NMR Study of Local Structure in Metallic $La_2CuO_{4+\delta}$

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We employ ^{139}La NMR spectroscopy as a structural probe of metallic $La_2CuO_{4+\delta}$. We find a distribution of lateral displacements of the oxygen atoms which form the apices of the oxygen octahedra. We directly observe a wide distribution of structures of the La-O layer; this distribution is strongly temperature dependent. We present copper NQR spectra which reveal a second, unexplained, copper site in the CuO_2 planes. We show that these features are not manifestations of disturbances of the lattice by interstitial dopants, but are the intrinsic response of $La_2CuO_{4+\delta}$ to doped holes.

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Structure is a key determinant of behavior in electronic systems; thus a detailed understanding of structural aspects of the superconducting cuprates is crucial. Furthermore, structural features with unusual properties or temperature dependences may hold clues vital to understanding the novel behavior of these materials. Although considerable work has been devoted to the study of the structure of the high-temperature superconductors many issues remain controversial [1]. In particular there is growing evidence that the periodic structure deduced from diffraction experiments may not adequately describe local structure, at least on some time scales [2]. An orthorhombic distortion may be necessary for superconductivity in $La_{2-x}Sr_xCuO_4$ [3] and, at least locally, in $YBa_2Cu_3O_{7-y}$ [4]. The sensitivity of superconductivity to structure in the $La_{2-x}Ba_xCuO_4$ and $(La,RE)_{2-x}Sr_xCuO_4$ (RE denotes rare earth) [5,6] systems emphasizes the critical role structure plays.

^{139}La NMR is a local probe which is extremely sensitive to certain details of structure in $La_2CuO_{4+\delta}$. Here, we report our studies of the structure of metallic $La_2CuO_{4+\delta}$: It closely resembles that of the undoped parent compound with the important difference that the presence of doped holes results in the development of a strongly temperature-dependent distribution of structures. This distributed structure is not a manifestation of the distortion in the proximity of an interstitial oxygen but is the intrinsic response of $La_2CuO_{4+\delta}$ to the presence of holes.

This study was performed on a 5 mg single crystal of $La_2CuO_{4+\delta}$ grown from a CuO flux and annealed in a 3 kbar oxygen atmosphere [7]. Studies of similarly prepared samples have shown [8] that $\delta \sim 0.03$ at high temperatures and that phase separation [9–11] into oxygen-rich and oxygen-poor domains (with dimensions of approximately 3000 Å [9]) occurs at a temperature T_{PS} in the vicinity of or just below room temperature. We have studied this phase separation process [12] and find a discontinuous change of δ at $T_{PS} \cong 265$ K. At $\sim$200 K the excess oxygen loses its mobility [13] so that δ for both phases remains constant below this temperature with values of $\delta \approx 0.01$ and 0.06. The superconducting T_c for this sample is 38 K.

The properties of the oxygen-rich metallic phase [12,14] are similar in many respects to those of metallic $La_{2-x}Sr_xCuO_4$. For comparable hole dopings the two materials have similar temperature-dependent spin susceptibilities (as determined by the Knight shift) and spin-lattice relaxation rates (both copper and oxygen); these imply similar electronic structure. The structure of metallic $La_2CuO_{4+\delta}$ [8–10,15] is controversial. One study finds that the orthorhombic structure is *Bmab*, as in undoped La_2CuO_4 [8]; another finds a related orthorhombic *Fmmm* structure [9,10] in which the apex oxygen lies directly above the copper.

Our study focuses on the electric field gradient (EFG) at the La site which is described by a symmetric traceless tensor [16]. The characteristics of the EFG are determined by the distribution of charge surrounding the site. In its principal axis frame this tensor is diagonal and can be described by two parameters: the quadrupole frequency ν_Q which specifies the magnitude of the largest component of the diagonal EFG tensor V_{zz}, and the asymmetry parameter η which specifies the degree of departure from axial symmetry. We determine these two quantities from zero-field (NQR) measurements.

Our interest is in the orientation of this principal axis frame with respect to the crystalline axes. The shift $\nu^{(2)}$ of the $m=\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition frequency by an axially symmetric EFG depends on the angle θ ($\mu \equiv \cos\theta$) between the applied magnetic field and V_{zz}: $\nu^{(2)} = (\frac{15}{16}) \times (\nu_Q^2/\nu_Z)(1-\mu^2)(1-9\mu^2)$. The Zeeman frequency is $\nu_Z = (1+K)\gamma H_0$, where K is the Knight shift, γ the ^{139}La gyromagnetic ratio, and H_0 the magnitude of the applied magnetic field (applied along the c axis).

There are two features of this NMR shift which are important in what follows. The first is that $\nu^{(2)} = f(\cos^2\theta)$. In the present case one might imagine a situation in which the EFG is tilted by a small angle away from the c axis but rotating about it in such a way that $\langle\theta\rangle = 0$ on the NMR time scale ($\langle f \rangle \equiv$ time average of f). In this case $\langle\cos^2\theta\rangle$ is not zero and $\langle\nu^{(2)}\rangle$ will not vanish.

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Thus, even in the case of a fluctuating structure we will observe a shift reflecting this time average. The field dependence of the quadrupole shift ($\propto 1/H_0$) allows it to be easily distinguished from magnetic shifts ($\propto H_0$). Spectra were taken at 52.5900 and 30.3629 MHz at all temperatures and occasionally at 39.1983 MHz as well to establish that the shifts were linear in $1/H_0$.

At high temperature La_2CuO_4 is tetragonal; at 530 K it undergoes a transition to an orthorhombic structure in which the oxygen octahedra rotate about the tetragonal 110 or $1\bar{1}0$ axes in a periodically ordered fashion [17]. This rotation causes a single well-defined tilt of V_{zz} at the La site. We have studied this tilt in several insulating, antiferromagnetic (AF) samples having Néel temperatures as high as 320 K by monitoring the substantial resultant NMR shift. On cooling from room temperature to 4 K the tilt increases from 15° to 19°; there is very little effect on the asymmetry of the EFG [18]: $0.01 < \eta < 0.02$.

The AF phase in the oxygen-annealed sample behaves identically. The values of η and ν_Q agree well with those observed in the undoped compounds and $\theta(T)$ is nearly identical to that in the undoped material. The three sharp lines in the spectra shown in Fig. 1(a) arise from this phase. A misalignment ($\approx 2°$) of the c axis of the sample with respect to the applied field is responsible for the splitting of the line. For an arbitrary orientation of $\mathbf{H}_0$ relative to $\mathbf{c}$, there will be four (in a twinned crystal) polar angles Θ between $\mathbf{H}_0$ and V_{zz} and so four NMR lines; two of these overlap in the present case. This small misalignment will be disregarded ($\theta \equiv \Theta$) in the analysis of the metallic phase.

We turn now to the results which we wish to emphasize: the determination of the tilt of V_{zz} in the metallic phase and its description in terms of a distribution of angles. Above and just below T_{PS} the ^{139}La NMR line is sharp. The signal from a small fraction of La nuclei neighboring an interstitial oxygen is unobservable due to the substantial displacements [8] of oxygens in its immediate vicinity. The sharp, unshifted line observed at high temperature shows that the interstitial oxygen does not intrinsically distort the EFG at La sites outside the near-neighbor shell. Note that oxygen motion alone cannot produce an unshifted, narrow line. As we will show, this structure is not affected by the structural disorder from the interstitial defects. At high temperature the resonance frequency does not vary with field showing that the quadrupole shift, and thus θ, is zero. At lower temperatures the metallic ^{139}La NMR line becomes broadened due to a distribution of tilt angles, so the separation of magnetic from quadrupole shifts must be handled differently (see Fig. 1). We first assume a Knight shift K and subtract the magnetic shift from the total shift leaving the quadrupole shift $\Delta\nu = \nu - \nu_z$ which will vary as ν_z^{-1}; thus $\nu_z \Delta\nu$ will be independent of applied field. In practice we transform the spectra $I(\nu)$ to $I(\mu)$ according to the expression: $\nu_z \Delta\nu = (\frac{15}{16})\nu_Q^2(1-\mu^2) \times (1-9\mu^2)$. The proper value of K is that for which the various $I(\mu)$ for different fields all fall on a single curve (the relative intensities of the spectra are allowed to vary). Figure 1(b) shows $I(\mu)$ for spectra at three fields which have been transformed and superposed. The signals for the metallic phase coincide completely within the noise; those from the AF phase do not because the magnetic shift for this phase is different from that for the metallic phase.

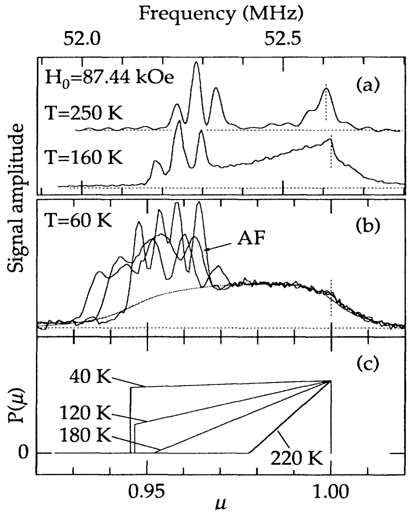

FIG. 1. Evolution of the ^{139}La NMR spectra. In panel (a) the vertical lines indicate the zero of the quadrupole shift, i.e., $\nu = (1+K)\gamma H_0$. In panel (b) data taken at three different frequencies have been transformed ($\mu \equiv \cos\theta$) as described in the text and superposed. The dashed line compares the tilt distribution described in the text to the data. The distribution does not, of course, describe the sharp lines arising from the AF phase. Panel (c) shows the evolution of $P(\mu)$ with temperature (normalized at $\mu = 1$). Note that at low temperature the distribution approaches a uniform one, e.g., $P(\mu) = \text{const}$. To produce the fit such as shown in panel (b) a delta function is added to $P(\mu)$ at $\mu = 1$ and the sum is convoluted with a Lorentzian. The quality of the resulting fits to spectra at all temperatures is comparable to that shown in (b).

The uncertainty in determining tilt angles in the metallic phase is due to uncertainty in the measured values of ν_Q and η and our neglect of the small misalignment of the sample. This uncertainty will affect the overall scale of the distribution of angles we determine but will not alter our primary results, which are the temperature dependence of the distribution and the relationship of the metallic tilts to that observed in the AF phase. The quadrupole frequency decreases with decreasing temperature and also becomes distributed: $\nu_Q = 5.9 \pm 0.35$ MHz at low temperatures. Note that the distribution of $\nu^{(2)}$ *cannot result from the distribution of* ν_Q since $\nu^{(2)}$ varies from zero to large shift while the distribution of ν_Q is only 12% of its center value and does not extend to zero. The asymmetry parameter η cannot be determined with high accuracy due to the increased width and nonsymmetric lineshape, but $\eta < 0.1$ at all temperatures. We estimate the error in the overall scale of θ to be approximately 10%.

We have simulated the effect of various motions of the nine oxygens coordinating the La site, including rigid rotations of the octahedra and both lateral and vertical motions of a single apex oxygen. The orientation of V_{zz} is very sensitive to lateral motions of the apex oxygen atom directly above the La site; it is much less sensitive to vertical motions and the motions of planar oxygen associated with rigid rotations. We find that the most plausible way to achieve substantial values of θ while leaving η small is through lateral (as opposed to vertical) motions of the apex oxygens.

In order to fit to $I(\mu)$, we find that a simple trapezoidal distribution successfully models the line shape: $P(\mu) = m\mu + b$; $\mu_c < \mu < 1$, $P(\mu) = 0$ otherwise, where $\mu_c = \cos(\theta_{\max})$. We add a delta function at $\mu = 1$ to account for sites having untilted V_{zz} and convolute this with a Lorentzian to simulate magnetic broadening. We vary five fit parameters: (i) μ_c, (ii) scaling of the NMR signal intensity, (iii) m/b, (iv) the relative weight in the delta function ($< 10\%$ below 120 K), and (v) the magnetic broadening width. The Knight shift is determined separately as described above. In Fig. 1(b) we show the quality of the fit achieved at 60 K.

There are three features of the tilt distribution $P(\mu)$ which indicate that it is not a manifestation of the distortion of the structure by the proximity of the interstitial oxygen. These features are (i) its temperature dependence, (ii) the existence of a cutoff at $\theta_{\max} = \theta_{\mathrm{AF}}$, and (iii) at low temperature, there is a *uniform* distribution of tilts; this simple distribution is not that expected to arise from a local expansion of the lattice by the interstitial. Figures 1(c) and 2 show that $P(\mu)$ evolves smoothly with temperature. The instantaneous distortion associated with an interstitial is independent of temperature, and motional effects cannot cause an unshifted line since $\langle \nu^{(2)} \rangle \propto \langle \cos^2\theta \rangle$, indicating that the observed temperature dependence does not simply reflect motional time scales. The smooth dependence on temperature through 200 K where motional time scales become smaller than the Larmor frequency supports this point. Thus the observed temperature dependence is not consistent with the distortion due to an interstitial. At low temperature we find a remarkable but quite simple distribution of structures in $La_2CuO_{4+\delta}$: $P(\mu) \cong \text{const}$ for $\mu_c < \mu < 1$, i.e., the distribution is *uniform* (any point on the unit sphere with $\theta < \theta_{\max}$ is occupied with equal probability). In contrast, the distortion due to an interstitial would have strong, monotonic dependence on μ with weak tails out to large deviations from $\mu = 1$ and with a high probability of very small tilts. The absence of any intensity in the spectra in Figs. 1(a) and 1(b) for quadrupole shifts larger than the quadrupole shift of the AF phase signal shows that there are no tilts greater than $\theta_{\max}(T)$. Figure 2 shows that for $T < 220$ K, $\theta_{\max}(T) = \theta_{\mathrm{AF}}(T)$; this reveals a close relationship to the structure of the undoped AF material which would not be expected for the distortion due to the interstitial. For these reasons we conclude that *this distributed structure is not a manifestation of the distortion associated with an interstitial defect.*

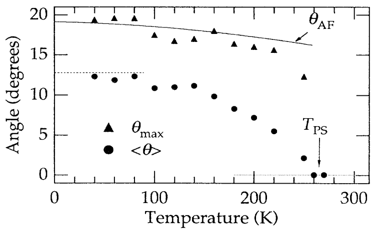

FIG. 2. Temperature dependence of the inhomogeneous tilt distribution. The solid line indicates the temperature dependence of the tilt observed in undoped La_2CuO_4 ($T_N = 320$ K), the filled triangles indicate $\theta_{\max}$; note that below ~220 K $\theta_{\max}(T) = \theta_{\mathrm{AF}}(T)$. The filled circles indicate the average of the distribution: $\langle\theta\rangle = \int \theta P(\theta) d\theta / \int P(\theta) d\phi$, and the dashed line $\langle\theta\rangle$ for a uniform distribution.

Copper NQR has been employed extensively as a probe of local structure in $La_{2-x}Sr_xCuO_4$ [19–24]. The copper NQR spectrum contains two peaks revealing the existence of two copper sites, in contrast to the single site expected on the basis of crystallography. The second site is believed to arise from the distortion of the local environment by a neighboring substitutional Sr atom. The quite unexpected appearance of the second site in the copper NQR spectrum in oxygen-annealed $La_2CuO_{4+\delta}$, shown in Fig. 3, argues against this explanation: It is essentially identical to that in $La_{2-x}Sr_xCuO_4$. We find (inset, Fig. 3) that the frequencies of the two peaks observed in $La_2CuO_{4+\delta}$ agree with those observed in $La_{2-x}Sr_xCuO_4$ to better than 2%. Note that the second peak is not related to the zero-field copper spectrum originating in the AF phase since that appears at $\nu \sim 100$ MHz due to the large hyperfine field of the ordered copper moments. In stoichiometric $La_2CuO_{4.0}$ [24] the second peak is absent above T_N.

The existence of two copper sites in $La_2CuO_{4+\delta}$ reveals an inhomogeneity in the CuO_2 planes not observed in crystallographic studies. Comparison to $La_{2-x}Sr_xCuO_4$ shows this is independent of the specific dopant, e.g., its location in the lattice and its charge. It is inconceivable that local distortions associated with the two very different dopants, one substituting for La and the second located interstitially, could result in nearly identical copper NQR spectra. Rather, the feature which distinguishes the second copper site must be common to both materials, e.g., it must arise as a consequence of the presence of doped holes regardless of the detailed method of doping. Note that the trait which distinguishes the second site need not be structural, e.g., it may be distinguished by a difference in charge distribution around the copper nucleus. Thus, although we do not understand the microscopic feature which distinguishes the two sites,

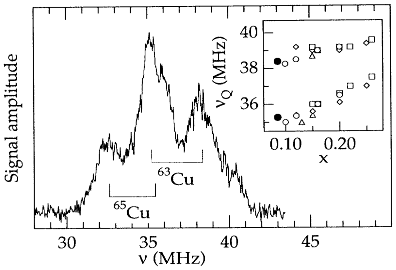

FIG. 3. The copper NQR spectrum (composed of ^{63}Cu and ^{65}Cu signals as indicated) from the metallic phase of oxygen-annealed $La_2CuO_{4+\delta}$ (AF spectrum appears at ~100 MHz). This spectrum is nearly identical to that observed in $La_{2-x}Sr_xCuO_4$; the x dependences of the two NQR frequencies shown in the inset demonstrate this. The data for $La_{2-x}Sr_xCuO_4$ from Refs. [19–22] are represented with open symbols: circles [19], triangles [20], diamonds [21], and squares [22]. The values for the oxygen doped material (present work) are plotted as closed circles at the value of x (0.09) which produces an equivalent level of hole doping of the planes [12].

it is clear that *this inhomogeneity is the intrinsic response of the material to the presence of doped holes.*

Recent neutron diffraction studies of the metallic phase in electrochemically prepared $La_2CuO_{4+\delta}$ [10] have found a complex structure which appears to be largely consistent with our conclusions. They find the apex oxygen located directly above the copper (*Fmmm* structure) *on average*; however, superstructure peaks indicate a long-wavelength, commensurate modulation of the oxygen position. Given evidence of long-range order, we conclude that the varying lateral displacements of the apex oxygens we observe locally are described by a long-wavelength modulation commensurate with the lattice. We are unable to elucidate the relationship between the distributed structure observed in the La-O layers and the two discrete sites in the CuO_2 planes. Experiments designed to understand the relationship between these are planned. We note that pair distribution analysis of neutron scattering data in other cuprates has revealed [2] variations in local structure which lack long-range order. Studies [25] of $La_{2-x}Sr_xCuO_{4+\delta}$ ($x \leq 0.02$ and $\delta \approx 0$) provide evidence for microscopic phase separation of doped holes which could also cause variations on a local scale.

In conclusion, metallic $La_2CuO_{4+\delta}$ displays a complex and strongly temperature-dependent structure, very different from that observed in the parent compound. The structural effects we observe are not manifestations of the distortion associated with the interstitial; rather they are the intrinsic response to hole doping. The striking coincidence between the onset of oxygen displacement and phase separation emphasizes the relationship between the level of hole doping and the structural effects. It is remarkable that the addition of a rather low concentration of holes can have such a marked structural effect. Copper NQR has revealed the appearance of a second copper site. The spectra from $La_2CuO_{4+\delta}$ and $La_{2-x}Sr_xCuO_4$ are essentially identical. This coincidence demonstrates that the agent differentiating the two sites must be common to these two systems; again we suggest doped holes.

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