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Nonbonding oxygen holes and spinless scenario of magnetic response in doped cuprates

A. S. Moskvin

Department of Theoretical Physics, Ural State University, 620083 Ekaterinburg, Russia

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Both theoretical considerations and experimental data point to a more complicated nature of the valence hole states in doped cuprates than it is predicted by Zhang-Rice model. Actually, we deal with a competition of conventional hybrid Cu 3d-O 2p $b_{1g} \propto d_{x^2-y^2}$ state and purely oxygen nonbonding state with $e_u x, y \propto p_{x,y}$ symmetry. The latter reveals a non-quenched Ising-like orbital moment that gives rise to a novel spinless purely oxygen scenario of the magnetic response in doped cuprates with the oxygen localized orbital magnetic moments of the order of tenths of Bohr magneton. We consider the mechanism of ^{63,65}Cu-O 2p transferred orbital hyperfine interactions due to the mixing of the oxygen O 2p orbitals with Cu 3p semicore orbitals. Quantitative estimates point to a large magnitude of the respective contributions both to local field and electric field gradient, and their correlated character.

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I. Introduction. The role played by magnetism, particularly the nature of magnetic fluctuations, is one of the central issues of the high-T$_c$ cuprate physics. Nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) are believed to provide the basic experimental grounds for a spin-fluctuation mechanism of high temperature superconductivity. It is worth to note that namely the spin-lattice relaxation rates and the Knight shift measurements by the NMR and NQR stimulated the elaboration of the well known antiferromagnetic spin-fluctuation scenario for the cuprates.[1] NMR first revealed a suppression of the low-energy magnetic excitations below what is called the spin gap temperature. In the underdoped region, it is thought that above T_c a pseudo-gap opens up in the spin fluctuation spectrum. Since the spin-gap state is believed to be related to the pairing mechanism, a large number of experimental and theoretical studies have focused on the origin of the spin gap. Despite some criticism [2] the spin-fluctuation scenario continues to be very popular both in the NMR/NQR and HTSC community. However, a conventional approach to the hyperfine coupling and the nuclear resonance in cuprates implies a treatment within simple models usually applied to the conventional metals or vice versa to the weakly covalent and weakly correlated insulator. The magnetic response is assumed to be provided by the only contribution of the spin degrees of freedom. As in parent antiferromagnetic oxides the Cu^{2+} center with $s = 1/2$ is considered to be a main resonating center whereas the doped holes are considered to form an usual Fermi-liquid. Meanwhile, a hole doping in the framework of the strongly-correlated scenario results in a formation of the well isolated Zhang-Rice $^1A_{1g}$ singlets. The hyperfine interactions and NMR-NQR experiments in cuprates right up to now are interpreted within the Shastri-Mila-Rice (SMR) spin Hamiltonian [3]. A conventional approach to the analysis of the ^{63,65}Cu NQR/NMR experiments in the hole-doped cuprates corresponds to the model of uniform lattice and indirectly implies the 100% volume fraction of the equivalent resonating nuclei.

Despite a great many of experimental and theoretical papers the nature and proper description of the magnetic correlations in cuprates is still a subject of controversy. Results of the recent NQR/NMR experiments for "classic" cuprate systems 214 and 123 together with a number of early data cast doubt on a validity of the popular concepts to be widely used as a starting point for analysis of the nuclear resonance and in a more broad sense for many other physical effects. First, it should be noticed that the ^{63,65}Cu NQR lines in the doped cuprates are sometimes unusually inhomogeneously broadened ($2 \div 4$ MHz), practically irrespective of the doping level [4 – 12]. Experimental Cu NQR study in $La_{2-x}Sr_xCuO_4$, $La_2CuO_{4+\delta}$ has revealed two distinct Cu(2) sites (A and B) with distinguishing relaxation rates and universal difference in corresponding quadrupole frequencies. Subsequently, a precise measurement of the nuclear relaxation in $La_{2-x}Sr_xCuO_4$ has revealed a composite structure of the separate Cu NQR lines with strong frequency dependence of T_1^{-1} across the spectrum. At last, first Cu NQR measurements have revealed either an unexpectedly small value of the asymmetry parameter η or rather large difference of η for A and B components. J. Haase et al. [13] have shown that the broadening of the Cu line in 214 system cannot be explained by spin effects and evidences the orbital shift modulation of a short-length scale. The full planar oxygen spectra show a correlated modulation of the electric field gradient with the spin susceptibility. NMR spin-echo double-resonance experiments uncovered the large distribution of the local magnetic fields at the planar Cu sites [14]. They found that a single fluid spin-only picture could not reproduce the experimental data.

Above we address mainly the NMR-NQR studies, however, a close inspection of other magnetic data evidences the same controversies. The absence of an ESR signal is strong evidence that local moments in cuprates do not exist. The polarised neutron results presented by Smith et al. [15] have demonstrated that there is neither an elastic nor a quasi-elastic magnetic response in the normal state of nearly optimally doped $YBa_2Cu_3O_{6.95}$. Their data are inconsistent with the existence of local spin magnetic moments in the CuO_2 planes. Little scattering they observed can be assigned to $\sim 3\%$ of the Cu atoms carrying a spin 1/2. They note that neither the variation in magnitude of the susceptibility in 123 system with oxygen content nor the temperature variation is consistent with the existence of local moments. The integral intensity of the famous resonanse peak in 123 cuprate does not exceed 1–2% from that for spin-wave resonanse in parent system [16]. A drastic decreasing of the AF susceptibility amplitude as a function of doping is found by INS, that disagrees with NMR data and questions the role of spin fluctuations in HTSC as the magnetic fluctuations seem to vanish for samples with largest T_c [16].

Both the NMR-NQR and neutron measurements cannot discriminate between the spin and orbital origin of electron magnetic moments. Thus, we cannot definitely state that current experimental data unambiguously confirm the spin nature of the magnetism in the doped cuprates. Furthermore, recently there appeared many indications to the orbital magnetism in cuprates. Possible formation of antiferromagnetism below the superconducting transition temperature was found by several experimental techniques in underdoped $YBa_2Cu_3O_{6+x}$ and $La_{2-x}Sr_xCuO_4$ [17–21]. The relatively small values of the observed magnetic moments [17–19] $(0.01 \div 0.05\beta_e)$ have indicated an orbital rather than a spin origin of the observed antiferromagnetism. Most recent ARPES observation of the circular dichroism in the normal state of underdoped and overdoped Pb-Bi2212 samples [22] also may be related to the persistent orbital currents.

The NQR study provides a more direct prove for the formation of orbital magnetism since it is performed in zero magnetic field. Thus, the internal magnetic moments if they are present will result in an NQR line splitting. The first experimental evidence for the formation of the internal magnetic moments in the underdoped three-CuO_2-layer $Hg_{0.8}Cu_{0.2}Ba_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) high-T_c cuprate superconductor below $T_c = 134$ K has been presented by Breitzke et al. [23]. Using NQR technique they show that Cu NQR-lines split below T_c due to a Zeeman splitting originating from the internal magnetic fields within the CuO_2-layers. These results strongly favor a formation of staggered orbital currents as an origin of the observed phenomenon. The values of the internal magnetic fields vary from the inner to the outer CuO_2-layer and are of order of several hundred Gauss. Note, the fields occur below T_c and their intensities increase with decreasing temperature. The ^{199}Hg Knight shift measurements in $HgBa_2CuO_{4+\delta}$ [24] have revealed very large anisotropic shifts which were assigned to orbital magnetic moments $\mu \approx 0.04\beta_e$ localized on the oxygen positions. The ^{63,65}Cu shift distribution in $La_{1.85}Sr_{0.15}CuO_4$ is found recently to be of *orbital* (!) origin [14].

In our opinion, these and many other experimental observations point to an inconsistency of a conventional model of the well isolated spin and orbital Zhang-Rice (ZR) singlet $^1A_{1g}$ [25] believed to be a ground state of the hole-doped CuO_4 center in the CuO_2 layers. Here, it should be noted that when speaking of a Zhang-Rice singlet as being "well isolated", one implies that the $^1A_{1g}$ ground state for the CuO_4 plaquette with the two holes of the $b_{1g}(d_{x^2-y^2})$ symmetry is well separated from any other excited two-hole states. Both, experimental data and theoretical model considerations evidence in favor of the more complicated structure of the valence multiplet for the hole-doped CuO_4 center rather than simple ZR singlet albeit namely the latter is a guideline in the overwhelming majority of current model approaches.

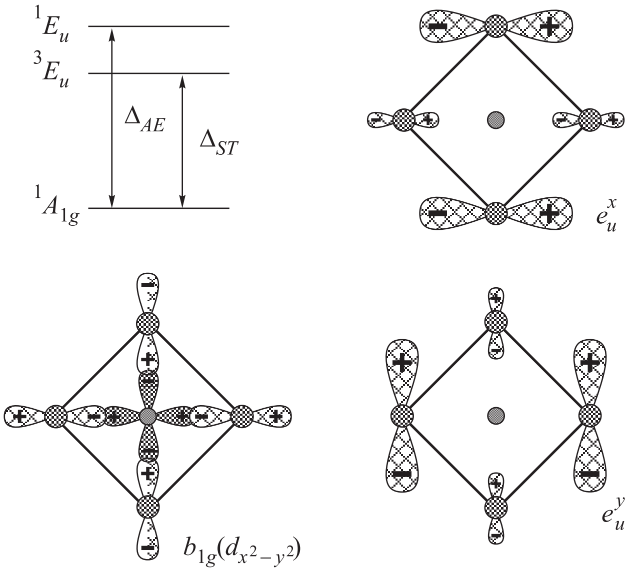
So, Y. Yoshinari et al. [26] have undertook the Cu NQR study of the isolated hole centers in $La_2Cu_{0.5}Li_{0.5}O_4$. Their results could be interpreted as convincing evidence of the singlet-triplet structure of the hole center. The authors have revealed the spin singlet ground state ($S = 0$) and the low lying spin triplet state ($S = 1$) with the singlet-triplet separation $\Delta_{ST} = 0.13$ eV which is comparable with the Cu-Cu nearest neighbor exchange integral in parent oxide La_2CuO_4. An experimental indication to the appreciable role of the O $2p\pi$ orbitals in the ^{17}O hyperfine coupling was obtained by Y. Yoshinari [27]. This implies a complicated nature of the ground state manifold for the

CuO_4 center with a significant mixing of the Zhang-Rice singlet and some other molecular term, whose symmetry should be distinct from $^1A_{1g}$. This conclusion conflicts with the widespread opinion regarding the well isolation of the Zhang-Rice singlet.

The nature of the valent hole states in doped cuprates is considered as being of great importance for the high-T_c problem. Having solved the problem we could justify the choice of the relevant effective Hamiltonian together with the opportunities of a mapping to the single band $t-J$ or Hubbard model.

Below we show that the outgoing beyond ZR model does predict a novel spinless scenario of magnetic response in cuprates.

II. A-E orbital structure of hole CuO_4 centers in cuprates. Intrinsic nature of electron and hole centers in oxides is related to the self-trapped charge transfer (CT) excitons. Both experimental observations and theoretical analysis point to a complex two-component structure of the low-energy CT band near 2 eV in parent insulating cuprates [28, 29]. Here, we deal with a superposition of rather well-defined one- and two-center CT excitons. The former is associated with a dipole-allowed transition $b_{1g} \to e_u$ from the ground state b^b_{1g} to the purely oxygen non-bonding doublet $e_u(\pi)$ in the CuO_4 plaquette, which is allowed in the "in-plane" polarization $\mathbf{E} \perp C_4$. The latter is attributed to a $b_{1g} \to b_{1g}$ CT between two neighboring CuO_4 plaquettes with the formation of electron CuO_4^{7-} and hole CuO_4^{5-} centers. Here, the electron center nominally represents the system of Cu^{1+} and O^{2-} ions with completely filled shells, whereas the hole one does the system with two b^b_{1g} holes forming the ZR-singlet [25]. The one-center CT exciton formally consists of the conventional electron center and unconventional hole center with actually two-hole configuration $b_{1g}e_u$ resulting in a spin singlet ^1E_u or triplet term ^3E_u, respectively. Both CT excitons can interact with each other. Hence, to describe the $el-h$-structure of both excitons on an equal footing one needs to consider the conventional electron center CuO_4^{7-} and unconventional CuO_4^{5-} hole center with actual $^1A_{1g},^{1,3}E_u$ multiplet. Hence, unlike a simple ZR-model our model assumes a quasi-degeneracy in the ground state of hole CuO_4^{5-} center with two close in energy $^1A_{1g}$ (ZR-singlet) and $^{1,3}E_u$ terms of b^2_{1g} and $b_{1g}e_u$ configurations, respectively. This implies two near equivalent locations for the additional hole, either in the Cu 3d-O 2p hybrid $b_{1g}(d_{x^2-y^2})$ state to form ZR singlet $^1A_{1g}$, or in a purely oxygen nonbonding doublet $e_{ux,y}$ state to form the $^{1,3}E_u$ state. Figure shows the term structure of the actual *valent A-E multiplet* for hole CuO_4^{5-} center together with the single-hole basis orbitals. These orbitals are defined as follows:



The term structure of the actual valent $A-E$ multiplet for hole CuO_4^{5-} center together with single-hole basis b^b_{1g} and $e^b_{ux,y}$ orbitals

$$|b^b_{1g}\rangle = \cos\alpha_{b_{1g}}|b_{1g}(3d)\rangle + \sin\alpha_{b_{1g}}|b_{1g}(2p)\rangle, \quad (1)$$

where $b_{1g}(3d) = 3d_{x^2-y^2}$ and $b_{1g}(2p)$ are copper and oxygen molecular orbitals with b_{1g} symmetry. There are two types of purely oxygen nonbonding orbitals with e_u symmetry: $e_u(\sigma)$ and $e_u(\pi)$, respectively, that hybridize with each other (equally for both types (x,y) of such orbitals):

$$|e^b_u\rangle = \cos\alpha_e\,|e_u(\pi)\rangle + \sin\alpha_e\,|e_u(\sigma)\rangle;$$

$$|e^a_u\rangle = \sin\alpha_e\,|e_u(\pi)\rangle - \cos\alpha_e\,|e_u(\sigma)\rangle, \quad (2)$$

where

$$\tan 2\alpha_e = \frac{2t^{pp}_{e_u}}{\epsilon_{pe_u(\sigma)} - \epsilon_{pe_u(\pi)}}, \quad (3)$$

and

$$t^{pp}_{e_u} = -(t_{pp\sigma} + t_{pp\pi})$$

is an effective transfer integral with $t_{pp\sigma} < 0$, $t_{pp\pi} > 0$ being two types of pp transfer integrals, for σ and π bonding, respectively ($|t_{pp\pi}| \approx \frac{1}{2}|t_{pp\sigma}|$). Hereafter, we preserve the notations $e_u(\sigma), e_u(\pi)$ for dominantly σ, or π orbital, respectively. Interestingly, that $e_u(\sigma), e_u(\pi)$ orbitals could form two types of circular current $p_{\pm1}$-like states: $e_{u\pm1}(\sigma), e_{u\pm1}(\pi)$, respectively, with Ising-like orbital moment

$$\langle e_{u\pm1}(\pi)|l_z|e_{u\pm1}(\pi)\rangle = \\ = -\langle e_{u\pm1}(\sigma)|l_z|e_{u\pm1}(\sigma)\rangle = \pm\sin 2\alpha_e \quad (4)$$

or two types of currentless $p_{x,y}$-like $e_{ux,y}(\sigma), e_{ux,y}(\pi)$ states with a quenched orbital moment. The $A-E$ model with a $b_{1g} - e_u$ competition goes essentially beyond the well-known ZR-model. In a sense, the valence $(b_{1g}^2)^1A_{1g} - (b_{1g}e_u)^{1,3}E_u$ multiplet for the hole center represents an unconventional state with Cu valence resonating between Cu^{3+} and Cu^{2+}, or "ionic-covalent" bonding. In other words, we deal with a specific version of the "correlation" polaron, introduced by Goodenough and Zhou [30]. Such centers are characterized by strong coupling with lattice and can reveal the (pseudo)Jahn-Teller effect [31].

The orbital doublet terms $^{1,3}E_u$ for hole CuO_4^{5-} center are straightforwardly derived from two-hole $b_{1g}e_u$ configuration, whereas the configurational interaction is surely to be taken into account when deriving the ZR-singlet $^1A_{1g}$. For the reasonable values of parameters (in eV): $U_d = 8.5$, $U_p = 4.0$, $V_{pd} = 1.2$, $\epsilon_d = 0$, $\epsilon_p = 3.0$, $t = 1.3$ [28] its wave function can be written as follows

$$\Psi_1 = |ZR\rangle = -0.25|d^2\rangle + 0.95|dp\rangle - 0.19|p^2\rangle,$$

where three b_{1g}^2-like configuration are mixed. This function reflects the well-known result that the ZR-singlet represents a two-hole configuration with one predominantly Cu $3d$ and one predominantly O $2p$ holes, however, having the same b_{1g} symmetry.

The $b_{1g} - e_u$ hole competition reflects the subtle balance between the gain in electron-electron repulsion ($U_{dd} > V_{pd}$) and the loss in one-particle energy both affected by a lattice polarization. The $b_{1g} - e_u$, or $A-E$ model is supported both by local-density-functional calculations [32] and *ab initio* unrestricted Hartree-Fock self-consistent field molecular orbital (MO) method (UHF-SCF) for copper-oxygen clusters [33, 34]. To the best of our knowledge the one of the first quantitative conclusions on a competitive role of the hybrid copper-oxygen $b_{1g}(d_{x^2-y^2})$ orbital and purely oxygen O $2p_\pi$ orbitals in the formation of valent states near the Fermi level in the CuO_2 planes has been made by McMahan et al. [32] and Tanaka et al. [33, 34]. Namely these orbitals, as they state, define the low-energy physics of copper oxides.

In connection with the valent $^1A_{1g} - {}^{1,3}E_u$ manifold model for copper oxides one should note and comment the results of paper by Tjeng et al. [35] where the authors state that they "...are able to unravel the different spin states in the single-particle excitation spectrum of antiferromagnetic CuO and show that the top of the valence band is of pure singlet character, which provides strong support for the existence and stability of Zhang-Rice singlets in high-T_c cuprates". However, in their photoemission work they made use of the Cu $2p_{3/2}(L_3)$ resonance condition that allows to detect unambiguously only copper photohole states, hence they cannot see the purely oxygen photohole e_u states.

Interestingly to note, that among three possible states for trapped hole in cuprate: ZR-singlet $^1A_{1g}$, spin singlet ^1E_u, and spin triplet ^3E_u, only the latter provides relevant conditions for the hole transport through antiferromagnetic background. In other words, one might speak about the spin-triplet channel of $e_u(\pi)$ hole transport as a main mechanism of conductivity in insulating cuprates [36].

A. Unconventional magneto-electric CuO_4 hole centers beyond simple ZR singlet picture. Unconventional orbital $A-E$ structure of the hole CuO_4^{5-} center in EH droplet goes beyond simple ZR-singlet picture and deserves more close examination. Neglecting the spin degree of freedom we introduce a pseudo-spin formalism to describe the orbital states of the CuO_4 centers in the framework of the valent $(^1A_{1g}, {}^1E_u)$ multiplet model. Three orbital states of the $(^1A_{1g}, {}^1E_u)$ multiplet we associate with three states of *orbital pseudo-spin* $S = 1$: $|z\rangle = |^1A_{1g}\rangle; |x,y\rangle = = |^1E_u x,y\rangle$. Then the pseudospin matrix has a very simple form: $\langle i|\hat{S}_k|j\rangle = i\epsilon_{ikj}$. A complete set of the pseudo-spin operators should include both $\mathbf{S}$ and five spin-quadrupole operators

$$\widetilde{\{\hat{S}_i, \hat{S}_j\}} = \{\hat{S}_i, \hat{S}_j\} - \frac{2}{3}\hat{\mathbf{S}}^2\delta_{ij}.$$

These pseudo-spin operators are not to be confused with real physical spin-operators as they act in a pseudo-space. Nevertheless, all these correspond to real physical quantities. First, the z-component of pseudo-spin defines the only non-zero z-component of the Ising-like orbital magnetic moment: $\hat{\mathbf{M}} = \hat{g}^M\hat{\mathbf{S}}$, with the only nonzero g_{zz} component of g^M-tensor. Microscopically, the effective magnetic moment is generated by the orbital currents for the e_u hole. Taking into account only local oxygen contributions one may write

$$\hat{\mathbf{M}} = \beta_e \sum_{n=1}^{4} \hat{\mathbf{l}}_n,$$

and

$$g_{zz}^M = \imath\beta_e\langle E_u x|\sum_{n=1}^{4}\hat{l}_{nz}|E_u y\rangle,$$

where $\hat{\mathbf{l}}_n$ is the orbital momentum operator for n-oxygen. Second, the $S_{x,y}$ pseudo-spin components define the unconventional quantity with spatio-transformational properties of polar vector like electric field, and time-inversion symmetry like magnetic field. This is a so-called toroidal moment which can be defined for the CuO_4 plaquette as follows: $\hat{\mathbf{T}} = [\mathbf{g}^T \times \hat{\mathbf{S}}]$, where the g^T-vector has the only non-zero z-component. Microscopically, the effective toroidal moment can be derived through the local oxygen effective orbital moments as follows:

$$\hat{\mathbf{T}} = \beta_e \sum_{n=1}^{4} [\mathbf{R}_n \times \hat{\mathbf{l}}_n],$$

and

$$g_z^T = \imath\beta_e \langle A_{1g}| \sum_{n=1}^{4} R_{nx}\hat{l}_{nz}|E_u y\rangle. \qquad (5)$$

It should be emphasized that both magnetic and toroidal moment are generated by the orbital currents for the oxygen holes. The numerical magnitude of the effective orbital magnetic moment in E_u state is determined mainly by the mixing of O $2p\pi$ and O $2p\sigma$ orbitals (see (2) and (3))

$$g_{zz}^M = \beta_e \sin 2\alpha_e,$$

where $\sin\alpha_e$ is a covalency parameter for $e_u(\pi) - e_u(\sigma)$ bond. For a relatively small $\pi - \sigma$-mixing

$$g_{zz}^M \approx \beta_e \tan 2\alpha_e = \frac{2\beta_e t_{e_u}^{pp}}{\epsilon_{pe_u(\sigma)} - \epsilon_{pe_u(\pi)}} \approx 0.2\beta_e$$

given the reasonable values $t_{e_u}^{pp} \approx 0.3$ eV and $|\epsilon_{pe_u(\sigma)} - \epsilon_{pe_u(\pi)}| \approx 3.0$ eV. For the g^T-vector we readily obtain

$$g_z^T = \frac{1}{\sqrt{2}}\beta_e R_{\mathrm{CuO}} \cos\alpha_e \sin\alpha_{b_{1g}},$$

where $\sin\alpha_{b_{1g}}$ is a covalency parameter for $b_{1g}(3d) - b_{1g}(2p)$ bond. This expression together with (5) implies that the toroidal moment is generated by oxygen orbital moments

$$l_z = \frac{1}{2\sqrt{2}}\beta_e \cos\alpha_e \sin\alpha_{b_{1g}},$$

which value can be estimated to be of the order of $0.2\beta_e$ given $|\sin\alpha_{b_{1g}}| \approx 0.6$. It is quite probable that the toroidal fluctuations will be comparable, or even more pronounced than that of conventional magnetic moment. The toroidal moment is distributed on CuO_4 plaquette and produces a nonzero dipole magnetic field. For all points lying in the CuO_4 plane the field has c-axis orientation whereas it has ab-orientation for all points lying in other symmetry planes.

Above we estimated the maximal values of magnetic and toroidal moments for the $A-E$ model of CuO_4 center. Puzzlingly, these compete with Cu^{2+} spin magnetic moments in parent oxides, which are markedly reduced by a quantum reduction and covalent effects. Actually, we should deal with the quenching effect of "single-ion" anisotropy or other crystalline fields on the orbital magnetism.

The symmetric quadratic pseudo-spin operators define effective electric dipole and quadrupole moments. The former has a planar character with two non-zero components: $\hat{d}_x = d_0\{\hat{S}_x\hat{S}_z\}, \hat{d}_y = d_0\{\hat{S}_y\hat{S}_z\}$, where d_0 is effective dipole moment length. The latter has three non-zero components: $\hat{Q}_{A_1} = Q_{A_1}(\hat{S}_z^2 - \frac{2}{3})$, $\hat{Q}_{B_1} = Q_{B_1}(\hat{S}_x^2 - \hat{S}_y^2)$, $\hat{Q}_{B_2} = Q_{B_2}\{\hat{S}_x\hat{S}_y\}$ with three quadrupole parameters Q_Γ. Thus, the CuO_4 plaquette with $({}^1A_{1g}, {}^1E_u)$ valent multiplet forms an unconventional magneto-electric center characterized by eight independent orbital order parameters. Generally speaking, our model represents a theory that predicts broken time-reversal (T) symmetry, two-dimensional parity (P), and basic tetragonal symmetry.

B. Oxygen holes and orbital hyperfine interactions beyond the Shastry-Mila-Rice model. Below we address some unconventional properties of $^{63,65}Cu$ hyperfine interactions for the spin-singlet ${}^1A_{1g} - {}^1E_u$ valence multiplet of the CuO_4 center resulting from its non-quenched orbital moment.

The nuclear resonance experiments right up to now are interpreted within the Shastri-Mila-Rice spin-Hamiltonian [3]

$$\hat{H}_{hf} = \sum_{mn} {}^{63}\mathbf{I}(n)[\hat{A}(n)\mathbf{s}(n) + B(nm)\mathbf{s}(m)], \qquad (6)$$

based on the assumption that the spin density in the CuO_4 centers is localized on the copper ions. Here $\hat{A}(n)$ is the hyperfine tensor for the direct, on-site coupling of the $^{63,65}Cu$ nuclei to the Cu^{2+} spins ($s = 1/2$), B(nm) is the strength of the transferred hyperfine coupling of the $^{63,65}Cu$ nuclear spin to the four nearest neighbor Cu^{2+} spins.

Effective Hamiltonian of nuclear quadrupole interactions for $^{63,65}Cu$ nuclei has a conventional form as follows

$$\hat{H}_Q = \frac{Q}{4I(2I-1)}\big[V_{zz}(3\hat{I}_z^2 - \hat{\mathbf{I}}^2) + \\ + \eta V_{zz}(\hat{I}_x^2 - \hat{I}_y^2) + \epsilon V_{zz}(\hat{I}_x\hat{I}_y + \hat{I}_y\hat{I}_x)\big], \qquad (7)$$

where for CuO_4 center

$$V_{zz} = V_{zz}(\mathbf{R}) = (V_{zz}^E - V_{zz}^A + V_{zz}^p)\langle\hat{S}_z^2\rangle_{\mathbf{R}} + V_{zz}^A,$$

$$\eta V_{zz} = 3V_{zz}^p\langle\hat{S}_x^2 - \hat{S}_y^2\rangle_{\mathbf{R}}, \qquad \epsilon V_{zz} = 3V_{zz}^p\langle\{\hat{S}_x, \hat{S}_y\}\rangle_{\mathbf{R}},$$

where $\mathbf{R}$ is the radius-vector of CuO_4 center. Parameters V_{zz}^A and V_{zz}^E determine the b_{1g} contribution to V_{zz}

for $^1A_{1g}$ and ^1E_u terms, respectively, while V^p_{zz} does the total contribution of the Cu p electrons. The ^{63,65}Cu NQR frequency can be written as follows

$$\nu_Q = \frac{1}{2}|QV_{zz}|\sqrt{1+\frac{1}{3}(\eta^2+\epsilon^2)}\,.$$

A variety of the model EFG calculations were carried out. [37 − 40] First, we would like to note the extreme sensitivity of the EFG to the calculated anisotropic charge distribution of the semicore Cu $3p$ states which are characterized by the very large magnitude of the effective quadrupole parameter $\langle 1/r^3\rangle_{3p} \simeq 150$ (Ref. [37]), or 170 *a.u.* (Ref. [39]). This parameter governs the magnitude both of the EFG tensor and local magnetic field induced by Cu $3p$ electron on copper nucleus:

$$V_{ij} = -\frac{2e}{5}\langle 1/r^3\rangle_{3p}\langle(3\widetilde{\hat{l}_i\hat{l}_j} - 2\delta_{ij})\rangle; \qquad (8)$$

$$\mathbf{H}_{loc} = -2\beta_e\langle 1/r^3\rangle_{3p}\mathbf{l}, \qquad (9)$$

where $\mathbf{l}$ is an orbital momentum for Cu $3p$ electron, and $\widetilde{\hat{l}_i\hat{l}_j} = 1/2(\hat{l}_i\hat{l}_j + \hat{l}_j\hat{l}_i)$. Thus, the Cu $3p$ contribution to the EFG and to the local field can reach colossal values such as 100 (in $10^{22}\,\mathrm{Vm}^{-2}$) and 10^3 T, respectively. In conventional cuprate scenarios with valence $b_{1g} \propto d_{x^2-y^2}$ holes there is no hybridization between Cu $3p$ and valence states, and the semicore Cu $3p$ contribution to electric and magnetic hyperfine interactions can be taken into account in frames of Sternheimer shielding-antishielding effects. However, the semicore Cu $3p$ role becomes of particular significance for the $^1A_{1g}, {}^1E_u$ valence multiplet of electron and hole centers with varying hole density in oxygen e_u states which have the same symmetry as Cu $3p_{x,y}$ states, that is these can hybridize with each other. As a result, the purely oxygen e_u orbital turns into O $2p$-Cu $3p$ hybrid MO

$$\phi^{e_u}_{x,y} \to \Phi^{e_u}_{x,y} = c_{2p}\phi^{e_u}_{x,y} + c_{3p}\phi^{3p}_{x,y}$$

with MO coefficients $c_{3p} \ll c_{2p}$. Thus we arrive at the effective magnetic and electric "oxygen-to-copper" transferred orbital hyperfine interaction. The effective $e_u(\pi)$ contribution to the local field on the copper nucleus can be written in terms of pseudo-spin formalism as (in Tesla)

$$H^z_{loc} = -2\beta_e\langle 1/r^3\rangle_{3p}|c_{3p}(\pi)|^2\langle S_z\rangle \approx$$
$$\approx 2.0\cdot 10^3|c_{3p}(\pi)|^2\langle S_z\rangle \qquad (10)$$

irrespective of the magnitude of the orbital moment for CuO_4 center. For the nonzero EFG components $V_{zz}, V_{xx}, V_{yy}, V_{xy}$ we obtain (in $10^{22}\,\mathrm{Vm}^{-2}$)

$$V_{ij} = -\frac{2e}{5}\langle 1/r^3\rangle_{3p}|c_{3p}(\pi)|^2\langle(3\widetilde{\hat{S}_i\hat{S}_j} - 2\delta_{ij})\rangle \approx$$
$$\approx 2.7\cdot 10^2|c_{3p}(\pi)|^2\langle(3\widetilde{\hat{S}_i\hat{S}_j} - 2\delta_{ij})\rangle. \qquad (11)$$

Interestingly, that Eqs.(10) and (11) imply that the ratio between local field and EFG is governed only by the ratio between respective pseudo-spin averages:

$$H^z_{loc} : V_{ij} = \beta_e\langle S_z\rangle : \frac{e}{5}\langle(3\widetilde{\hat{S}_i\hat{S}_j} - 2\delta_{ij})\rangle). \qquad (12)$$

Simple relation between local field and EFG governed only by the respective pseudo-spin averages implies a rather subtle interplay between magnetic and electric contributions both to NMR-NQR frequencies and the spin-lattice relaxation rate for copper nuclei. The numerical calculations allow us to expect the O $2p$-Cu $3p$ mixing coefficient c_{3p} to be of the order of several hundredth. Indeed, the overlap contribution to this coefficient given the Cu-O separations $R_{CuO} \approx 1.9$ Å is estimated [41] to be $c_{3p}(overlap) = S^\sigma_{\mathrm{Cu3}p-\mathrm{O2}p} \approx -0.05$ for the strongest Cu $3p$ – O $2p$ σ-bonding and $S^\pi_{\mathrm{Cu3}p-\mathrm{O2}p} \approx \approx -0.5S^\sigma_{\mathrm{Cu3}p-\mathrm{O2}p}$. In such a way the oxygen $e_u(\pi)$ hole contribution to the orbital hyperfine interactions due to the Cu $3p\pi$-O $2p\pi$ overlap can be estimated as $|H_{loc}| \leq 1$ Tesla and $|V_{ij}| \leq 0.3\cdot 10^{22}\,\mathrm{Vm}^{-2}$ for magnetic and electric terms, respectively. It should be noted that the respective maximal values correspond to the very large magnitude of effective NMR and NQR frequencies of the order of 10 MHz. Moreover, the oxygen $e_u(\sigma)$ hole contribution can be approximately four times bigger.

III. Conclusion. We showed that outgoing beyond a simple ZR model we arrive at a complex $^1A_{1g} - {}^{1,3}E_u$ structure of the valent multiplet for the hole CuO_4^{5-} center in cuprate with engaging orbital degree of freedom. Moreover, it should be emphasized that simple $^1A_{1g} - {}^1E_u$ model implies a spinless purely orbital and purely oxygen scenario of magnetic response and hyperfine interactions in doped cuprates. However, we do not completely reject the spin degree of freedom. Indeed, our model implies a near degeneracy for singlet ^1E_u and triplet ^3E_u terms with many interesting manifestations of the spin singlet-triplet magnetism [42]. Moreover, both spin and orbital degrees of freedom are likely to be involved into a formation of the complex magnetic response of doped cuprates with a relative weight that manifests itself diversely depending on the energy range and experimental conditions (NMR-NQR, magnetic susceptibility, magnetic neutron scattering,...).

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