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## Direct evidence of non-Zhang-Rice $\text{Cu}^{3+}$ centers in $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$

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A well-isolated Zhang-Rice (ZR) singlet as a ground state of the  $\text{Cu}^{3+}$  center in hole-doped cuprates is a leading paradigm in modern theories of high-temperature superconductivity. However, a dramatic temperature evolution of the  $^{6,7}\text{Li}$  NMR signal in  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ , a system with a regular lattice of well-isolated  $\text{Cu}^{3+}$  centers, reveals significant magnetic fluctuations and suggests a quasidegeneracy to be a generic property of their ground state at variance with the simple ZR model. We argue for a competition of the ZR state with nearby states formed by a "doped" hole occupying purely oxygen nonbonding  $a_{2g}(\pi)$  and  $e_u(\pi)$  orbitals rather than a conventional  $b_{1g}(d_{x^2-y^2})$   $\text{Cu}$   $3d$ - $\text{O}$   $2p$  hybrid. The temperature variation of the  $^{6,7}\text{Li}$  NMR line shape and spin-lattice relaxation rate point to a gradual slowing down of some magnetic order parameter's fluctuations without distinct signatures of a phase transition down to  $T = 2$  K. This behavior agrees with a stripelike ferrodistorptive fluctuating  $Ammm$  order in a two-dimensional structure of the  $(\text{CuLi})\text{O}_2$  planes accompanied by unconventional oxygen orbital antiferromagnetic fluctuations.

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**Introduction.** The nature of the doped-hole state in the cuprates with nominally  $\text{Cu}^{2+}$  ions such as  $\text{La}_2\text{CuO}_4$  is a matter of great importance in understanding both the mechanism leading to high-temperature superconductivity and the unconventional normal state behavior of the cuprates. A single hole  $b_{1g}(\propto d_{x^2-y^2})$  state of the  $\text{Cu}^{2+}$  ion is a typical one for copper ions with the square-planar coordination of oxygen ions, whereas a two-hole  $\text{Cu}^{3+}$  state with the same coordination of oxygen ions seldom exists.

In 1988 Zhang and Rice<sup>1</sup> proposed that the doped hole forms a well-isolated local spin and orbital  $^1A_{1g}$  singlet state which involves a phase coherent combination of the  $2p\sigma$  orbitals of the four nearest neighbor oxygens with the same  $b_{1g}$  symmetry as for a bare  $\text{Cu}$   $3d_{x^2-y^2}$  hole. However, there are both theoretical considerations and many experimental observations (for a short overview, see Refs. 2, and Refs. 3 and 4 for the most recent publications) that unambiguously point to an inconsistency of the simple Zhang-Rice (ZR) model and a competition of the conventional ZR state with another electron removal state.

Although the concept of a well-isolated ZR singlet for the doped-hole state in cuprates (the first ionization state for an insulating cuprate) remains widely accepted as a guideline in an overwhelming majority of current model approaches, 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 a strong coupling of the corner-shared  $\text{CuO}_4$  plaquettes in the  $\text{CuO}_2$  planes and, in particular, to the difficulty of discerning the magnetic behavior of the ZR singlet in a background of antiferromagnetically correlated copper moments in parent cuprates. A unique opportunity to study the doped-hole state, or nominally  $\text{Cu}^{3+}$  ions in isolated  $\text{CuO}_4$  clusters without the confounding contributions of the nearest

neighbor antiferromagnetically correlated  $\text{CuO}_4$  clusters, is provided in  $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$  at  $x = 0.5$ .<sup>5</sup> At this composition the Li and Cu ions form an ideally ordered superlattice<sup>6,7</sup> in which all Cu ions are surrounded by four in-plane Li ions ( $1s^2$ , closed shell electronic configuration) and thus create weakly coupled, almost isolated  $\text{CuO}_4$  clusters. Surprisingly, the first experimental studies of  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  (Refs. 6–9) have uncovered several unexpected properties, indicating the importance of phenomena not previously appreciated. On the one hand, most researchers assign  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  to the  $\text{K}_2\text{NiF}_4$  ( $I4/mmm$ ) crystal structure in full accordance with a ZR singlet ground state of the  $\text{Cu}^{3+}$  centers, hereafter termed the ZR phase. On the other hand, the first low-temperature ( $T = 5$  K) neutron-diffraction structural determination<sup>6</sup> and later electron-diffraction studies<sup>7</sup> revealed clear signatures of the orthorhombic  $Ammm$  space group that cannot be directly reconciled with the ZR scenario.

The diamagnetic susceptibility of  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  (Ref. 8) strongly suggests the scenario of well-isolated ZR singlets in  $(\text{CuLi})\text{O}_2$  planes. However, the analysis of the temperature dependence of the  $^{63,65}\text{Cu}$  nuclear quadrupole resonance (NQR) relaxation rates<sup>9</sup> unambiguously evidences that the singlet state has a 130 meV gap to magnetic excitations. In other words, it appears the energy of the excited spin-triplet state relative to the ground state is radically smaller than predicted by Zhang and Rice<sup>1</sup> and many other authors. Whereas this paper has generated a revival of the interest in the low-energy electronic structure of the hole centers in cuprates, the theoretical studies of the non-ZR effect in  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  are limited to two papers,<sup>10,11</sup> with some conjectures regarding the origin of the low-energy spin triplet. Furthermore, the  $^{63,65}\text{Cu}$  NQR study<sup>9</sup> has posed other puzzles which remain unexplained. For example, below 170 K, the  $^{63,65}\text{Cu}$  nuclear

relaxation is dominated by quadrupolar fluctuations, however, with a weak yet distinct intrinsic *magnetic orbital* contribution having the same  $T$  dependence. The distribution of  $T_1^{-1}$ 's demonstrates that not all Cu sites are equivalent and the local crystal structure seems to vary on a nanoscopic length scale. The muon spin rotation ( $\mu$ SR) studies of  $\text{La}_2\text{Cu}_{0.5}\text{Li}_{0.5}\text{O}_4$  (Ref. 12) revealed that below about 200 K a magnetically inhomogeneous state evolves with magnetic clusters in about 15% of the sample volume and the remaining nonmagnetic volume.

All these puzzles stimulated our  $^{6,7}\text{Li}$  nuclear magnetic resonance (NMR) studies of  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ . An extremely ionic character of the Li-O bond makes the  $^7\text{Li}$  nuclei as very instructive NMR probes of the valence states of oxygen and copper ions. First room temperature (RT)  $^7\text{Li}$  NMR measurements in powder  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  samples<sup>8,13</sup> revealed a very narrow [ $\approx 5$  kHz (Ref. 13)] bare linewidth that allowed for the quadrupole effects to be resolved even in powder samples. Furthermore, this pointed to an opportunity to make use of  $^7\text{Li}$  NMR spectra for the detection of subtle non-ZR effects predicted theoretically. Indeed, estimates for oxygen orbital magnetic moments  $\mu \leq 0.1\mu_B$  (Refs. 2 and 4) point to rather large dipole magnetic fields on  $^7\text{Li}$  nuclei,  $H_{\text{dip}} \leq 100$  Oe, that correspond to a very large  $^7\text{Li}$  NMR line shift,  $\Delta\nu \leq 160$  kHz, which is considerably larger than the quadrupole splitting  $\sim 40$  kHz.<sup>8,13</sup> At the same time these dipole fields in the case of  $^{63,65}\text{Cu}$  nuclei correspond to smaller shifts of  $\leq 100$  kHz hardly resolved given the  $^{63,65}\text{Cu}$  NQR linewidth in  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ , FWHM  $\approx 700$  kHz at  $T = 1.5$  K.<sup>8</sup> In other words, the  $^7\text{Li}$  NMR seems to be a more sensitive tool for an inspection of subtle effects than the  $^{63,65}\text{Cu}$  NMR-NQR.

In this Rapid Communication we report results of the  $^{6,7}\text{Li}$  NMR measurements in  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  samples which directly point to an inconsistency of the conventional model of the well-isolated spin and orbital ZR singlet  $^1A_{1g}$  believed to be the ground state of the hole-doped  $\text{CuO}_4$  center in the  $\text{CuO}_2$  layers. Our data suggests the involvement of some other low-lying states into the excitation of the doped-hole state in cuprates.

**Experiment.** The sample preparation procedure has been described elsewhere.<sup>5</sup> The RT x-ray powder diffraction pattern of the pristine cuprate  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  was indexed to fit a tetragonal  $\text{K}_2\text{NiF}_4$ -type structure (space group  $I4/mmm$ ,  $a = b = 3.731$  Å,  $c = 13.20$  Å).  $^{6,7}\text{Li}$  NMR experiments were performed utilizing a Tecmag Apollo FT NMR spectrometer equipped with a high homogeneity superconducting Varian NMR magnet with a fixed magnetic field  $\mu_0 H = 9.3956$  T and an Oxford Instruments continuous flow cryostat.  $^{6,7}\text{Li}$  NMR spectra were recorded in the temperature range of 1.9–300 K at the frequencies  $^7F_0 = 155.462$  MHz and  $^6F_0 = 58.864$  MHz for  $^7\text{Li}$  and  $^6\text{Li}$ , respectively, using the conventional spin-echo pulse sequence  $\pi/2-\pi$  with the subsequent Fourier transformation of half of the spin-echo signal in the time domain. The  $^7\text{Li}$  nuclear spin-lattice relaxation was measured by the saturation-recovery method in the temperature range 4.2–300 K.

**Results.** Our main results are presented in Figs. 1 and 2. The upper panel in Fig. 1 shows the  $^7\text{Li}$  NMR spectra measured at different temperatures. The RT spectrum is a textbook example of the  $I = 3/2$  NMR powder pattern with almost zero chemical

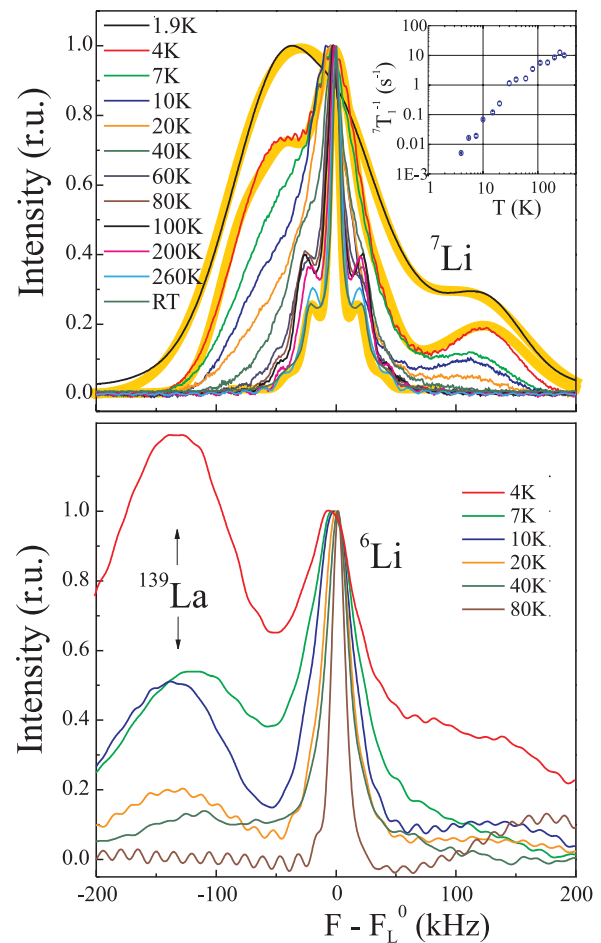


FIG. 1. (Color online) Upper panel:  $^7\text{Li}$  NMR spectra ( $^7F_0 = 155.462$  MHz). The thick solid lines are Gaussian powder fitting. Bottom panel:  $^6\text{Li}$  NMR spectra ( $^6F_0 = 58.864$  MHz). All line shapes are normalized to equal heights for purposes of comparison.

shift and the first order quadrupole splitting of 0.045 MHz, which is in perfect agreement with the  $^7\text{Li}$  NMR spectra reported in Refs. 8 and 13. This is completely consistent with the ZR scenario and seemingly does not arouse any suspicion of its validity. However, our  $^7\text{Li}$  NMR measurements revealed a dramatic counterintuitive change in the  $^7\text{Li}$  NMR line shape upon lowering the temperature (see Fig. 1), particularly below 10 K. Several remarkable features of the spectra should be noted: (i) a strong inhomogeneous broadening with a marked change of the line shape already below  $T \approx 200$  K and a clearly visible asymmetry below  $T \approx 100$  K; (ii) the relative intensity of the high-temperature central NMR line gradually falls down upon lowering the temperature with a simultaneous rise of the intensity of two broad satellite lines distinctly separated only below 10 K (these are different from the quadrupolar satellites which are still present); and (iii) the left satellite line shifted by  $-0.06$  MHz ( $T = 4$  K) from the Larmor frequency becomes a dominant component of the  $^7\text{Li}$  NMR spectra below 2 K. The relative spectral weight of the less intensive right satellite line shifted by  $+0.012$  MHz ( $T = 4$  K) from the Larmor frequency falls with lowering the temperature.

The lower panel in Fig. 1 presents the observed temperature evolution of the  $^6\text{Li}$  NMR spectra in  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ . Due

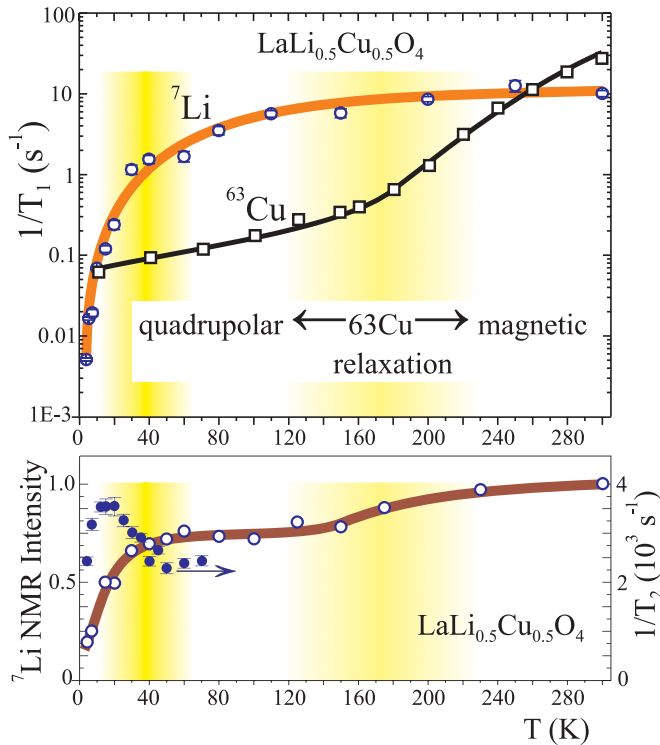


FIG. 2. (Color online) Upper panel: Temperature dependence of the spin-lattice relaxation rate for  ${}^7\text{Li}$  (open circles) and  ${}^{63}\text{Cu}$  (open squares, Ref. 9). Bottom panel: Integrated  ${}^7\text{Li}$  NMR intensity scaled for the Boltzmann factor and  $T_2$  spin-echo decay, and normalized to intensity at  $T = 300$  K (open circles, left Y axis);  $1/T_2$  values (blue solid circles, right Y axis). The solid curves are guides for the eye.

to the very low quadrupole moment of  ${}^6\text{Li}$  nuclei ( ${}^6Q = -0.0008$  b) as compared to  ${}^7\text{Li}$  ( ${}^7Q = -0.045$  b) the  ${}^6\text{Li}$  NMR spectra are almost free of any quadrupole effects, providing a unique opportunity to distinguish between the magnetic and charge distribution caused phenomena. Unfortunately, the gyromagnetic ratio of the  ${}^6\text{Li}$  nuclei,  ${}^6\gamma/2\pi = 6.27$  MHz/T, only slightly exceeds that of  ${}^{139}\text{La}$ ,  ${}^{139}\gamma/2\pi = 6.01$  MHz/T, therefore the  ${}^6\text{Li}$  NMR signal is superimposed on a broad  ${}^{139}\text{La}$  NMR line peaked at about  $-150$  kHz (marked by an arrow in Fig. 1) growing up upon lowering the temperature. The line is revealed to be the right hand singularity of the central transition line powder pattern of the  ${}^{139}\text{La}$  nuclei strongly broadened by the second order quadrupole effects. Nonetheless, as seen from Fig. 1 (lower panel) the  ${}^6\text{Li}$  NMR spectra demonstrate a single distinct peak line shape which starts to broaden below  $80$  K with a clear asymmetry at the lowest temperatures, thus unequivocally validating the presence of a magnetic mechanism of line broadening both for  ${}^6\text{Li}$  and  ${}^7\text{Li}$  with fluctuations of the local field,  $|\delta H_{\text{loc}}| \leq 100$  Oe. The spin-lattice relaxation (SLR) rate  $T_1^{-1}$  for  ${}^7\text{Li}$  decreases continuously towards low temperatures, revealing a three orders of magnitude slowing down between  $300$  and  $4$  K with no anomalies corresponding to the onset of a structural or magnetic long-range order. Its behavior differs radically from that of  $T_1^{-1}$  for  ${}^{63}\text{Cu}$  (see Ref. 9 and Fig. 2, upper panel), pointing to an absolutely different leading mechanism of the low-temperature SLR for the two nuclei, quadrupole for  ${}^{63}\text{Cu}$  (Ref. 9) and the magnetic one for  ${}^7\text{Li}$ . On the other hand,

the  ${}^7T_1^{-1}(T)$  dependence resembles that of  $T_1^{-1}$  for  ${}^{63,65}\text{Cu}$  in the normal state of many superconducting cuprates, where it is considered to be a signature of a pseudogap behavior or a very gradual and inhomogeneous glassy slowing of stripe fluctuations.<sup>14</sup> A relatively weak rise of the spin-spin relaxation rate  ${}^7T_2^{-1}$  under lowering the temperature turns into a sharp fall below  $10$  K. As for  ${}^{63,65}\text{Cu}$  NQR in typical striped cuprates<sup>14</sup> the integrated  ${}^7\text{Li}$  NMR intensity scaled for the Boltzmann factor and  $T_2$  spin-echo decay shows a *wipeout* effect, or a dramatic loss of signal intensity below  $50$  K, with a precursor at temperatures below  $180$  K (Fig. 2, bottom panel), where the  ${}^{63,65}\text{Cu}$  SLR mechanism switches abruptly from purely magnetic to one dominated by quadrupolar fluctuations<sup>9</sup> (see Fig. 2, upper panel).

*Discussion.* Our experimental findings support earlier suggestions<sup>9</sup> and point to a clear inconsistency of the simple ZR model for the  $\text{CuO}_4^{5-}$  hole centers in  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ . These data evidence that the  $\text{CuO}_4^{5-}$  centers should have nontrivial magnetic orbital order parameters whose fluctuations and ordering are clearly seen by  ${}^6,{}^7\text{Li}$  rather than  ${}^{63,65}\text{Cu}$  nuclei. The temperature evolution of the  ${}^7\text{Li}$  NMR signal points to an instability of the high-temperature ZR phase and its competition with another low-temperature phase which does condense below  $T = 2$  K. In other words, experimental data suggest some kind of (quasi)degeneracy in the valence state of the hole centers with a competition of the conventional ZR state with another low-lying state(s). Direct information about these states can be retrieved from the neutron structural data<sup>6</sup> on the  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  system which revealed a  $B_{2g}$ -type (rectangular) distortion of both  $\text{CuO}_4$  and  $\text{LiO}_4$  plaquettes with acute in-plane O-M-O bond angles of  $86^\circ$  and  $87^\circ$ , respectively. This finding cannot be reconciled with the concept of the well-isolated ZR singlet but agrees with a static pseudo-Jahn-Teller (PJT) effect induced by a vibronic coupling of the  ${}^1A_{1g}$  ZR singlet with a nearby  ${}^1B_{2g}$  singlet. Such a  ${}^1A_{1g}$ - ${}^1B_{2g}$  quasidegeneracy is one of the main points in the model of the non-ZR valence multiplet proposed in Refs. 2 and 4 whose results are summarized in Fig. 3. Cluster model calculations show that the ground state of a two-hole  $\text{CuO}_4^{5-}$  center arises from a competition of the conventional hybrid  $\text{Cu } 3d\text{-O } 2p$   $b_{1g} \propto d_{x^2-y^2}$  state and *purely oxygen nonbonding* O  $2p\pi$  states with  $a_{2g}$  and  $e_{u,x,y} \propto p_{x,y}$  symmetry<sup>15</sup> [see Fig. 3(a)]. Accordingly, the ground state of such a non-ZR  $\text{CuO}_4^{5-}$  hole center with  $D_{4h}$  symmetry as a cluster analog of the  $\text{Cu}^{3+}$  ion should be described by a complex  ${}^1A_{1g}$ - ${}^1B_{2g}$ - ${}^1E_u$  multiplet to be an interplay of three two-hole configurations,  $b_{1g}^2$ ,  $b_{1g}a_{2g}$ , and  $b_{1g}e_u$ , rather than the well-isolated spin and orbital ZR singlet  ${}^1A_{1g}$ .<sup>16</sup>

The vibronic mixing of the  ${}^1A_{1g}$  and  ${}^1B_{2g}$  terms gives rise to a two-well adiabatic potential with two types of the bond-bending  $B_{2g}$  distortion of the  $\text{CuO}_4$  plaquette ( $B_{2g}^x$  and  $B_{2g}^y$ , respectively). Their in-plane long-range ferrodistorptive ordering with a rectangular distortion both of  $\text{CuO}_4$  and  $\text{LiO}_4$  plaquettes [see Fig. 3(d)] gives rise to the orthorhombic  $Ammm$  structure.<sup>6,17</sup> However, the  ${}^1A_{1g}$ - ${}^1B_{2g}$  doublet is characterized by two purely orbital order parameters<sup>2,4</sup> [see Fig. 3(d)]. These are a conventional electric quadrupole moment ( $Q_{xy}$ ) of  $B_{2g}$  symmetry and an unconventional antiferromagnetic  $G_z$  ordering of the oxygen orbital magnetic

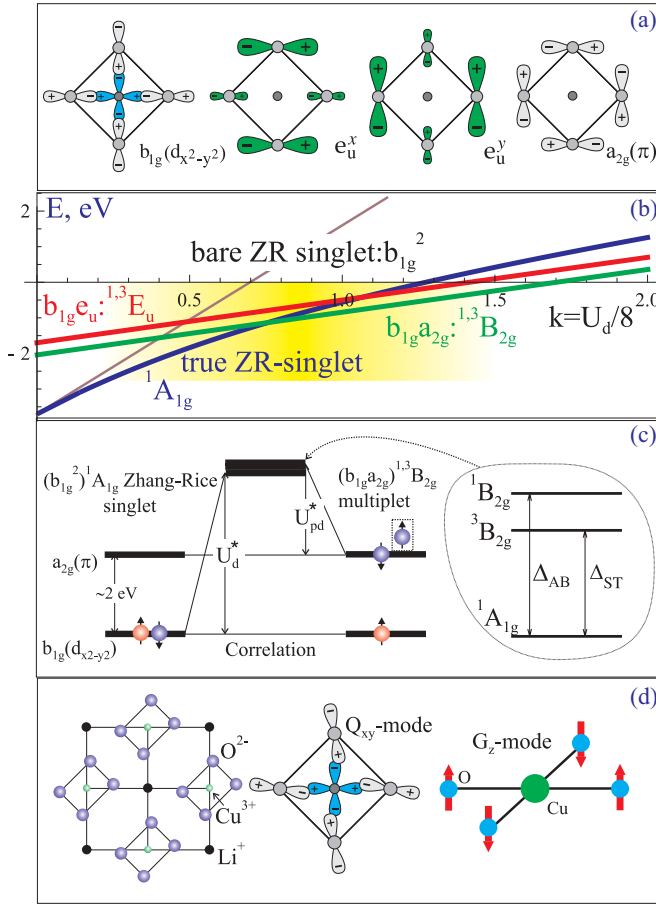


FIG. 3. (Color online) (a) Hole orbitals active in forming the non-ZR center. (b) Energies of the competing terms (true ZR singlet,  $b_{1g}a_{2g} : {}^{1,3}B_{2g}$ , and  $b_{1g}e_u : {}^{1,3}E_u$ ) as functions of the effective “screening” parameter  $k = U_d/U_d^0$  (bare ZR singlet = true ZR singlet given  $U_d = 0$ ). Filling points to the (quasi)degeneracy region. (c) Simple illustration of the formation of the valence  $(b_{1g})^2 ({}^1A_{1g})^1$  Zhang-Rice singlet and  $(b_{1g}a_{2g})^1 ({}^{1,3}B_{2g})^1$  multiplet; (d) from left to right, illustration of the ferrodistortive  $B_{2g}$ -type order, the oxygen quadrupole  $Q_{xy}$ , and antiferromagnetic orbital  $G_z$  orders, respectively.

moments ( $\leq 0.1\mu_B$ ) both localized on four oxygen sites.<sup>18</sup> The latter was proved recently<sup>4</sup> to be responsible for an unusual translational-symmetry preserving antiferromagnetic order which was revealed by the spin-polarized neutron diffraction in the pseudogap phase of several hole-doped high- $T_c$  cuprates.<sup>19</sup> The staggered  $G_z$ -type orbital magnetic fluctuations are seen only by  ${}^6,{}^7\text{Li}$  and  ${}^{17}\text{O}$  rather than  ${}^{63,65}\text{Cu}$  nuclei that explains a radically different mechanism of the low-temperature SLR for Li and Cu nuclei. Our  ${}^6,{}^7\text{Li}$  NMR data together with the  ${}^{63,65}\text{Cu}$  NQR data<sup>9</sup> point to a step-by-step condensation of the ferrodistortive stripelike lattice-orbital  $Ammm$ - $G_z$  mode.

We fitted the  ${}^7\text{Li}$  NMR spectra by trial and error down to  $T = 4$  K as a superposition of three main powder patterns with a temperature dependent spectral weight, a central NMR line at the Larmor frequency, and two (left and right) satellite lines. At the lowest temperature,  $T = 1.9$  K, the spectral weight of the central NMR line sharply falls almost down to zero. The results of the fitting for room temperature,  $T = 4$  and 1.9 K shown in Fig. 1, nicely demonstrate an evolution of the  ${}^7\text{Li}$

NMR signal from that which is typical for the RT ZR phase to a response of a low-temperature phase. It is worth noting that at variance with the narrow central NMR line the fitting for both the satellite lines implied a local magnetic field on the order of 20–25 Oe directed perpendicular to  $(\text{Li})\text{CuO}_4$  plaquettes. Such a field can be induced by adjacent oxygen orbital moments on the order of  $0.02\mu_B$ .

The  $A$ - $B$ - $E$  quasidegeneracy of the valence multiplet does not necessarily produce large positive magnetic susceptibility for the hole  $\text{CuO}_4^{5-}$  centers. Indeed, given the ZR singlet as a ground state we arrive at a dominant contribution of the fluctuations induced by the  $A$ - $B$  or  $A$ - $E$  “linear” mixing which does not produce the net spin or orbital magnetic moment. This agrees with the negative susceptibility observed for  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  down to very low temperatures,  $T \sim 10$  K,<sup>8</sup> which was considered earlier to be a strong argument in favor of the well-isolated spin singlet ZR ground state. On the other hand, a low-temperature Curie-like susceptibility upturn<sup>8</sup> points to the contribution of a net spin and/or orbital bulk magnetic moment fluctuations induced by a coupling of the  $A$ - $B$ - $E$  valence multiplets for adjacent centers. The shift of the NMR lines in such a system should include both the spin and orbital contributions. The two-satellite structure in the  ${}^7\text{Li}$  NMR response of the low-temperature phase can most likely reflect an orbital domain structure. Then simple estimates yield for the non-ZR phase, at  $T = 4$  K,  $K_{\text{spin}} \approx +0.02\%$ ,  $K_{\text{orb}} \approx -0.06\%$ .

**Summary.** We observed a dramatic temperature evolution of the  ${}^6,{}^7\text{Li}$  NMR signal in  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  which cannot be explained in frames of the simple ZR scenario for the ground state of the hole  $\text{CuO}_4^{5-}$  centers and suggests a quasidegeneracy to be a generic property of their ground state. We argue a competition of the ZR state with nearby states formed by a “doped” hole occupying *purely oxygen nonbonding*  $a_{2g}(\pi)$  and doublet  $e_{u,x,y}(\pi)$  orbitals rather than a conventional  $b_{1g}(d_{x^2-y^2})$   $\text{Cu } 3d$ - $2p$  hybrid. The temperature variation of the  ${}^6,{}^7\text{Li}$  NMR line shape and the SLR rate point to a gradual slowing down of some order parameter’s fluctuations without distinct signatures of a phase transition down to  $T = 2$  K. This behavior agrees with a quantum disordered stripelike<sup>20</sup> ferrodistortive fluctuating  $Ammm$  order in a two-dimensional structure of the  $(\text{CuLi})\text{O}_2$  planes accompanied by unconventional oxygen orbital antiferromagnetic fluctuations. At present, there are no published NMR or ZF- $\mu\text{SR}$  studies which revealed signatures of the static  $G_z$ -type mode in cuprates (see Ref. 19 and references therein). The failure to detect orbital-like magnetic order of the kind observed by spin-polarized neutron diffraction<sup>19</sup> surely indicates that the local fields are rapidly fluctuating outside the  $\mu\text{SR}$  or NMR time window. In this regard our  ${}^6,{}^7\text{Li}$  NMR measurements can be addressed as an indication of a quasistatic  $G_z$ -type mode realized in  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ . Further work implies direct  ${}^{17}\text{O}$  NMR studies on samples enriched with  ${}^{17}\text{O}$ .

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- <sup>15</sup>O  $2p\pi$ -type  $e_u$  orbitals acquire a small O  $2p\sigma$  mixture [Fig. 3(a)] due to a  $\pi$ - $\sigma$  hybridization (Ref. 2).
- <sup>16</sup>The  $A$ - $B$ - $E$  model suggests even two candidate spin triplets,  ${}^3E_u$  or  ${}^3B_{2g}$ , for the magnetic excitation at 0.13 eV observed in the  ${}^{63,65}\text{Cu}$  NQR studies of  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$  (Ref. 9).
- <sup>17</sup>Prior to the findings of Attfield and Férey (Ref. 6) an antiferrodistortive  $B_{2g}$  ordering with the rectangular distorted  $\text{CuO}_4$  plaquettes but square  $\text{LiO}_4$  plaquettes was addressed (Ref. 5) to be the most preferred low-temperature crystal mode in  $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ .
- <sup>18</sup>In general, the  $A$ - $B$ - $E$  multiplet of the  $\text{CuO}_4^{5-}$  hole centers is characterized by a set of different order parameters, including conventional spin and Ising-like orbital magnetic moments, toroidal moment, electric dipole, and quadrupole moments (Ref. 2).
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