

Singlet and triplet doped-hole configurations in $\text{La}_2\text{Cu}_{0.5}\text{Li}_{0.5}\text{O}_4$

V. I. Anisimov and S. Yu. Ezhov

Institute of Metal Physics, Russian Academy of Sciences, 620219 Ekaterinburg GSP-170, Russia

T. M. Rice

Theoretische Physik, Eidgenössische Technische Hochschule-Hönggerberg, 8093 Zürich, Switzerland

(Received 20 September 1996)

The ordered alloy $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ is found to be a band insulator in local density approximation (LDA) calculations with the unoccupied conduction band having predominantly $d_{x^2-y^2}$ symmetry and substantial weight in O $2p$ orbitals. This is equivalent to a predominant local singlet configuration d^9L or a low-spin Cu^{3+} ion with both holes in orbits having $d_{x^2-y^2}$ symmetry, i.e., Zhang-Rice singlets. A fairly modest reduction of the apical Cu-O bond length is sufficient to stabilize a high spin triplet Cu^{3+} ionic configuration with holes in both $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbits in LDA + U calculations. This leads us to identify the low energy triplet excitation found in nuclear quadrupole resonance studies by Yoshinari *et al.* as a local high-spin Cu^{3+} ionic configuration accompanied by a substantial reduction of the apical Cu-O separation, i.e., an anti-Jahn-Teller triplet polaron. [S0163-1829(97)02319-9]

The substitution of lithium for copper in La_2CuO_4 is formally equivalent to Sr doping on the La site as each donates one hole per dopant. In lightly doped samples Li and Sr doping have essentially indistinguishable effects on the magnetic properties and lattice structure.^{1,2} However, in-plane substitutions for Cu and out-of-plane substitutions for La were found to be very different in the conductivity. Li^{+1} has an ionic radius essentially the same as that of Cu^{+2} , and brings a hole with it into the plane. But the alloys $\text{La}_2\text{Cu}_{1-x}\text{Li}_x\text{O}_4$ are never metallic nor superconducting so that this hole must be localized in contrast to the mobile holes introduced by out-of-plane substitutions. The solid solubility of Li is such that complete filling of the copper band (at 50% Li) can be achieved. At this composition the Li and Cu ions form an ordered superlattice³ in which all Cu ions are surrounded by four in-plane Li^{+1} ions ($1s^2$, closed shell electronic configuration), leading to isolated CuO_4 clusters. This compound was found to be a diamagnetic insulator.

The nuclear quadrupole resonance (NQR) study of $\text{La}_2\text{Cu}_{0.5}\text{Li}_{0.5}\text{O}_4$ (Ref. 4) reveals a magnetic excitation of the doped-hole state with an energy of ≈ 130 meV. This energy is much smaller than the estimation of the singlet-triplet splitting of the local Zhang-Rice singlet⁵ which is of the order of few eV. There are also indications that this magnetic excitation is coupled to the charge fluctuation or lattice distortion around the Cu site.⁴

$\text{La}_2\text{Cu}_{0.5}\text{Li}_{0.5}\text{O}_4$ is not the only compound with formally trivalent copper which is a diamagnetic insulator. Another example is NaCuO_2 .⁶ Spectroscopy measurements and configuration interaction (CI) calculations by Mizokawa *et al.*⁷ led them to conclude that the ground state of NaCuO_2 is dominated by d^9L (L : ligand hole) configurations and not by d^8 as for a simple Cu^{3+} ion. The ligand holes L are not metallic because strong p - d hybridization between d^8 and d^9L configurations leads to a split-off d^9L -like discrete state above the oxygen continuum.

The calculation of the electronic structure of NaCuO_2 in a local (spin) density approximation⁸ [L(S)DA] showed that this compound can be described as a conventional insulator with a band gap arising from simple covalent effects (p - d hybridization). The unoccupied band has more oxygen character than copper thus confirming the conclusion from CI calculations that “doped” holes are situated predominantly on oxygen orbitals. The key structural element of the crystal structure of NaCuO_2 is the same as in layered cuprates (for example, La_2CuO_4): CuO_4 plaquettes with the Cu atoms in the center of a square of oxygen atoms. However in layered compounds the squares are corner-sharing and the Cu-O-Cu bond angles are nearly 180° resulting in very broad $pd\sigma$ band, while in NaCuO_2 the squares are edge-sharing and those angles are close to 90° and the corresponding bandwidth is much smaller.

In $\text{La}_2\text{Cu}_{0.5}\text{Li}_{0.5}\text{O}_4$ the CuO_4 plaquettes are separated by Li ions, so that there are no Cu-O-Cu bonds at all and one can expect an even narrower $pd\sigma$ band than in NaCuO_2 . We have performed LDA calculation for $\text{La}_2\text{Cu}_{0.5}\text{Li}_{0.5}\text{O}_4$ using the linearized muffin-tin orbital method in an atomic-spheres approximation (LMTO-ASA).⁹ The results (Fig. 1) show that, indeed, the ground state is a nonmagnetic insulator with a sizable gap value (≈ 1 eV), compared to the 0.3 eV value in NaCuO_2 .⁸ The unoccupied band is again rather narrow and with a symmetry of Cu centered $d_{x^2-y^2}$ orbitals. It contains 40% Cu $3d$ orbitals and 60% O $2p$ states, indicating the strongly covalent nature of the singlet ground state. The top of the valence band is predominantly oxygen in origin, however there is significant admixture of $d_{3z^2-r^2}$ orbitals of copper.

Our results shows that in order to reproduce singlet ground state of the doped hole in $\text{La}_2\text{Cu}_{0.5}\text{Li}_{0.5}\text{O}_4$ there is no need to take into account Coulomb interaction corrections to the one-electron LDA. However the magnetic excited state cannot be explored in a calculation scheme which does not include Coulomb interactions inside the d shell of copper.

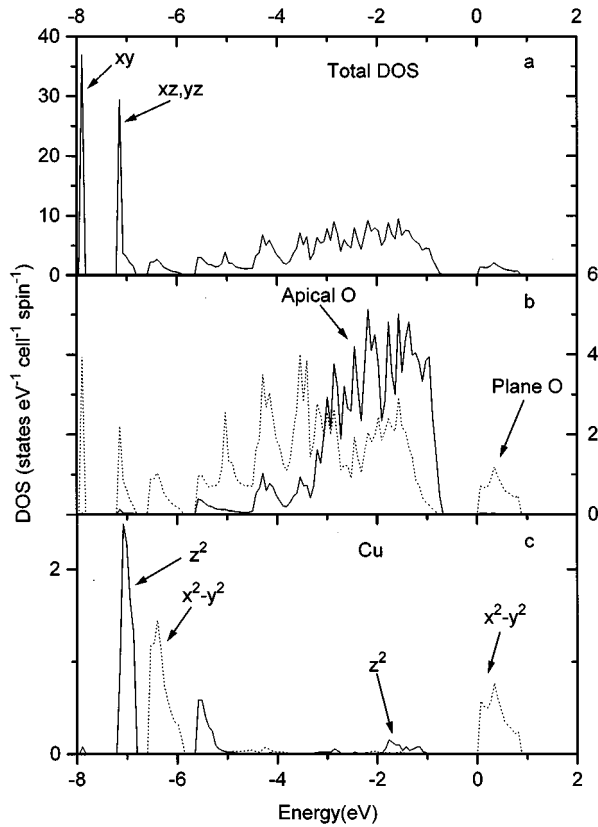


FIG. 1. The total (a) and partial [O 2p (b) and Cu 3d (c)] densities of states (DOS) for $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ calculated in the undistorted crystal structure. The bands formed by different d orbitals are marked by arrows.

For example, the undoped cuprates experimentally are antiferromagnetic insulators while LDA gives a paramagnetic metallic ground state. The reason for this discrepancy is that while in a LSDA the splitting between majority and minority spin states is driven only by the exchange interaction with a value of the Stoner parameter of ≈ 1 eV, the real driving force for the antiferromagnetic insulator solution must be the much larger direct Coulomb interaction parameter $U \approx 8$ eV. This contradiction was resolved in the so-called LDA+U method where orbital-spin polarization caused by the Coulomb interaction is directly taken into account.^{10,11}

The main idea of the LDA + U method is that LDA gives a good approximation for the average Coulomb energy of d - d interactions E_{av} as a function of the total number of d electrons $N = \sum_{m\sigma} n_{m\sigma}$, where $n_{m\sigma}$ is the occupancy of a particular $d_{m\sigma}$ orbital:

$$E_{\text{av}} = \frac{1}{2} UN(N-1) - \frac{1}{4} JN(N-2). \quad (1)$$

But LDA does not properly describe the full Coulomb and exchange interactions between d electrons in the same d shell. So Anisimov *et al.*^{10,11} suggested subtracting E_{av} from

the LDA total energy functional and to add orbital- and spin-dependent contributions to obtain the exact (within a mean-field approximation) formula:

$$E = E_{\text{LDA}} - E_{\text{av}} + \frac{1}{2} \sum_{m,m',\sigma} U_{mm'} n_{m\sigma} n_{m'-\sigma} + \frac{1}{2} \sum_{m \neq m', m', \sigma} (U_{mm'} - J_{mm'}) n_{m\sigma} n_{m'\sigma}. \quad (2)$$

Taking the derivative with respect to $n_{m\sigma}$ gives the orbital-dependent one-electron potential:

$$V_{m\sigma}(\vec{r}) = V_{\text{LDA}}(\vec{r}) + \sum_{m'} (U_{mm'} - U_{\text{eff}}) n_{m'-\sigma} + \sum_{m' \neq m} (U_{mm'} - J_{mm'} - U_{\text{eff}}) n_{m\sigma} + U_{\text{eff}} \left(\frac{1}{2} - n_{m\sigma} \right) - \frac{1}{4} J, \quad (3)$$

with $U_{\text{eff}} = U - \frac{1}{2}J$. The Coulomb and exchange matrices $U_{mm'}$ and $J_{mm'}$ are expressed through the integrals over products of three spherical harmonics and screened Coulomb and exchange parameters U and J .¹⁰

A nontrivial problem is what value of the screened Coulomb interaction U to use. For insulators, such as late transition-metal oxides a good approximation is to calculate static screening of the d - d intrashell Coulomb interaction in a supercell LDA calculation.¹²

The question is what symmetry should the lowest energy excited states have? The band gap separates states which are both mainly oxygen but due to the hybridization with Cu 3d orbitals the states have a symmetry of x^2-y^2 and $3z^2-r^2$ for the unoccupied and occupied bands, respectively. The x^2-y^2 band is higher in energy due to the Jahn-Teller-distorted CuO_6 octahedra in $\text{La}_2\text{Cu}_{0.5}\text{Li}_{0.5}\text{O}_4$ crystal structure: the length of the Cu-O bond in the ab plane is 1.8 Å the distance to the apical oxygen is larger — 2.4 Å.³ It follows that the lowest energy excitation will be from the (formally) $d_{x^2-y^2\uparrow} d_{x^2-y^2\downarrow}$ singlet configuration to the $d_{x^2-y^2\uparrow} d_{3z^2-r^2\downarrow}$ triplet configuration.

We have performed LDA+U method calculations for both singlet and triplet configurations. We find that a starting triplet configuration is not a stable solution but self-consistently converges to the singlet solution. (The singlet solution of LDA+U method is practically the same as for pure LDA, because in the absence of the orbital-spin polarization the LDA+U correction to LDA is irrelevant.) However, if the copper-apical oxygen bond length is contracted by 16% (0.38 Å), then a stable *triplet solution appears and becomes the ground state*. For 16% contraction the total energy of the magnetic solution is still 0.06 eV higher than the nonmagnetic one, however already for 17% contraction the triplet energy is 0.1 eV lower.

It is instructive to follow the changes, with copper-apical oxygen bond contraction, of the two bands below and above Fermi energy (Fig. 2). For the undistorted structure [Fig.

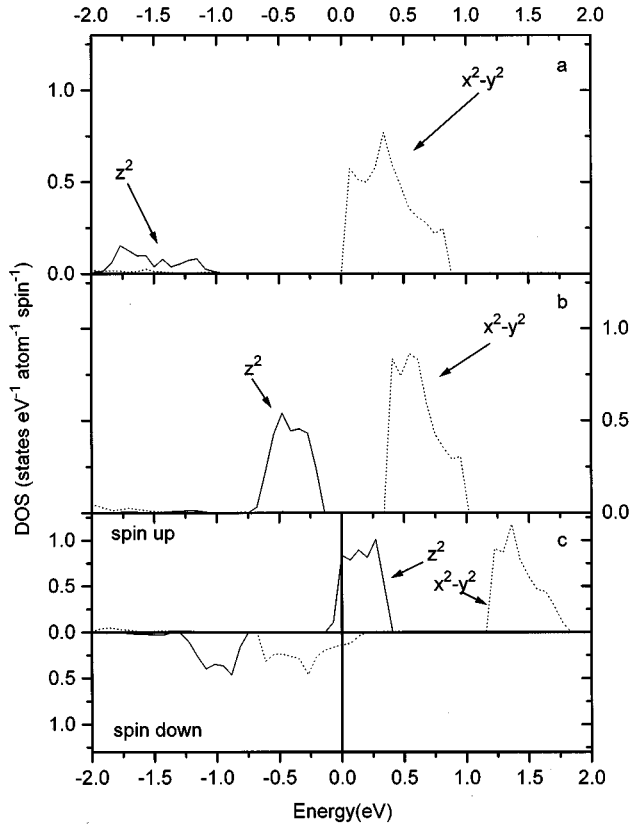


FIG. 2. The partial Cu 3d densities of states (DOS) for $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ for the LDA+U calculation. Upper panel (a): non-magnetic solution in the undistorted crystal structure. Middle panel (b): non-magnetic solution with 16% contraction of the copper-apical oxygen bond length. Lower panel (c): magnetic solution with 16% contraction of the copper-apical oxygen bond length.

2(a)] those bands (the lower one of $d_{3z^2-r^2}$ symmetry and the higher one of $d_{x^2-y^2}$) are well separated from each other and the admixture of the $d_{3z^2-r^2}$ orbitals to the valence band is relatively small. With distortion the hybridization of the $\text{Cu}3d_{3z^2-r^2}$ orbitals with the apical oxygen $2p_z$ orbitals becomes stronger and the antibonding band goes higher in energy and the admixture of the $d_{3z^2-r^2}$ orbitals in this band becomes stronger [Fig. 2(b)]. In order for the magnetic state to be stable, the splitting between spin-up and spin-down bands must become large enough that the top of the spin-up $d_{x^2-y^2}$ band does not overlap with the bottom of spin-down $d_{3z^2-r^2}$ band (in other words magnetic energy must over-

come kinetic energy). Figure 2(c) shows that for the critical value of the distortion (16%) this condition is nearly satisfied.

Similar effects were found in a supercell LDA+U calculation for a doped hole in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.¹³ In that work two solutions were found for a hole introduced in the CuO_2 plane: one solution had the symmetry x^2-y^2 with the hole spin antiparallel to the d hole of Cu atom, while the other one had $3z^2-r^2$ symmetry and spin parallel to the Cu spin. The latter solution was present only for a contracted apical Cu-O distance (0.26 Å contraction). The total energy calculation in a full-potential scheme including the lattice relaxation showed that the total energy minima for these two solutions were very close in energy with the triplet state only 54 meV higher than the ground state singlet.

As the hopping between CuO_6 octahedra in $\text{La}_2\text{Cu}_{0.5}\text{Li}_{0.5}\text{O}_4$ is smaller than in La_2CuO_4 , one would expect more localized states in the former and, hence, a larger separation between the singlet ground state and excited triplet state. The value found in NQR measurements⁴ 130 meV looks quite reasonable from this point of view.

We would like to emphasize that while the excited magnetic state is a triplet with $S=1$, the actual magnetic moment residing in Cu 3d orbitals found in the LDA+U calculation is very small: $0.8\mu_B$. That is due to the fact that the bands (or Wannier orbitals) of x^2-y^2 and $3z^2-r^2$ symmetry have only 40% of Cu 3d orbitals contribution, being mainly oxygen in origin as implied by the predominance of d^9L many electron configurations in model CI calculations.⁷

In conclusion, we find that LDA correctly gives a band insulator ground state for $\text{La}_2\text{Li}_{0.5}\text{Cu}_{0.5}\text{O}_4$ with the unoccupied conduction band having predominantly $d_{x^2-y^2}$ -symmetry and substantial weight in O 2p orbitals — a state equivalent to a formal valence Cu^{3+} in a low-spin configuration or a Zhang-Rice singlet. A reduction of the Cu-O apical distance stabilizes a high-spin configuration and this leads us to identify the 130 meV triplet excitation observed in NQR with such a local configuration, i.e., an anti-Jahn-Teller polaron. Two aspects of the experiments remain to be clarified — the origin of the low energy nuclear spin relaxation process which dominates at lower temperature at $T \lesssim 170$ K and secondly the absence of a significant activated contribution to the uniform susceptibility from the 130 meV triplet excitations — at least below room temperature.

The work was partly supported by Russian Basic Research Foundation (RFBR Grant No. 96-02-16167). One of us (V.I.A.) wishes to thank the ‘‘Zentrum für Theoretische Studien’’ at the Institute for Theoretical Physics, ETH-Zürich for hospitality.

¹A. Rykov, H. Yasuoka, and Yu. Ueda, *Physica C* **247**, 327 (1995).

²M.A. Kastner, R.J. Birgeneau, C.Y. Chen, Y.M. Chiang, D.R. Gabbe, H.P. Jenssen, T. Junk, C.J. Peters, P.J. Picone, T. Thio, T.R. Thurston, and H.L. Tuller, *Phys. Rev. B* **37**, 111 (1988).

³J.P. Attfeld and G. Ferey, *J. Solid State Chem.* **80**, 112 (1989).

⁴Y. Yoshinari, P.C. Hammel, J.A. Martindale, E. Moshopolou, J.D. Thompson, J.L. Sarrao, and Z. Fisk, *Phys. Rev. Lett.* **77**, 2069 (1996).

⁵F.C. Zhang and T.M. Rice, *Phys. Rev. B* **37**, 3759 (1988).

⁶P. Steiner, V. Kinsinger, I. Sander, B. Siegwand, S. Huefner, C. Politics, R. Hoppe, and H.P. Muller, *Z. Phys. B* **67**, 497 (1987).

⁷T. Mizokawa, H. Namatame, A. Fujimori, K. Akeyama, H. Kondoh, H. Kuroda, and N. Kosugi, *Phys. Rev. Lett.* **67**, 1638 (1991).

⁸D.J. Singh, *Phys. Rev. B* **49**, 1580 (1994).

⁹O.K. Andersen, *Phys. Rev. B* **12**, 3060 (1975).

- ¹⁰V.I. Anisimov, J. Zaanen, and O.K. Andersen, Phys. Rev. B **44**, 943 (1991); V.I. Anisimov, I.V. Solovyev, M.A. Korotin, M.T. Czyzyk, and G.A. Sawatzky, *ibid.* **48**, 16 929 (1993).
- ¹¹A.I. Liechtenstein, V.I. Anisimov, and J. Zaanen, Phys. Rev. B **52**, 5467 (1995).
- ¹²V.I. Anisimov and O. Gunnarsson, Phys. Rev. B **43**, 7570 (1991).
- ¹³V.I. Anisimov, M.A. Korotin, J. Zaanen, and O.K. Andersen, Phys. Rev. Lett. **68**, 345 (1992).