Magnetic Excitations of the Doped-Hole State in Diamagnetic $La_2Cu_{0.5}Li_{0.5}O_4$

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Substitution of Li for Cu in $La_2Cu_{1-x}Li_xO_4$ donates holes; at $x = 0.5$ the Li ions form an ordered superlattice which isolates individual CuO_4 plaquettes from one another, and the number of doped holes is sufficient that each plaquette is occupied. Above 170 K, an activated temperature dependence of the Cu nuclear spin relaxation rate reveals a magnetic excitation of the doped-hole state with an energy of ~130 meV. Below 170 K relaxation is primarily due to fluctuations of the electric field gradient; the temperature dependence of this rate is anomalously slow: $T_1^{-1} \propto \sqrt{T}$. [S0031-9007(96)01098-8]

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The nature of the doped-hole state [1] in the cuprates is a matter of great importance in understanding both the normal state behavior of the cuprates and the mechanism leading to superconductivity. Compounds containing formally trivalent copper are rare, $La_2Cu_{0.5}Li_{0.5}O_4$ providing one of the few examples [2]. In the cuprates doped holes are believed to occupy oxygen $2p_\sigma$ orbitals which hybridize with the Cu $d_{x^2-y^2}$ orbital to form a $d^9\bar{L}$ ($\bar{L}$ ligand hole) configuration. Zhang and Rice [1] proposed in particular that the doped hole forms a local singlet state which involves a phase coherent combination of the $2p_\sigma$ orbitals of the four nearest neighbor oxygens. Although this description of the doped-hole state in the cuprates is widely accepted, there is still a lack of straightforward experimental evidence that such a local singlet state forms when holes are doped into the cuprates. This is partially due to the difficulty of discerning the magnetic behavior of such a singlet in a background of antiferromagnetically correlated copper moments.

Here we report a Cu nuclear quadrupole resonance (NQR) study of the properties of La_2CuO_4 hole doped by substitution of lithium for copper, a compound [2,3] which provides a unique opportunity to study the doped-hole state of the cuprates. In lightly doped $La_{2-y}Sr_yCu_{1-x}Li_xO_4$, Li and Sr doping (each donate one hole per dopant) have essentially indistinguishable effects on the magnetic properties and lattice structure of lanthanum cuprate [3]. For $y = 0$ this compound is insulating; for $x \gtrsim 0.1$, $\rho \propto \exp[(\text{const}/T)^{1/4}]$ [4]. The solid solubility of Li is such that a hole density of one hole per copper (at $x = 0.5$, $y = 0$) can be readily achieved. At this composition the Li and Cu ions form an ordered superlattice [5] in which all Cu ions are surrounded by four in-plane Li ions ($1s^2$, closed shell electronic configuration) and thus create isolated CuO_4 clusters. This material is unique amongst cuprates in that one is able to study the magnetic behavior of the doped hole confined by the four Li neighbors and in the absence of the confounding contributions of the antiferromagnetically correlated copper moments. For instance, the relaxation rate we observe at $T = 100$ K is smaller than that observed in $La_{1.85}Sr_{0.15}CuO_4$ by over 4 orders of magnitude.

As we will show, this singlet state has a ~130 meV gap to magnetic excitations. The energy of the excited state relative to the ground state is smaller than predicted by Zhang and Rice, and strikingly similar to the value of the effective exchange interaction J in the lightly doped cuprates. Below 170 K this gapped magnetic excitation mechanism becomes sufficiently weak that relaxation is dominated by a charge-fluctuation mechanism which is unusual in two respects. It has a fractional magnetic component indicating that the mechanism responsible for the charge-fluctuation-induced relaxation also induces a magnetic fluctuation which contributes to relaxation. Furthermore, the suppression of this relaxation mechanism with decreasing temperature is quite slow ($T_1^{-1} \propto \sqrt{T}$). In particular, phononic mechanisms (the most common source of charge-fluctuation driven relaxation in nonmagnetic insulators) usually exhibit larger power law exponents.

The sample preparation procedure has been described elsewhere [3]. Two samples (labeled 1 and 2) were prepared for this study: sample 2 exhibited more intense superlattice peaks in the x-ray diffraction pattern. The concentration of magnetic impurities (estimated from the Curie contribution to the magnetic susceptibility at low T) was 0.5% (0.1%) for sample 2 (1). All results for the two samples were essentially the same (although measurements on the smaller sample 1 suffered from weak signals at high T). We will focus primarily on the results from sample 2. All measurements were carried out in zero applied field using NQR techniques. The recovery curve was recorded by integrating the spin echo intensity obtained after a $\frac{\pi}{2}$-t_s-$\frac{\pi}{2}$-τ-π pulse sequence in which the separation time t_s is swept. For $H_1 \gtrsim 50$ G, T_1 is independent of H_1; thus for our measurements ($H_1 \sim 70$ G) spin diffusion does not contribute to relaxation. The measured recovery curves exhibit a nonsingle exponential decay in all measurements

due to a distribution of T_1's. In order to extract the characteristic time constant of the distributed recovery curve, we fit our recoveries by the expression $M(t) = M_0\{1 - \exp[-(3t/T_1)^{\alpha}]\}$. (The factor of 3 is appropriate for a NQR measurement on a $I = 3/2$ nuclear spin [6].) The distribution is essentially temperature independent: $\alpha = 0.6 \pm 0.1$ for $10 < T < 300$ K.

In order to examine the degree of Li/Cu ordering, structural studies employing room temperature electron and neutron diffraction measurements were carried out on sample 2. The absence of diffuse scattering in long-exposure electron-diffraction patterns implies a high degree of Li/Cu ordering. Rietveld refinement of neutron diffraction data (based on the model of Ref. [5]; $R_p = 3.9\%$, $R_{wp} = 6.5\%$) confirms this. Furthermore, the Cu NQR frequency is very sensitive to the substitution of Li for Cu: $\nu_Q \simeq 36$ MHz in La_2CuO_4 and $\simeq 45$ MHz in $La_2Cu_{0.5}Li_{0.5}O_4$. Thus Cu linewidth is a sensitive indicator of Li disorder. Above 170 K, the NQR linewidth (FWHM) is $\lesssim 300$ kHz, only slightly larger than linewidths in the best samples of $YBa_2Cu_4O_8$, the most defect-free cuprate, ($\Delta\nu \sim 200$ kHz) and much less than in $La_{2-x}Sr_xCuO_4$ (typically 0.6–2 MHz for nonzero x). Cu NQR signals originating in significantly Li-poor regions of the sample (if they exist) will have a different NQR frequency and so will have no influence on the measurements.

For nuclei such as ^{63,65}Cu which have a nonzero quadrupole moment, nuclear spin relaxation can arise either from fluctuations of the hyperfine field of the electronic spin or fluctuations of the electric field gradients (EFG's) which arise from charge surrounding the probe nucleus [7]. (Hereafter, we will use the term "charge fluctuations" to describe the latter situation which can arise from any process which causes the electric field gradient at the nucleus to fluctuate.) The availability of two copper isotopes provides an opportunity to distinguish between these. If Q, γ, and n are, respectively, the nuclear quadrupole moment, gyromagnetic ratio, and the atomic number for a given nucleus, then ${}^nT_1^{-1}$ is proportional to ${}^n\gamma^2$ if relaxation is due to spin fluctuations and proportional to ${}^nQ^2$ if due to charge fluctuations. Thus, measuring the ratio $R \equiv {}^{63}T_1^{-1}/{}^{65}T_1^{-1}$ unambiguously distinguishes between these two mechanisms: the experimental value of R will equal $R_\gamma \equiv ({}^{63}\gamma/{}^{65}\gamma)^2 = 0.8720$ [$R_Q \equiv ({}^{63}Q/{}^{65}Q)^2 = 1.1378$] in the event that relaxation is due to spin fluctuations (charge fluctuations). This capability has been frequently exploited in studying the cuprates [8,9]. In Fig. 1(a) we show the T dependence of T_1^{-1}. Figure 1(b) shows the T dependence of R in $La_2Cu_{0.5}Li_{0.5}O_4$. Above 170 K, $R \simeq R_\gamma$ demonstrating that relaxation is due entirely to magnetic excitations; below this temperature the mechanism switches abruptly to one dominated by quadrupolar fluctuations.

The distribution of T_1^{-1}'s demonstrates that not all Cu sites are equivalent. This inequivalence of the various Cu sites could arise if relaxation were due to magnetic impurities randomly located in the lattice [10]. As we will show, however, the data do not support this explanation. Rather, we believe the distribution of Cu environments is due to local variations in the crystal structure similar to those observed in neutron diffraction experiments in $La_{2-x}Ba_xCuO_4$ [11]. These have shown that the local crystal structure (e.g., the local CuO_6 octahedral tilt order) varies on a length scale of ~ 10 Å. It is now evident that similar local variations in the crystal structure are present in the majority of, if not all, cuprates [12,13]. Such a local variation in the lattice structure will render different Cu sites inequivalent, and, in principle, the different sites will have different T_1^{-1}'s. Relaxation due to a dipolar coupling of the nuclear spins to randomly located magnetic impurities leads to distributed relaxation with $\alpha = \frac{1}{2}$ [10]. However, this mechanism cannot

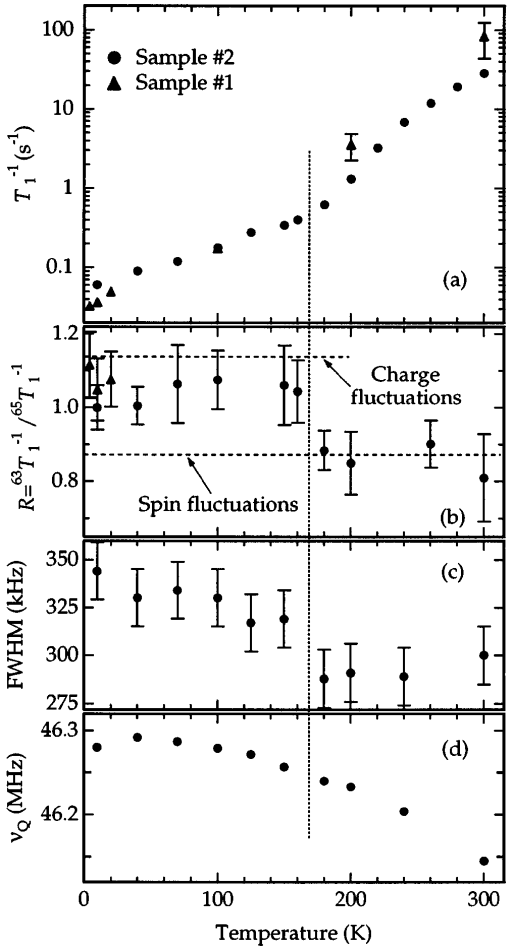

FIG. 1. The T dependencies of various quantities are shown for sample 1 (triangles) and sample 2 (circles). In panel (a), ${}^{63}T_1^{-1}$; in panel (b), $R \equiv {}^{63}T_1^{-1}/{}^{65}T_1^{-1}$. The broken horizontal lines show the values of the ratios $R_Q \equiv ({}^{63}Q/{}^{65}Q)^2 = 1.1378$ (charge fluctuations, upper line) and $R_\gamma \equiv ({}^{63}\gamma/{}^{65}\gamma)^2 = 0.8720$ (spin fluctuations, lower line). We show the full width at half maximum (FWHM) of the ^{63}Cu NQR line in panel (c) and the ^{63}Cu quadrupole frequency ν_Q in panel (d).

explain our data. At 170 K the T_1^{-1} relaxation mechanism abruptly shifts from a magnetic to a *quadrupolar* one. Yet the value of $\alpha = 0.6$ is unchanged at low temperatures where the magnetic impurity mechanism is clearly not responsible for relaxation. This makes clear that the origin of the distribution of T_1^{-1}'s is much more general than the specific magnetic impurity relaxation mechanism, and apparently more fundamental.

The NQR data fall into two temperature regimes. Above 170 K T_1^{-1} increases rapidly with increasing T; this regime is well described by an activated process: $(T_1T)^{-1} = C_0 \exp(-E_a/k_BT)$ with $E_a = 130$ meV and $C_0 = 14\ \mathrm{s}^{-1}\,\mathrm{K}^{-1}$ (see Fig. 2). With decreasing temperature this rapidly weakening relaxation rate decreases sufficiently to reveal a mechanism arising from charge fluctuations. This is demonstrated by the abrupt shift of R toward R_Q [see Fig. 1(b)]. The relevant charge fluctuations could arise from distortions of the CuO_6 octahedra or from charge fluctuations within the Cu ion. However, R ($\simeq$1.05) is constant within the error and less than R_Q (=1.1378) indicating the presence of an intrinsic *magnetic* contribution to relaxation at low T having the same T dependence as the charge-fluctuation mechanism. (The downturn in R below 40 K in sample 2 probably reflects the influence of impurities.) This implies a coupling between the charge and spin fluctuations which would suggest that the mechanism responsible for the charge fluctuation also introduces a weak magnetic component into the doped-hole state. The observed temperature dependence of T_1^{-1} is unusually slow: $T_1^{-1} \propto \sqrt{T}$ (see Fig. 2 inset). For example, our measurements in the diamagnetic, Cu^{1+} compound Cu_2O find $R = R_Q$ and $T_1^{-1} \propto T^2$, behavior more characteristic of a phononic nuclear spin relaxation mechanism.

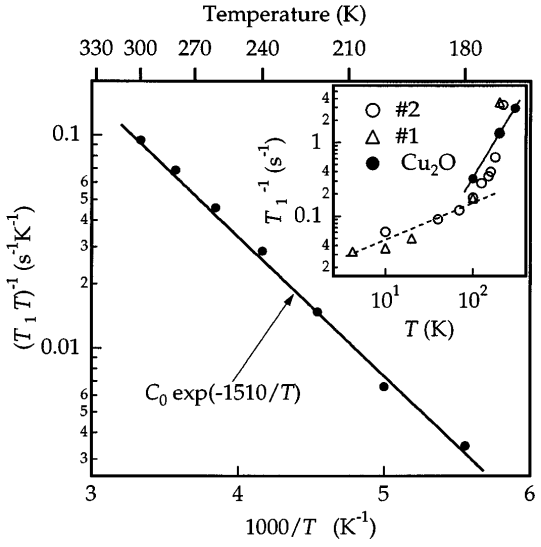

FIG. 2. The activated behavior at high temperature is shown: we plot $(^{63}T_1T)^{-1}$ versus $1000/T$. The solid line shows the function $f(T) = C_0 \exp(-E_a/k_BT)$ where $E_a/k_B = 1510$ K and $C_0 = 14\ \mathrm{s}^{-1}\,\mathrm{K}^{-1}$. Inset: power law behavior for $La_2Cu_{0.5}Li_{0.5}O_4$ (open symbols) and Cu_2O (closed symbols); lines indicate T^2 (solid) and $\sqrt{T}$ (dashed line) behavior.

To better understand the shift at 170 K, we examined the evolution of the Cu NQR spectrum with temperature. Figures 1(c) and 1(d) show the T dependencies of the width (FWHM) and frequency, ν_Q, of the ^{63}Cu NQR line. While ν_Q increases essentially monotonically with decreasing T, the FWHM exhibits an anomaly near 170 K, where the relaxation mechanism changes. As ν_Q is proportional to the EFG at the nuclear site, this increase indicates increased inhomogeneity. Since ν_Q has contributions from both electronic charge on the same site and from all surrounding ions straightforward, interpretation of these results is difficult.

Our results do not definitively determine the spin of the ground state of a doped hole occupying a CuO_4 plaquette. The uniform (wave vector $q = 0$) magnetic susceptibility of $La_2Cu_{0.5}Li_{0.5}O_4$ is diamagnetic [2]. However, taking into account an estimate of the core diamagnetic contributions to the susceptibility, it is not clear that one can rule out the possibility of a finite, but weakly temperature dependent spin susceptibility. Were it not for the small magnetic contribution to the low temperature ($T < 170$ K) T_1^{-1}, the observation of an activated temperature dependence of the nuclear spin relaxation, which decreases until it becomes unobservable in a background of charge-fluctuation induced relaxation, would provide convincing evidence that the ground state of the local doped-hole state is indeed a magnetic singlet, in agreement with expectations. The presence of a magnetic component in the low-T relaxation leaves open the possibility that the ground state has nonzero spin. The apparent coupling to the charge-fluctuation mechanism strongly suggests, however, that the doped-hole ground state is indeed singlet, but that a low-lying excited state has both spin and an altered charge distribution around the Cu nucleus.

We turn now to the magnetic excitation observed above 170 K. The small value of the gap to a magnetic state is unexpected. E_a is very close to the value of the effective coupling, J between Cu moments in the undoped and lightly doped cuprates. Given the isolated nature of the copper moments in this material it is hard to understand how a similar value of J would be observed in this material. Nonetheless, while possibly coincidental, the appearance of a fundamental energy scale for cuprates in the spectrum of an isolated singlet is striking. Zhang and Rice [1] argue that the energy gap between the ground state singlet and the lowest-lying triplet state will be $6(t_1 + t_2)$, where $t_1 = t_0^2/(U - \epsilon_p)$ and $t_2 = t_0^2/\epsilon_p$. Here t_0 is the amplitude of the hybridization between Cu($d_{x^2-y^2}$) and O($2p\sigma$) orbitals, U is the on-site Coulomb repulsion at the copper site, and ϵ_p is the O site energy. Using reasonable values for these parameters this gives a gap of $\sim$6 eV, much larger than the observed 130 meV. *Ab initio* cluster calculations [14] find a similar singlet-triplet splitting (5.4 eV). This

energy is large because the singlet is confined to a single CuO_4 plaquette. However, increasing the size of the local singlet would lead to overlap between neighboring states and, presumably, delocalization, inconsistent with observed insulating behavior.

Polaron formation [15] has been implicated in the local deviations in crystal structure [12,13] noted earlier. Theoretical studies by Yonemitsu *et al.* [16] find a breathing mode polaron in the CuO_2 planes involving contraction of the Cu-O distance which alters the mixing of the Cu and ligand holes, thereby reducing the magnitude of the Cu moment. If this polaronic state were time dependent, this could cause a fluctuation of the Cu electronic moment and thus Cu nuclear-spin relaxation. Very interestingly, Anisimov *et al.* [17] find a low-lying anti-Jahn–Teller polaron which *carries a triplet spin*. This state involves hole occupation of the $Cu(3d_{3z^2-r^2})$ orbital. The tendency of the spherical Li^{1+} ion to prefer a nonplanar coordination may encourage such local structural deformations. If these were dynamic, Li motion would modulate the Cu-O bond length and thus, possibly, the Cu moment. Finally, we note that $\ln\rho \propto T^{-(1/4)}$ behavior is observed in the case of hopping between localized states [18].

In summary, the compound $La_2Cu_{0.5}Li_{0.5}O_4$ provides the opportunity to study the doped-hole state which results from adding a hole to a CuO_4 plaquette. We observe a low-lying excitation with an energy of 130 meV. This is much lower than expectations based on calculations of the spectrum of a singlet localized on a single CuO_4 plaquette. This suggests the involvement of some other physics which introduces low-lying states into the excitation of the doped-hole state. In the low-T regime, the anomalously slow T dependence of the charge-fluctuation-induced T_1^{-1} is not understood, but this process involves coupled charge fluctuation and magnetic mechanisms. This and the simultaneous occurrence of anomalies in T_1^{-1} and the NQR linewidth suggest that the electron-lattice coupling is significantly involved. The doped-hole state is the fundamental element from which high temperature superconductivity arises. We find that this state has several unexpected properties indicating the importance of phenomena not previously appreciated. Further investigations of this and related materials are warranted. Studies of local structure and spectroscopic measurements capable of directly probing the 130 meV excitation could provide important insight into the origin of the unusual normal state properties and the nature of high temperature superconductivity in the cuprates.

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