Nuclear Quadrupole Resonance Spectrum of La_2CuO_4

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I report the results of *ab initio* quantum chemistry calculations addressing the nuclear quadrupole resonance (NQR) spectra of hole-doped La_2CuO_4. The experimental spectra point to two Cu environments, with a main peak, corresponding to a predominantly d^9 Cu site, and a satellite at ~3 MHz higher frequency. The cluster calculations exhibit broken-symmetry solutions in which an additional hole localizes on a single CuO_6 unit, and predict a satellite in the NQR spectrum 2.7 MHz above the main peak. The satellite corresponds to Cu sites neighboring a localized hole. I conclude that some (~25%) of the holes doped in to $La_{2-x}Sr_xCuO_4$ are localized on the NQR time scale of ~1 μsec.

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The interpretation of the nuclear quadrupole resonance (NQR) spectra of "hole-doped" derivatives of La_2CuO_4 [1–6] presents an intriguing puzzle. The frequency at which the NQR signal appears measures the energy difference between nuclear spin sublevels split by the coupling between the electric field gradient at the nucleus and the nuclear quadrupole moment. In the case of a spin $I = 3/2$ nucleus such as ^{63}Cu, one expects a single peak in the NQR for every unique ^{63}Cu environment. Thus the ^{63}Cu NQR spectrum of La_2CuO_4 consists of a narrow peak at 33.0 MHz, corresponding to the single Cu site present (the inset in Fig. 1) [5]. The additional peak at ~30.6 MHz arises from the other naturally abundant isotope, ^{65}Cu. Because the spectrum of this second isotope simply echoes that of ^{63}Cu, I will concentrate in what follows on the ^{63}Cu signature.

Upon replacing La with Sr, $La_{2-x}Sr_xCuO_4$, holes are doped into the CuO planes. This substitution causes the width of the main peak (A) at 33 MHz to increase dramatically [3] (Fig. 1), and its frequency gradually shifts upward until it appears near 36 MHz for $x = 0.16$. In addition, a second resonance (B) appears whose intensity grows [6] as x and whose position is ~3 MHz to higher frequency. A reasonable early assignment of this peak [2] attributed it to Cu nuclei whose immediate environment includes a Sr site.

This interpretation became suspect when Hammel *et al.* [7] reported the spectrum of $La_2CuO_{4+\delta}$. Excess oxygen also dopes holes into the planes, in this case the electrons going to the additional oxygen atoms which occupy interstitial positions in the lattice [8]. Figure 2 shows the NQR spectra for $\delta = 0.06$ and $\delta = 0.12$. Interestingly, this material also shows a satellite ~3 MHz higher in frequency than the main peak, and a third feature which appears in the vicinity of 41–43 MHz. Hammel *et al.* convert the composition δ into an equivalent hole concentration x, thereby allowing the position of the primary line and the satellite to be compared with $La_{2-x}Sr_xCuO_4$ as shown in the inset in Fig. 2. Importantly, the data for $La_2CuO_{4+\delta}$ fall on the same line as that for $La_{2-x}Sr_xCuO_4$. This strongly suggests that the satellite is associated with the properties of the hole, and not the specific way it is doped into the plane. Since a homogeneous distribution of holes should give a single average Cu environment, the presence of this

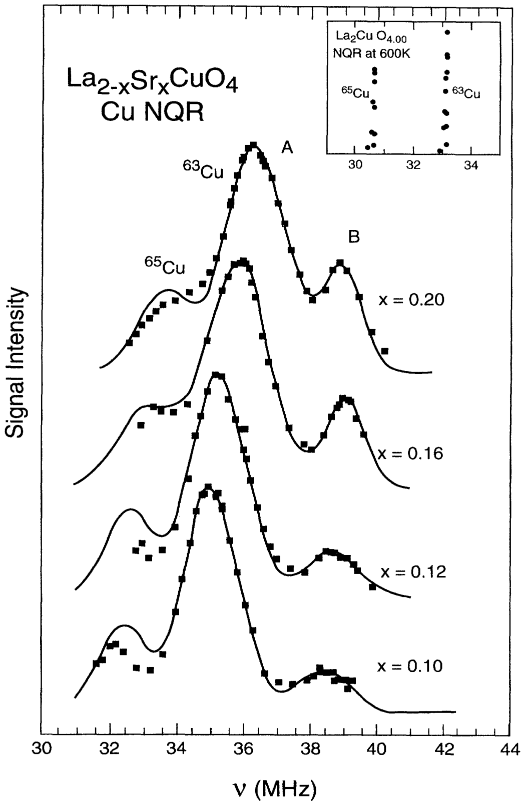

FIG. 1. The copper NQR spectra in $La_{2-x}Sr_xCuO_4$ (Song *et al.* [3]). The inset reproduces the $x = 0$ spectrum of Imai *et al.* [5]. Note the appearance and growth of site B as x increases.

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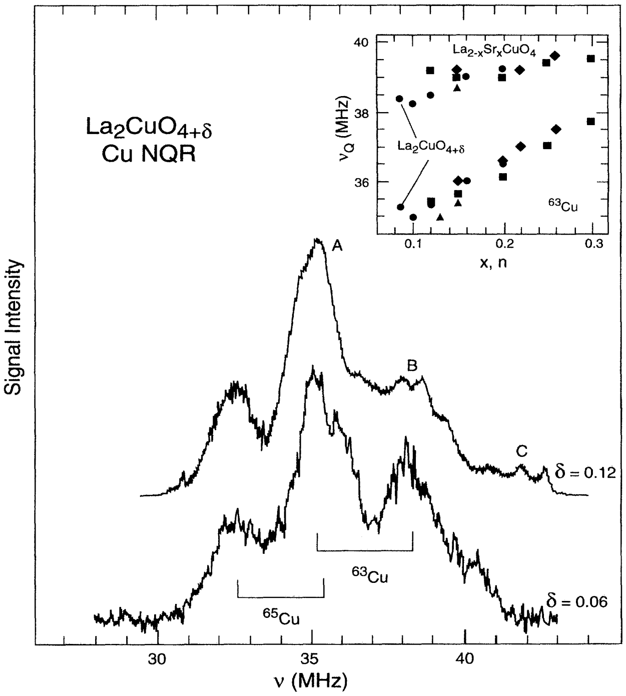

FIG. 2. The Copper NQR spectrum of $La_2CuO_{4+\delta}$ (Hammel *et al.* [7]). Note the satellite (B) apparent in Fig. 1, as well as new structure in the 41–43 MHz region (C). The inset compares the frequency of the main peak and satellite with that observed in $La_{2-x}Sr_xCuO_4$ [1–6] .

additional peak is puzzling. Because many of the models which address the strong correlations characteristic of the cuprates predict specific charge inhomogeneities (phase separation, polarons, and charge density waves), the origin of this additional resonance is of some interest.

In this Letter, I report theoretical NQR frequencies from *ab initio* quantum chemistry calculations on cluster models of La_2CuO_4. The calculations suggest that the presence of neighboring Sr atoms in $La_{2-x}Sr_xCuO_4$ contribute to the width of the main resonance, but are not responsible for the satellite. Similarly, neighboring interstitial oxygen atoms in $La_2CuO_{4+\delta}$ lead to the feature observed in the 41–43 MHz region, but not the satellite. The calculations lead to the conclusion that some of the holes doped into these materials are localized on the NQR time scale of ~1 μsec. The satellite is assigned to Cu(d^9) sites neighboring a localized hole. The signature of the localized hole itself is predicted to occur in the region of ~90 MHz, and has not yet been observed experimentally.

The cluster models for La_2CuO_4 utilize a Madelung-Pauli embedding potential developed earlier [9]. In brief, a primary cluster such as CuO_6 is treated *ab initio* in an embedding potential constructed by placing formal point charges at the positions of a few neighboring shells of atoms. The point charges at the boundaries of this enlarged cluster are adjusted so as to reproduce the exact Madelung potential in the region of the primary cluster. In order to enforce orthogonality between the electrons in the primary cluster and the background ion cores, effective core potentials are used to represent the Cu^{2+} and La^{3+} sites immediately adjoining the primary cluster. The basis sets and other details of the calculation are identical to those reported previously, with one exception. Since the electric field gradient probes a property at the nucleus, the use of effective core potentials to describe Cu atoms in the primary cluster is a possible source of error. All electrons on the Cu were, therefore, considered explicitly using a $[9s/5p/3d]$ contraction of Wachters' primitive basis for Cu [10]. The charge state of the primary cluster dictates the correspondence with an experimental doping. For example, the $CuO_6{}^{10-}$ cluster corresponds to a formal $Cu^{2+}(d^9)$ site and models undoped La_2CuO_4 ($x = 0$). Similarly, $CuO_6{}^{9-}$ has an additional hole relative to the undoped cluster and corresponds to the situation in which the additional hole is completely localized on one CuO_6 unit ($x = 1$). While this charge state is formally $Cu^{3+}(d^8)$, the density loss is predominantly on the ligands, and the state is usually referred to as $d^9\underline{L}$, where $\underline{L}$ denotes a ligand hole. In deference to the single-band Hubbard model, however, it will be referred to in what follows by its formal d occupancy (d^8).

Before discussing the results, a few words are in order regarding why one would want to study this problem with clusters [11]. The NQR frequency for a spin $I = 3/2$ nucleus is given by

$$\nu = \frac{e^2qQ}{2h}\left(1 + \frac{\eta^2}{3}\right)^{1/2}, \tag{1}$$

where Q is the nuclear quadrupole coupling constant (0.18 b for ^{63}Cu), and q and η are the principal moment and asymmetry parameter characterizing the negative of the electric field gradient of the molecule evaluated at the nucleus of interest. The electric field gradient at nucleus A is given by

$$V_{ij}^A = e\sum_B Z_B\left[\frac{3X_{AB}^iX_{AB}^j - \delta_{ij}R_{AB}^2}{R_{AB}^5}\right] - e\langle\Psi|\sum_k\left[\frac{3x_{kA}^ix_{kA}^j - \delta_{ij}r_{kA}^2}{r_{kA}^5}\right]|\Psi\rangle, \tag{2}$$

where the first term is the contribution of all primary cluster nuclei and any background point charges B with charge Z_B, and the second term is the electronic contribution summed over all primary cluster electrons, k. X_{AB}^i, X_{AB}^j, x_{kA}^i, and x_{kA}^j refer to the x, y, or z components of $\mathbf{R}_{AB}$ and $\mathbf{r}_{kA}$, and Ψ is the electronic wave function for the primary cluster. An important point in Eq. (2) is that the field gradient goes as $\sim 1/r^3$ and so is a relatively short-ranged operator and a very local probe of the electronic structure. Since the cluster calculations treat the local environment with *ab initio* techniques while approximating the background, comparison with this measurement should be less susceptible to inadequacies in the cluster size and background potential than many others.

The results of Hartree-Fock calculations are given in Table I. Concentrate first on the entries for the CuO_6 cluster. The result for the d^9 charge state, 38.9 MHz, is in error compared with the experimental value of 33.0 MHz at $x = 0.0$ by ~18%. This overestimate is not unexpected given the limited basis set, the finite cluster, and, especially, the fact that no electron correlation is included in the Hartree-Fock approximation. Furthermore, the cluster geometry was chosen to be that appropriate to a doping level $x = 0.15$, as opposed to $x = 0.0$. In what follows, I shall be concerned only with changes in the *ab initio* frequency as a function of changes in the local environment; this approach minimizes the influence of the errors referred to above as they are expected to remain nearly constant.

It is initially of interest to determine where signals originating from "localized" d^{10} and d^8 sites would appear. The d^{10} situation resonates at ~69 MHz, well outside the region of the satellite. The signal from the d^8 hole state is predicted at even higher frequency, ~92 MHz. These results may be used to estimate the variation in the frequency of the main line with doping. This variation should reflect at least two effects. The first is the dependence of the frequency on the effective fractional charge on the Cu. If this is assumed to be linear between $x = 0$ and $x = 1$, then the results of Table I yield $d\nu/dx =$ 53 MHz. The other major effect is the change in frequency with a change in lattice constant. By contracting the CuO bond lengths in the primary cluster by 0.1 Å and repeating the calculation on ${CuO_6}^{10-}$, this was determined to be $d\nu/dR_{\mathrm{CuO}} = -91$ MHz/Å. Coupled with the experimental variation in bond length with x, $dR_{\mathrm{CuO}}/dx \sim$ 0.2 Å, this effect contributes $d\nu/dx \sim -18$ MHz and opposes the increase in frequency with charging. The net contribution is $d\nu/dx \sim 35$ MHz, roughly twice the experimentally observed slope of ~20 MHz in Fig. 2. I shall return to this overestimate later.

TABLE I. ^{63}Cu NQR frequencies from *ab initio* cluster calculations (MHz). The first column gives the Hartree-Fock NQR frequency for CuO_6 and Cu_2O_{11} models of undoped La_2CuO_4. The second column gives the shift in frequency from the d^9 reference state. For the Cu_2O_{11} entries, the center at which the electric field gradient is evaluated is underlined.

Model	ν	$\Delta\nu$
${CuO_6}^{10-}(d^9)$	38.9	0.0
${CuO_6}^{11-}(d^{10})$	68.8	29.9
${CuO_6}^{9-}(d^8)$	92.3	53.4
${CuO_6}^{10-}(d^9)/Sr^{2+}$		0.6
${CuO_6}^{10-}(d^9)/O^{2-}$		5.1
${Cu_2O_{11}}^{18-}(\underline{d}^9,\underline{d}^9)$	38.4	0.0
${Cu_2O_{11}}^{17-}(\underline{d}^8,\underline{d}^9)$		2.7
${Cu_2O_{11}}^{17-}(\underline{d}^8,\underline{d}^9)$		52.2

It has been suggested that the satellite in $La_{2-x}Sr_xCuO_4$ is associated with Cu(d^9) sites near a Sr site. In order to test this hypothesis, the calculations were repeated with a cluster background in which one of the near neighbor La sites was replaced by a 2+ point charge representing Sr. This increases the frequency by ~0.6 MHz. Such a shift is in reasonable agreement with the observed increase in the width of the signal which accompanies doping, but is too small to account for the satellite. In the case of $La_2CuO_{4+\delta}$, it is interesting to inquire where signals originating from a d^9 site next to an interstitial oxygen would appear. For this purpose, I examined a cluster in which the background potential was modified by placing a single 2-point charge at the position in the lattice taken by the addition O in $La_2CuO_{4.06}$. Doping with excess oxygen also causes a distortion of the CuO_6 octahedron [8], which was not included for the purposes of this rough calculation. The d^9 signal is now found ~5 MHz to higher frequency. This peak may be evident in Fig. 2 for $La_2CuO_{4.06}$ as a shoulder near 40 MHz; structure is clearly evident in the 40–43 MHz region for the more heavily doped $La_2CuO_{4.12}$. This peak is, therefore, assigned to d^9 sites in proximity to an interstitial oxygen. The additional fine structure evident in this region is not accounted for by this simple calculation.

The calculations discussed thus far leave the satellite ~3 MHz from the main peak unassigned. The third set of frequencies in Table I refer to the results of calculations on Cu_2O_{11}, a cluster composed of two of the CuO_6 units sharing a bridging oxygen [12]. The first entry corresponds to the model of the undoped material, d^9-d^9. The close agreement with the result for $CuO_6(d^9)$ is a reflection of the fact that the electric field gradient is converging rapidly with cluster size. When a hole is doped into this cluster, two solutions to the Hartree-Fock equations may be found [12,13]. In the first, the additional hole is symmetrically delocalized over both Cu sites in the gerade combination of the two Cu $d_{x^2-y^2}$ orbitals. This symmetry restricted solution lies 1.9 eV higher in energy, however, than a broken-symmetry solution in which the hole localizes on one of the CuO_6 units. This broken-symmetry state is degenerate with its mirror image in which the hole localizes on the other side. Table I presents the frequencies computed with the broken-symmetry wave function. The site with the localized hole resonates at ~91 MHz, close to the result for the $CuO_6(d^8)$ hole state. The other Cu site (d^9) resonates 2.7 MHz above the main peak, in good agreement with the position of the satellite.

The appearance of these broken-symmetry, "electronic polaron," solutions is driven by the same considerations governing a normal polaron. If the loss in kinetic energy caused by localization is smaller than the electronic polarization energy which can be recovered by localizing the hole, broken-symmetry solutions will be found by the variational Hartree-Fock approach. These solutions are not acceptable eigenstates of the Hamiltonian, however. Proper electronic eigenstates can be restored by taking linear combinations of the two broken-symmetry solutions. In essence, this result says that a better zeroth-order description of the band is obtained by fully dressing localized holes which are then allowed to delocalize, as opposed to beginning with a free-electron picture and introducing the correlations among the Cu $3d$ and O $2p$ electrons which dress the hole with polarization. I emphasize that this tendency to localize originates from correlations among the Cu $3d$ and O $2p$ electrons. In particular, it cannot reflect a confining influence generated from the desire of Cu d spins to maintain antiferromagnetic coupling. This effect may also be operative in the material, but it is irrelevant in such a small cluster as Cu_2O_{11}.

The electronic correlations just outlined act to reduce the effective bandwidth of the carries, but the stationary states by themselves will not produce distinct Cu sites. If the resonance were to result from a fluctuation into a localized hole state, then in order to observe two well defined peaks separated by 3 MHz, the localized hole would have to exist at least for times of this order, or ~ 1 μsec. This is quite a long time, and it seems reasonable to suggest that some of the holes are pinned to the lattice. This may occur through an interaction with the excess interstitial O in $La_2CuO_{4+\delta}$, or the Sr in $La_{2-x}Sr_xCuO_4$. Both sites generate a region of negative potential relative to the undoped background which may act to pin a hole. In addition, nuclear motion may reinforce this tendency.

It is possible to generate a rough estimate for the concentration of localized holes in $La_{2-x}Sr_xCuO_4$ as follows. It was noted earlier that the theoretical estimate for the change in frequency with doping, $d\nu/dx \sim 35$ MHz, is larger than experiment, ~ 20 MHz. That analysis assumed that all holes were mobile and contributed to the effective charge on each Cu. If one admits the possibility that not all the holes contribute to the effective Cu charge, then $\sim 30\%$ of the holes must be localized in order to make the theoretical estimate coincide with the experiment. This is obviously only a rough guide, but it is consistent with another check, the experimental variation of the intensity of the two peaks [6] with x. Each localized hole should have four neighbors, and so the relative intensity of the satellite should scale as $4x$ times the fraction of localized holes. The experimental intensity varies as $\sim x$, which suggests that 25% of the holes are localized.

In summary, the calculations suggest that the satellite observed in ^{63}Cu NQR corresponds to Cu sites adjacent to a localized hole and predict the direct signature of the localized hole to occur in the region of ~ 90 MHz. In $La_{2-x}Sr_xCuO_4$, a rough estimate suggests that $\sim 25\%$ of the holes are localized. The experimental verification of the high frequency peak would strengthen the conclusions of this work and permit a more precise measure of the relative concentration of these sites.

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