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Local symmetry of copper sites in $La_{2-x}Sr_xCuO_4$

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Nuclear quadrupole and magnetic resonances of copper ions in $La_{1.84}Sr_{0.16}CuO_4$ have been performed at temperatures between 300 and 5 K. The analysis of the spectra shows that there are two electronically distinct copper sites for which the symmetry of the electric-field-gradient tensors is uniaxial with the principal axis along the crystal c axis. This result constrains possible structural models.

Early nuclear quadrupole resonance (NQR) work on $La_{2-x}Sr_xCuO_4$ (Refs. 1 and 2) has been interpreted[2] as evidence for two copper sites with distinct electric-field gradients (EFG) in this compound. It has also been found[2-4] that the relative occupancy of two sites is sensitive to strontium doping. More recently our measurements[4] have shown that one copper site, the A site, is native to the undoped compound and that occupancy of the second site, the B site, is proportional to the doping level, x. The structural and electronic properties of the second site, and its effect on superconductivity, have been the subject of recent controversy[5,6] which we address in this paper.

Tan *et al.*[5] interpreted their x-ray absorption near-edge structure (XANES) data as evidence for a copper site with fivefold coordination to oxygen. It was argued[3,5] that in nonstoichiometric compounds an interstitial oxygen might be paired with an oxygen vacancy at the apical position, just above or below a copper ion along the c axis. This idea was motivated[3] in part by neutron-scattering observations of an interstitial oxygen defect in oxygen rich $La_2CuO_{4+\delta}$.[7] However, neutron-scattering experiments on $La_{2-x}Sr_xCuO_4$ (Ref. 6) appear to be inconsistent with an oxygen vacancy in the apical position. Another possibility is that the B site might correspond to the existence of a second phase, macroscopically distinct from that containing the A site, and one that is not observed by diffraction. Our experiments suggest otherwise. These results [4] indicate that the two copper sites belong to the superconducting compound with the same superconducting properties and consequently both reside in the conduction plane.

Existence of a second copper site with a substantially different local electronic environment situated in the copper-oxygen plane, may be important to our understanding of superconductivity in this system. For example, a non-s-wave pairing state is exponentially sensitive to potential scattering from impurities.[8] However, it is known[9] that T_c of $La_{2-x}Sr_xCuO_4$ increases with increasing strontium doping, for $x < 0.16$. This implies that T_c is not controlled by defects in the conduction plane introduced by strontium having concentration x. Consequently, it is likely that superconductivity is s wave.

In this paper, we discuss NMR and NQR measurements[4] on a $La_{1.84}Sr_{0.16}CuO_4$ sample and demonstrate that the symmetry of the EFG tensor at site B is uniaxial with negligible asymmetry and that the direction of the principal axis is along the crystal c axis. We will discuss the implications of this on structural models for site B.

The sample was prepared by the solid reaction of appropriate metal oxides of high purity and the product was found to be phase pure and homogeneous. The details of the synthesis and x-ray diffraction analysis have been published elsewhere.[4] The powder was finely ground and cast in epoxy (Stycast 1266, Emerson and Cumming Co.) and allowed to cure in a strong magnetic field. Alignment of the crystallite c axes was indicated by x-ray rocking curve[4] measurements having a full width at half maximum of 7.8°. A sharp ^{139}La NMR line ($\frac{1}{2}$ to $-\frac{1}{2}$ transition) and an angular study of the spectrum confirmed that there was substantial alignment. The superconducting transition was measured by static magnetization in a magnetic field of 10 Oe and T_c was found to be 36.4 K.[4] NQR measurements were performed on a powder sample of approximately 2 g. The NMR measurements were performed at 3.47 T on a sample of about 1 g with the alignment direction perpendicular to the magnetic field. The NMR and NQR spectra were measured with a spin-echo pulsed method.

An example of the ^{63}Cu and ^{65}Cu NQR and NMR spectra of $La_{2-x}Sr_xCuO_4$ at 5 K are shown in Fig. 1. All spectra consist of pairs of peaks attributable to the two isotopes. The NQR spectrum is consistent with earlier results.[1-3] The spectrum can be understood as a superposition of two copper sites with different EFG tensors. The *B* site is assigned to the smaller peak at 39 MHz, with the main peak, site *A*, to the peak at 36 MHz. Note that by NQR alone the EFG tensor cannot be determined. The NQR frequencies of the two sites are listed in Table I. The spin-spin relaxation, T_2, was measured at each site and the T_2 data were used to determine the correct relative intensities. The intensity of site *B* was found to be 15% ± 3% of the total spectrum, equal to the strontium doping.

The Hamiltonian, including both magnetic and electric interactions for a copper nucleus, is[10]

$$H=-\gamma\mathbf{H}_{\rm ext}\cdot\hbar\mathbf{I}+V_c[3I_z^2-I(I+1)+\eta(I_y^2-I_x^2)]\,, \qquad (1)$$

where I_α $(\alpha=x,y,z)$ are spin operators in a coordinate frame that diagonalizes the EFG tensor and boldface denotes a vector. γ is the gyromagnetic ratio, $V_c=(eQ/12)V_{zz}$ where Q is the quadrupole moment, η is the asymmetry parameter, $\eta=(V_{yy}-V_{xx})/V_{zz}$, $0\le\eta\le 1$, and the indices indicate partial derivatives of the electrostatic potential $V(x,y,z)$. The magnetic shift has been neglected since it is a small effect compared with that of the quadrupolar term.[4] At zero field the NQR frequency can be shown to be

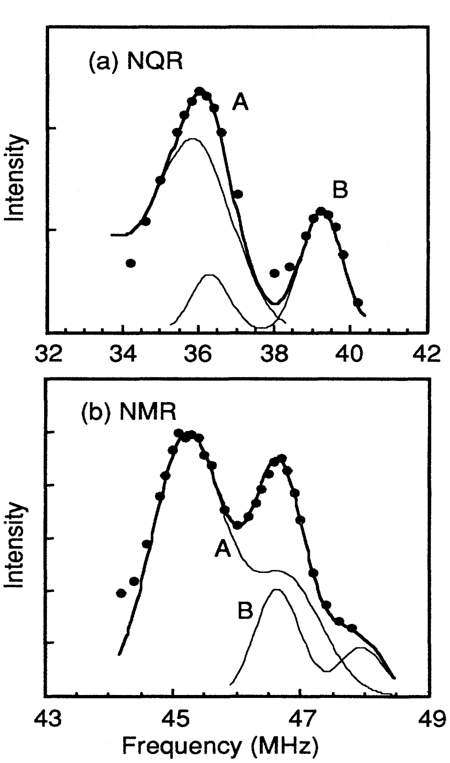

FIG. 1. (a) NQR and (b) NMR spectra of ^{63}Cu and ^{65}Cu of $La_{2-x}Sr_xCuO_4$ at 5 K (Ref. 4). The solid lines are fits for the two-site model. For the fitting of the NMR spectrum, the EFG tensors of both sites are taken to be uniaxial with the principal axis along the crystal *c* axis. The thin solid lines are the contributions from each site as labeled.

TABLE I. Peak frequencies and second moments σ of ^{63}Cu NQR and NMR spectrum (MHz).

Site	NQR frequency	NQR σ	NMR frequency	NMR σ
A	35.85	1.00	45.25	0.56
B	39.25	0.55	46.65	0.35

$$f_{\rm NQR}=2V_c(9+3\eta^2)^{1/2}\,. \qquad (2)$$

For a *c*-axis aligned sample the *a* and *b* axes are randomly oriented in a plane. In general, if the EFG principal axis **z** is at an angle θ to the crystal *c* axis, the NMR spectrum is an average over all **z** orientations forming a cone as shown in the inset of Fig. 3. It is sufficient to consider only the $\frac{1}{2}$ to $-\frac{1}{2}$ transition. To analyze the corresponding NMR spectrum of site *A*, it is reasonable to take $\theta=0$, since the *A* site is assigned to copper coordinated to six oxygen atoms in the tetragonal structure. In this case the magnetic field is perpendicular to $\mathbf{z}_A$ and the NMR frequency is a function of azimuthal angle ϕ for a nonzero η. The observed NMR spectrum will be a two-dimensional powder average over all ϕ, which we expect to have three singularities at $\phi=0°$, 90°, and approximate 28° (in the range $0.5<\eta<1$). Using the Hamiltonian, Eq. (1), we have calculated the frequencies of the three singularities as a function of η and show them in Fig. 2. Note that all three singularities become degenerate at $\eta=0$. The measured NQR frequency of site *A* was used as a constraint on V_c and η, as expressed in Eq. (2). The observed peak in the NMR spectrum at 45.3 MHz rules out the possibility of a large asymmetry parameter for site *A*, and consequently $\eta_A\approx 0$.

We can set a quantitative upper bound on η_A from an analysis of the second moment of the NMR spectrum.

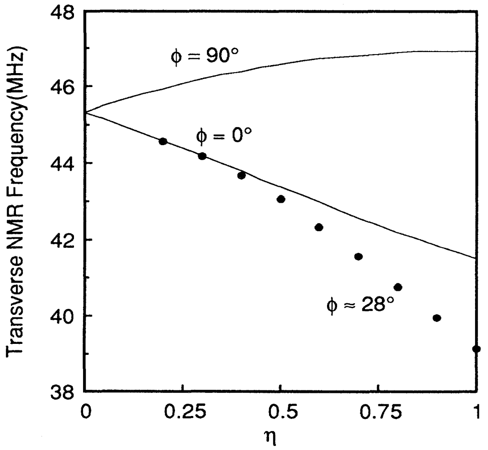

FIG. 2. Calculated transverse ^{63}Cu NMR frequencies of site *A* as a function of η at three singularities, $\phi=0$, 90°, and approximately 28° for $\eta>0.5$ (solid circles). The measured NQR frequency of site *A* is used as a constraint on V_c and η, Eq. (2).

For small nonzero η, the average over ϕ would appear as an additional broadening of the spectrum given by the difference between the NMR frequencies for $\phi = 0°$ and $90°$. Another contribution to the second moment of the NMR spectrum comes from distribution of the EFG tensor measured by the NQR linewidth which we estimate to be 0.34 MHz.[11] The remaining, unaccounted for broadening of 0.43 MHz establishes an upper bound on the value of η_A, $0 \leq \eta_A < 0.09$.

Turning to the analysis of site B, we cannot assume *a priori* that the symmetry axis of the EFG tensor is parallel to the c axis. In general, for a powder sample the NMR spectrum of a nucleus with a quadrupolar moment is an average over all possible orientations of the EFG relative to the magnetic field and the intensity is spread out over a broad range of frequencies resulting in a powder pattern. In a c-axis aligned sample this average is over a cone as displayed in the inset of Fig. 3. We have closely examined two situations for the principal axis of the site B EFG tensor, $\mathbf{z}_B$, both parallel and perpendicular to the c axis for different values of η. A selection of calculated spectra are shown in Fig. 3. A Gaussian broadening function was used in the calculations with a width similar to that observed in the NMR experiments. The general features of these spectra are that there are three singularities, and that the one at the lowest frequency has the largest weight. A singularity can occur in the frequency range of interest ($\sim$47.6 MHz) with an appropriate choice of η and orientation of $\mathbf{z}_B$; for example, one such case could be $\eta = 1$, $\mathbf{z}_B \perp c$, $\phi \approx 72°$. However, the intensity of such a singularity is about $\frac{1}{15}$ of the total intensity. In the special case where $\eta = 0$, $\mathbf{z}_B \| c$, such as for site A, the NMR frequency is independent of ϕ and the spectrum is a single resonance line with a full intensity shown by the thick line in Fig. 3.

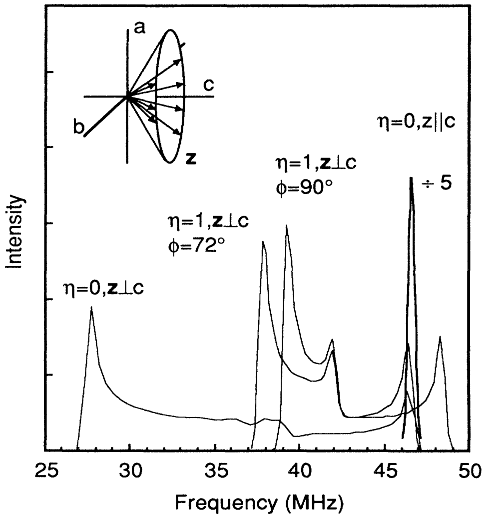

FIG. 3. Calculated spectra for a c-axis aligned sample with $\mathbf{z}_B$ parallel and perpendicular to the c axis and for different η and ϕ as labeled in the graph. The thick line is the spectrum for $\mathbf{z}_B \| c$, $\eta = 0$, whose intensity is reduced by a factor of 5 to fit the graph. A Gaussian broadening function is used with a width similar to that observed in the NMR experiment.

In our transverse NMR spectrum peak B is narrow. The deconvoluted spectrum shows that the relative intensity attributed to site B is 21% ± 4%, in reasonable agreement with the intensity of 15% ± 3% found for site B in the NQR measurement. This indicates that the NMR intensity of site B is not distributed in a two-dimensional powder average such as shown in Fig. 3. Thus $\mathbf{z}_B$ must be oriented along the crystal c axis and the asymmetry parameter must be small. A similar analysis of the NMR linewidth for site B, as for site A, requires that $\eta_B < 0.06$. More rigorously, the intensity argument leads to the conclusion that the two sites have identical symmetry. Having established the symmetry properties of the EFG tensor of site B, we now turn to discuss its implication for structural models.

We have measured[4] the total magnetic shift of both sites A and B, and found that they have the same temperature dependence, namely, temperature independent in the normal state with a sharp reduction in the superconducting state. There is a nonzero, constant difference between the NMR frequency shifts of sites A and B for all temperatures, $K_B - K_A = 0.40\% \pm 0.1\%$. This is attributed to a difference in orbital shift. A difference in the orbital shift of such magnitude and that in the EFG tensor imply a substantial change in the local electronic environment, such as a change in coordination by oxygen or in the valence structure. By way of comparison, in the compound $YBa_2Cu_3O_7$ the transverse orbital shift of the copper at plane and chain sites is 0.3% and the difference in their EFG is about 35%.[12]

The symmetry of the site B EFG tensor would rule out the possibility that this copper site was associated with an oxygen defect in the copper-oxygen plane, although such planar oxygen defects have been found to occur for $x > 0.25$.[13] An apical oxygen vacancy, as proposed by Tan *et al.*[5] satisfies the symmetry constraint on the EFG tensor as we infer from our measurements. However, it should not produce a significant change in the copper orbital shift due to the symmetry of the copper d and oxygen p orbitals. Generally, the transverse orbital shift is given by $K_{x(y)} \propto \sum |\langle 0 | L_{x(y)} | n \rangle|^2 / \Delta E$,[10] where $L_{x(y)}$ is the orbital angular momentum operator. $|0\rangle$ and $|n\rangle$ indicate ground and excited states, and ΔE is the excitation energy measured from the ground state. The sum is over excited states. In the case of copper d orbitals in $La_{2-x}Sr_xCuO_4$, $|0\rangle = x^2 - y^2$, $|n\rangle = xz, yz, xy$, and z^2. Due to the symmetry of the angular momentum operator, only xz and yz contribute to the transverse orbital shift. Note that to first-order approximation, the p_z orbital of apical oxygen has zero net overlap with orbitals $x^2 - y^2$, xz, or yz, so that the excitation specturm for them will not shift due to the loss of apical oxygen. Furthermore, the neutron-scattering data[6] does not support the existence of an apical oxygen vacancy.

It is generally believed that the introduction of strontium in $La_{2-x}Sr_xCuO_4$ stabilizes the hole doping which provides metallic conductivity in the normal state. In addition to this, strontium may affect copper locally, through either structure deformations or further oxidation of some copper, giving rise to site B. Since neutron diffraction[6] does not suggest a structural deformation identifiable with the second site, we have considered that copper at site *B* may be partially oxidized to a different level.[4] In this model the density of site *B* is proportional to x. Our measurements of the relative intensity of the *B* site in a series of samples $0.10 < x < 0.20$ show that the intensity of site *B* is equal to x within experimental error.[4] This implies that one copper is partially oxidized by one strontium. Such a difference in the oxidation level of copper would induce a significant change in the orbital shift. This model also preserves the c-axis symmetry of the EFG tensor which is consistent with what we infer from our measurements. It is also likely that further oxidation alters the magnitude of the EFG.

In summary, using copper magnetic resonance in $La_{2-x}Sr_xCuO_4$ we have demonstrated that the EFG tensors of two copper sites have uniaxial symmetry. This result, together with NMR frequency shift data, suggests that charge differentiation is a reasonable model for a second copper site in $La_{2-x}Sr_xCuO_4$. It is interesting to consider that the concentration of such defects in the conduction plane is sufficiently large that superconductivity in $La_{2-x}Sr_xCuO_4$ might be viewed as being inherently in the dirty limit.

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[1] K. Kumagai and Y. Nakamura, Physica C **157**, 307 (1989); K. Ishida, T. Kondo, Y. Kitaoka, and K. Asayama, J. Phys. Soc. Jpn. **58**, 2638 (1989).

[2] K. Yoshimura, T. Imai, T. Shimizu, Y. Ueda, K. Kosuge, and H. Yasuoka, J. Phys. Soc. Jpn. **58**, 3057 (1989).

[3] K. Yoshimura, K. Kosuge, T. Imai, T. Shimizu, and H. Yasuoka (unpublished).

[4] M. A. Kennard, Y.-Q. Song, K. R. Poeppelmeier, and W. P. Halperin, Chem. Mater. **3**, 672 (1991).

[5] Z. Tan, M. E. Filipkowski, J. I. Budnick, E. K. Heller, D. L. Brewe, B. L. Chamberland, C. E. Bouldin, J. C. Woicik, and D. Shi, Phys. Rev. Lett. **64**, 2715 (1990).

[6] G. H. Kwei and D. E. Partin, Phys. Rev. Lett. **65**, 3456 (1990); J. D. Jorgensen *et al.* (unpublished).

[7] C. Chaillout, S. W. Cheong, Z. Fisk, M. S. Lehmann, M. Marezio, B. Morosin, and J. E. Schirber, Physica C **158**, 183 (1989).

[8] L. P. Gor'kov, Sov. Sci. Rev. Sect. A **9**, 1 (1987).

[9] J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang, and S. S. P. Partin, Phys. Rev. Lett. **61**, 1127 (1988); S.-W. Cheong, J. D. Thompson, and Z. Fisk, Physica C **158**, 109 (1989).

[10] C. P. Slichter, *Principles of Magnetic Resonance,* 3rd ed. (Springer-Verlag, New York, 1989).

[11] $\delta f_{\rm NMR} = 27 V_c \delta V_c / 2\gamma H_{\rm ext}$, where $\delta f_{\rm NMR}$ is the frequency variation in the NMR spectrum due to that in the EFG, δV_c.

[12] C. H. Pennington and C. P. Slichter, *Physical Properties of High Temperature Superconductors II,* edited by D. M. Ginsberg (World Scientific, Singapore, 1990), Chap. 5.

[13] N. Nguyen, J. Choisnet, M. Hervieu, and B. Raveau, J. Solid State Chem. **39**, 120 (1981); L. Soderholm, D. W. Capone, D. G. Hinks, J. D. Jorgenson, and I. K. Schuller, Inorg. Chem. Acta **140**, 167 (1987).