (O) phase believed to exhibit long-range crystalline order. The T-O phase boundary decreases from 530 to 0 K for $0 \leq x < 0.2$. The material is antiferromagnetic for $x < 0.018$, superconducting for $0.06 < x < 0.3$, with a possible spin-glass phase in between.

X-ray and neutron diffraction have established *Cmca* symmetry in the orthorhombic phase for materials of the form $La_{2-x}M_xCuO_{4+\delta}$ (M denotes metal ion).[2-4] Nevertheless, the possibility remains that the low-temperature structure is more complicated.[5] Broadening of structural Bragg peaks beyond instrumental resolution has been noted for $La_{2-x}Sr_xCuO_{4+\delta}$,[6] $La_{2-x}Ba_xCuO_{4+\delta}$,[7] $La_2NiO_{4+\delta}$,[8] and $La_2CoO_{4+\delta}$.[9] In addition, below 70 K a first-order transition in $La_{2-x}Ba_xCuO_{4+\delta}$ has been observed by Axe *et al.*,[10] whereas for pure $La_2CuO_{4+\delta}$ similar local structure has been seen by Egami *et al.*[11]

The present work applies perturbed $\gamma\gamma$ angular correlations (PAC) to the low-temperature structure of $La_{2-x}Sr_xCuO_{4+\delta}$. Based on the extreme sensitivity of the electric-field gradient (EFG) to small deviations in the local symmetry, PAC studies can be used to draw distinctions between long- and short-range order. Because experiments may be performed on masses as low as ~ 5 mg at any temperature, the method has advantages over nuclear resonance and x-ray and neutron diffraction.

Like nuclear resonance, PAC provides details about the electronic environment of the probe nucleus. For counters set at an angle θ, nuclear hyperfine structure is revealed via the time-dependent coincidence rate $C(\theta,t)$ between γ rays that respectively populate and depopulate a given nuclear excited state.[12] Under favorable conditions this behavior is uniquely fitted by the principal components of the diagonalized EFG, V_{xx}, V_{yy}, V_{zz}, the magnetic hyperfine field, B_{hf}, and angles defining their relative direction.

Earlier PAC work on pure[13,14] and Sr-doped[15] $La_2CuO_{4+\delta}$ showed via linewidth analysis that our materials are *prima facie* oxygen stoichiometric. We observed that pure materials have a molecular-field dependence for $B_{hf}(T)$, and an EFG asymmetry, $\eta(T) \equiv (V_{yy} - V_{xx})/V_{zz}$, proportional to the crystallographic asymmetry, $\eta'(T) \equiv 2(c-a)/(c+a)$.[16] In addition, we argued that the ^{111}In probe occupies the La site.

In this paper we report evidence of a *new structural phase* in stoichiometric $La_{2-x}Sr_xCuO_{4+\delta}$ for $T < 150(20)$ K. As $T \rightarrow 0$ this phase is characterized by an *increase* in the inhomogeneous broadening of the EFG distribution, a parallel *increase* in the distribution of $\eta(T)$, and a *decrease* in the average value $\langle \eta(T) \rangle$. We interpret the distribution of η in terms of local deviations from orthorhombic symmetry, and conclude that the phase is *structurally disordered.*

Experiment.—Using near theoretical density ~ 10-mg samples, ~ 10-μCi sources were made by depositing carrier-free 2.8-d ^{111}In in a 0.05-M HCl solution, evaporating to dryness, and diffusing in oxygen at $\sim 1000\,^\circ$C. This implies an In concentration of $\leq 10^{-7}$ per formula unit. To prepare stoichiometric samples, the oxygen content was adjusted via vacuum annealing.[13] For both pure and Sr-doped material this produced quadrupole frequencies differing by less than 1%, indicating the structural equivalence of the ^{111}In site for various values of x. Samples with $x = 0$ had repeatable sharp magnetic transitions with $T_N = 317(1)$ K,[13] whereas for $x \geq 0.018$ no magnetically ordered phase could be found for $T > 20(2)$ K.

The prepared samples were measured in a Displex closed-cycle He refrigerator with stability of ± 1 K, and a range of $11 < T < 350$ K. A standard four-counter slow-fast coincidence system equipped with BaF_2 scintillation counters[17] produced four spectra that were combined via standard ratios to form the perturbation function $G_2(t)$.[18] Data for $G_2(t)$ and its Fourier transform

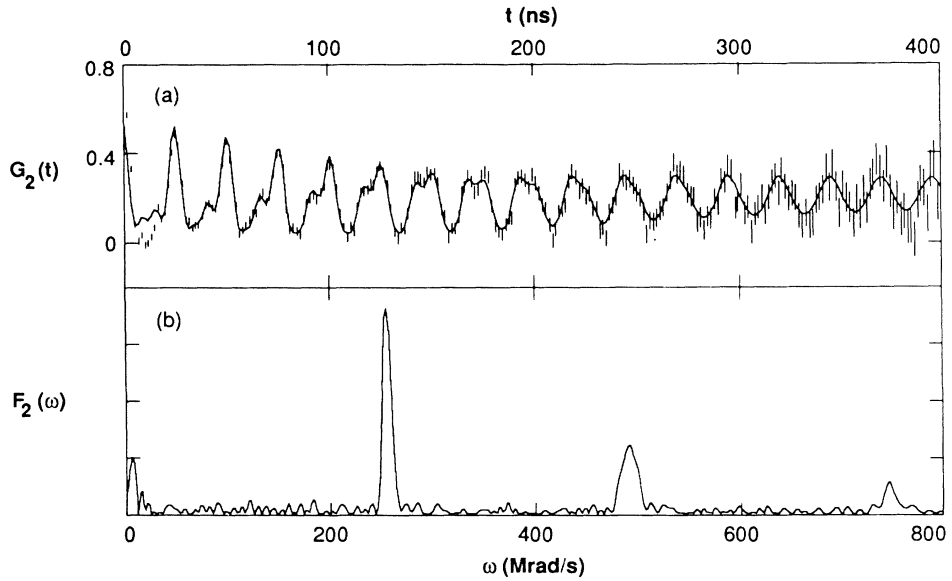

FIG. 1. (a) PAC spectrum $G_2(t)$ for $x=0.018$ and $T=196$ K, fitted as described in the text. (b) Fourier transform $F_2(\omega)$; this illustrates line broadening in excess of the natural linewidth determined by the Fourier time window.

$F_2(\omega)$ are illustrated in Fig. 1.

Data analysis.—With B_{hf} oriented relative to the principal axes of the EFG tensor by the polar angles (ϑ,Φ), the most general form of the hyperfine Hamiltonian for a nucleus of spin 1 is[19]

$$H=\hbar\omega_Q[3I_z^2-I(I+1)+(\eta/2)(I_+^2+I_-^2)]$$
$$+\hbar\omega_L[I_z\cos\vartheta+I_x\sin\vartheta\cos\Phi+I_y\sin\vartheta\sin\Phi]\,. \quad (1)$$

Here $\omega_L=\mu B_{hf}/I\hbar$ is the Larmor frequency, μ the nuclear magnetic moment, $\omega_Q=\frac{1}{40}eV_{zz}Q/\hbar$ the quadrupole frequency, and Q the nuclear quadrupole moment.

For a randomly directed EFG, $I=\frac{5}{2}$, and the case $\eta=\omega_L=0$, hyperfine splitting of the nuclear energy levels results in a perturbation function having the well-known exact form

$$G_2(t)=\tfrac{1}{5}[1+\tfrac{13}{7}\cos(\omega_1 t)+\tfrac{10}{7}\cos(\omega_2 t)+\tfrac{5}{7}\cos(\omega_3 t)]\,, \quad (2)$$

with $\omega_n=n\omega_0$, $n=1,2,3$, and $\omega_0=6\omega_Q$.

If $\eta\neq0$, the principal frequencies are not an integral multiple of ω_0 and the amplitudes are altered.[20] For $\eta<0.2$ the perturbation result, $2-\omega_2/\omega_1=2.59\eta^2$, may be used to estimate η within 1%.[21] To describe inhomogeneity due to Sr doping, $G_2(t)$ was fitted with each term in Eq. (2) multiplied by $\exp(-\delta\omega_n t)$, where $\delta\omega_n$ corresponds to the excess Fourier linewidth. Above 150 K this yielded excellent fits for $La_{2-x}Sr_xCuO_4$, with $\delta\omega_1:\delta\omega_2:\delta\omega_3=1:2.5:3$ (see Fig. 1).

If, in addition, $\omega_L\neq0$, the three quadrupole levels are each split into doublets (Fig. 2), and the Hamiltonian can no longer be solved exactly. However, for $y=\omega_L/\omega_Q\ll1$, and $\eta\ll1$, a sufficiently accurate perturbation expansion leads to approximate eigenvalues E_n and eigenstates $|n\rangle$,[19] with

$$G_2(t)=\sum S_n\cos(\omega_n t)\,, \quad (3)$$

where S_n and ω_n are amplitudes and frequencies corresponding to the twelve possible $(\Delta E\neq0)$ transitions between the magnetically split quadrupole levels.

For our material where $\cos\vartheta\ll1$ and $\eta\ll1$, the twelve frequencies are effectively reduced to five, ω_1 and ω_3 become doublets, and the splitting of ω_2 is negligibly small. This has been clearly demonstrated in earlier work,[13] and has the fortunate consequence that $\delta\omega_2$ reflects structural inhomogeneity alone, even in the presence of magnetic interactions.

Experimental spectra for $G_2(t)$ were fitted by an expli-

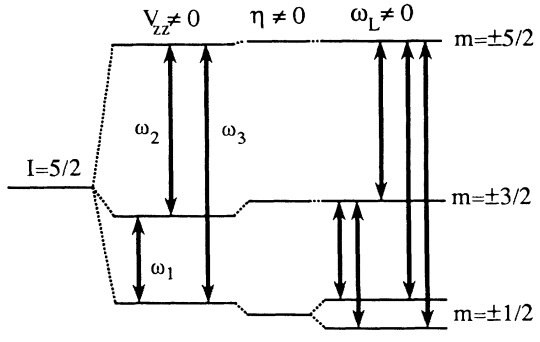

FIG. 2. Schematic energy-level diagram in $La_{2-x}Sr_xCuO_{4+\delta}$ for the full combined interaction with $\vartheta=90°$, and transitions that are resolvable shown by vertical lines. Magnetic splittings for $m=\pm\frac{5}{2}$ and $\pm\frac{3}{2}$ are too small to show, and all other level differences are exaggerated.

cit form of Eq. (3) with the parameters ω_Q, η, y, ϑ, and Φ, and the effective widths $\delta\omega_n$. Confidence in such fitting derives not from a single case, but from the fact that we have studied many spectra with and without Sr doping, above and below T_N, and above and below the structural transition reported below.

Results for $0 \leq x \leq 0.02$.—The temperature dependence of η is shown in Fig. 3(a) for a range of concentrations. The corresponding behavior of $\delta\omega/\omega$ is illustrated in Fig. 3(b) for the case of $x = 0.018$ (which has no magnetic splitting at any temperature > 20 K).

For $T \geq 150$ K and all values of x studied, the observed behavior is as expected for the orthorhombic distortion; i.e., $\eta(T)$ increases with decreasing T and has a narrow, temperature-independent distribution $\Delta\eta$, whereas $\delta\omega_1(T)$ and $\delta\omega_2(T)$ are nearly constant and understandable in terms of chemical inhomogeneity due to Sr doping.[15] We conclude that above 150 K we have a population of probe sites that accurately reflect the long-range crystalline order known from diffraction studies.

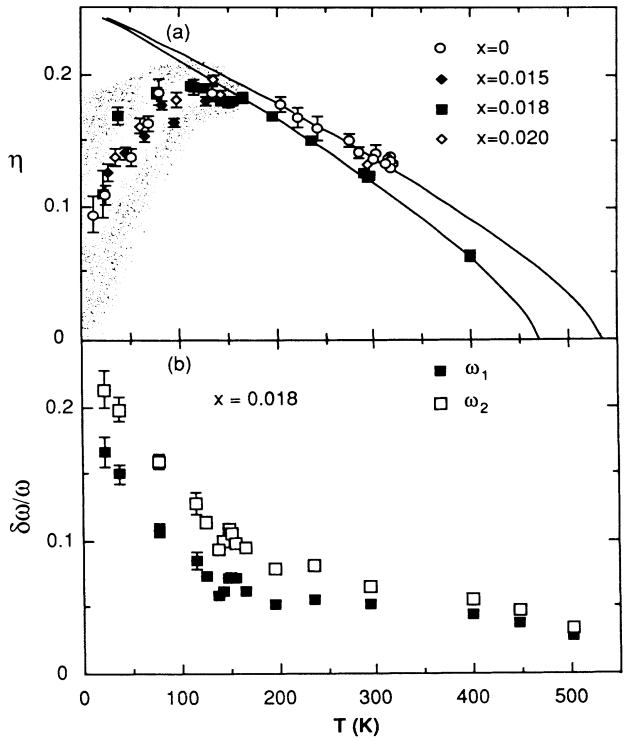

FIG. 3. (a) Variation of the mean EFG asymmetry parameter $\langle\eta\rangle$ for four values of x. In the range $T \geq 150$ K, η has a narrow distribution reflecting long-range order, and is proportional to the crystallographic asymmetry, as shown by the solid lines for $x = 0.00$ (top) and $x = 0.018$ (bottom). For $T \leq 150$ K, η has a broad distribution (shaded area), and reflects local disorder. (b) Excess linewidth below 150 K for $x = 0.018$, derived as described in the text. Above 150 K, $\delta\omega_2(T)$ reflects the effect of chemical inhomogeneity due to Sr doping. Below 150 K it reflects disorder as well.

For $T \leq 150$ K and all concentrations studied, the distribution $\Delta\eta(T)$ and the linewidths, $\delta\omega_1(T)$ and $\delta\omega_2(T)$, exhibit a dramatic *increase* even while the average value $\langle\eta(T)\rangle$ shows a corresponding *decrease*. At 12 K the width of the asymmetry is as large as the mean, i.e., $\Delta\eta \cong \langle\eta\rangle \cong 0.1$, indicating that η is as likely to be zero as 0.2, the value extrapolated from the orthorhombic phase. This implies that the site population has become microscopically inhomogeneous beyond chemical disorder, and now involves a distribution of local lattice symmetry. As indicated by the behavior of η, as $T \rightarrow 0$ this involves local lattice distortions for which the EFG approaches uniaxial structure, e.g., tetragonal symmetry. It is interesting to note that the observed behavior occurs independent of x for all x studied.

We interpret the change at $T_d = 150(20)$ K as a structural transition which involves freezing in of local disorder as the temperature decreases, very much like a spin-glass transition. The reversibility and the low temperature of the transition argues against phase separation. The reversibility is also evidence that the new phase is a property of the material, and not of the probe used to observe it.

As a further test of our picture of T_d, consider that 3D antiferromagnetic order in $La_{2-x}Sr_xCuO_4$ results from ferromagnetic interplanar coupling allowed only for the orthorhombic phase.[22] If the material undergoes a structural order-disorder transition near T_d, as proposed, the mechanism for 3D antiferromagnetism may be disrupted when x reaches a value such that $T_N(x) \sim T_d$. To test this hypothesis, we have measured $T_N(x)$ for $0 < x < 0.02$ via PAC and susceptibility using a SQUID magnetometer.

As shown in Fig. 4, between $x = 0$ and 0.015, $T_N(x)$ decreases linearly at the rate 90 K per 0.01 increase in x. For $0.015 < x < 0.018$, the region in which the extrapolated value of $T_N(x)$ falls below T_d, the former drops

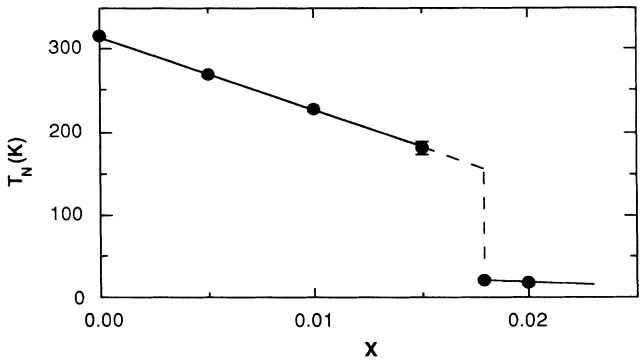

FIG. 4. Variation of Néel temperature, $T_N(x)$, measured in our PAC samples and confirmed with SQUID studies. The dotted line connecting the points at $x = 0.015$ and 0.018 extrapolates $T_N(x)$ through the proposed order-disorder transition at $T_d \approx 150$ K.

from 180 to 20 K. This clearly confirms our hypothesis.

Hence, stoichiometric $La_{2-x}Sr_xCuO_{4+\delta}$ not only suffers a structural order-disorder transition at T_d, but loses its long-range magnetic order at the appropriate concentration. This provides support for our characterization of T_d and, independently, additional support for the model of subtle spin canting that has been developed to explain 3D antiferromagnetic order.

Whereas diffraction studies have shown unexplained line broadening at low temperature, as already noted, the full extent of the order-disorder transition at T_d was not recognized. We believe there are three possible reasons for this: (1) The temperature dependence of the diffraction linewidth was not always systematically observed; (2) the transition at T_d may depend sensitively on oxygen concentration; and (3) the transition involves subtle inhomogeneous structural changes on the scale of the unit cell, without corresponding changes in long-range crystalline order.

Egami *et al.*[11] have discussed a model of case (3). They propose a random distribution of tilted CuO_6 octahedra arranged in "islands" with a different tilt direction. This would produce short-range disorder, a distribution of η, but no loss of overall long-range crystalline order. This model and pulsed neutron data[11] support a low-temperature order-disorder transition in pure $La_2CuO_{4+\delta}$.

Recent work extends the new phase to $x=0.07$. For this value we observe a PAC linewidth anomaly with $T_d=150$ K, as in Fig. 3. We also see the expected Meissner fraction in SQUID measurements on 10-mg samples, thus proving that they are superconducting. The new phase below 150 K may therefore be important in the theory of superconductivity for $La_{2-x}Sr_xCuO_{4+\delta}$.

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