Nonlocal interactions in doped cuprates: Correlated motion of Zhang-Rice polarons

L. Hozoi,[1,2] S. Nishimoto,[1] G. Kalosakas,[1,3] D. B. Bodea,[1] and S. Burdin[1]
[1]*Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Strasse 38, 01187 Dresden, Germany*
[2]*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany*
[3]*Department of Materials Science, University of Patras, 26504 Patras, Greece*
(Received 26 September 2006; published 31 January 2007)

Intercarrier correlations in hole doped cuprates are investigated by *ab initio* multiconfiguration calculations. The dressed carriers display features that are reminiscent of both Zhang-Rice (ZR) CuO_4 states and Jahn-Teller polarons. The interaction between these quasiparticles is repulsive. At dopings that are high enough, the interplay between long-range unscreened Coulomb interactions and long-range phase coherence among the O-ion half-breathing vibrations on the ZR plaquettes may lead to a strong reduction of the effective adiabatic energy barrier associated to each polaronic state. Tunneling effects cannot be neglected for a relatively flat, multiwell energy landscape. We suggest that the coherent, superconducting quantum state is the result of such coherent quantum lattice fluctuations involving in-plane O ions. Our findings appear to support phenomenological models where the superconductivity is related to a lowering of the in-plane kinetic energy.

DOI: 10.1103/PhysRevB.75.024517 PACS number(s): 71.27.+a, 71.28.+d, 71.38.−k

I. INTRODUCTION

There is increasing evidence that many properties of the doped copper oxide compounds cannot be understood without taking into account the lattice degrees of freedom. Experiments that indicate strong electron-phonon (EP) couplings are the inelastic neutron scattering,[1,2] angle-resolved photoemission (PE),[3,4] x-ray absorption fine structure (XAFS),[5] and electron paramagnetic resonance.[6] The anomalies in the phonon, PE, and XAFS spectra were previously addressed with *t-J* or Hubbard models supplemented with EP interaction terms.[7–11] Strong and anomalous electron-lattice couplings were also found by *ab initio*, wavefunction-based calculations.[12,13] In the case of hole doping,[15] multiconfiguration (MC) calculations[12–14] on clusters of a few CuO_6 octahedra show that the doped holes enter O $2p_x$ and $2p_y$ orbitals that form σ-bonds with the open-shell Cu $3d_{x^2-y^2}$ orbitals and give rise to *pd* singlet states similar to the type of configuration proposed by Zhang and Rice (ZR) a long time ago.[16] A major deviation from the original ZR picture is that the formation of such a singlet is associated with significant lattice deformations. The most stable configuration corresponds to Cu-O distances that are shorter by 5% to 6%. The stabilization energy due to the local lattice deformation is a few hundreds meV for an isolated $2p$ hole.[12] The interplay between O-ion (half)breathing vibrations and intercarrier Coulomb and spin interactions may induce, however, strong charge redistribution. The $2p$ hole, which for a distorted CuO_4 plaquette is approximately equally distributed over the four anions, can be partially transferred onto a single ligand to give an electronic wavefunction (WF) with a dominant contribution from a $\cdots$-Cu d^9-O p^5-Cu d^9-$\cdots$ configuration.

d^9-p^5-d^9 entities were postulated to exist in cuprates by several authors.[17,18] This single-oxygen $2p$ hole and the adjacent Cu holes are viewed as a spin-1/2 quasiparticle state in which the $3d$ spins are ferromagnetically (FM) polarized, i.e., coupled to a triplet, and the spin on the O ion is low-spin coupled to it. Interactions that could lead to the pairing of these quasiparticles and superconductivity (SC) were analyzed in Refs. 17 and 18 in terms of *p-d*, extended Hubbard Hamiltonians. It was pointed out[18,19] that such models imply different low-energy physics as compared to the effective single-band model proposed by ZR.[16]

Near-degeneracy effects between a quadrisinglet (QS) polaronic state similar to the ZR state and a two-site spin-singlet polaron were studied in the frame of a Holstein-Hubbard model in Ref. 20. Although some details are quite different, the two-site spin-singlet resembles a two-hole d^9-p^5 singlet configuration. It was shown that in the parameter region with near-degeneracy, the effective mass of the QS polaron is sharply reduced. Near-degeneracy plus quantum tunneling effects associated with a rather flat energy landscape are believed to be[20] crucial ingredients in the theory of "bipolaronic" SC.[21]

We investigate in this paper interactions between two or more spatially separated ZR *polarons* (ZRPs). We find that long-range phase coherence among the O-ion half-breathing vibrations on the ZR CuO_4 plaquettes may lead to a correlated motion of the $2p$ holes. Several effects come into play here. The local electron-lattice couplings make possible the transfer of the ZR singlet to an adjacent plaquette. The longer-range intercarrier interactions are responsible, at dopant concentrations that are high enough and in a "dynamic" regime, for a significant lowering of the effective energy barrier seen by each ZR quasiparticle. This is exactly the kind of picture proposed, in a somewhat different context, by Hirsch:[22] single carriers are heavily dressed at very low concentrations by the interaction with the local environment; they partially "undress" and their effective mass decreases at higher concentrations due to collective intercarrier interactions. Our analysis is mainly based on results obtained by *ab initio* electronic structure methods from traditional quantum chemistry. The calculations are performed on finite clusters. The many-electron WF is constructed as a full configuration-interaction (CI) expansion in the space defined by a limited set of so-called active orbitals. These are chosen as those orbitals which are expected to contribute to degeneracy effects, that is, strong mixing between configurations which have the same, or nearly the same, energy. The rest of the

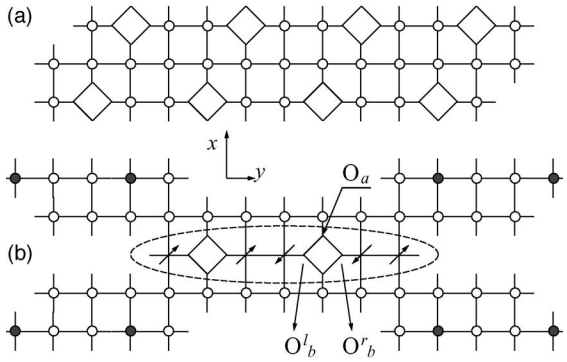

FIG. 1. (a) 1/3-doped stripes at optimal doping in a ZR-like picture, see text. (b) The 7-plaquette cluster employed for the CASSCF calculations and the positions of the extra positive charges (the filled circles) within the PC embedding. These correspond to the situation where every second pair of ZRPs along the 1/3-doped stripes is removed. One of the two symmetry-equivalent lowest-energy configurations is sketched for the "quantum" cluster. Only the Cu sites are displayed. The squares represent distorted ZR plaquettes. O_b are bridging "chain" oxygens, O_a are ions adjacent to the CuO_b chain.

orbitals are either doubly occupied in all configurations or empty. The former set of orbitals is called inactive, the latter is referred to as the virtual orbital set and spans the rest of the orbital space, defined from the basis set used to build the "molecular" orbitals (MOs). This is known as the complete active space (CAS) MC approach.[23] The variational parameters of the WF are *both* the CI and MO coefficients.

II. CHARGE-LATTICE INTERACTIONS

Intercarrier interactions are studied by doping a 7-plaquette $[Cu_7O_{22}]$ linear cluster with two holes. The length of the cluster corresponds roughly to the scale of the superconducting coherence length. We used the lattice parameters of the hole doped $La_{1.85}Sr_{0.15}CuO_4$ compound,[24] with the in-plane lattice constant $a=3.78$ Å. The 7-plaquette cluster is embedded in an array of formal point charges (PCs) at the experimental lattice positions that reproduce the crystal Madelung potential. The Cu^{2+} and La^{3+} nearest neighbors (NN) are represented by effective model potentials.[25] Trial calculations were first performed with embedding PCs that correspond to a fully ionic picture of the undoped material, La_2CuO_4. In this situation, due to the large mutual repulsion, the CAS self-consistent field (SCF) calculations converge to solutions where the $2p$ holes are each located on the outermost CuO_4 plaquettes. However, at not too small doping other $2p$ holes exist in the immediate vicinity. In a next step, we decided to take into account the presence of other doped holes by introducing a few extra elementary positive charges around the cluster. The results discussed in the following paragraphs were obtained with a PC embedding where eight positive charges were added. The positions of these extra PCs are shown in Fig. 1. The reason behind choosing this type of arrangement is discussed below.

It is widely accepted[26,27] that charge and magnetic inhomogeneities appear in cuprates at least dynamically. Goodenough[28] argued that at optimal doping ($x\approx 1/6$) and low temperatures, 1/3-doped (fluctuating) stripes are formed on every second chain of plaquettes. In a ZR-like picture, the 1/3-doped stripes could be represented as in Fig. 1(a), for example. The SC is associated in Ref. 28 with the formation of traveling charge-density-waves[27] along the doped chains. In models with EP coupling, the relevant phonon modes would be the O-ion half-breathing modes with $\mathbf{q}=(1/3,0,0)$. Experimental data that appear to support Goodenough's model are the strong anomalies at such wave vectors, $\mathbf{q}=(0.25-0.33,0,0)$.[1,2] These anomalies are actually observed in both hole and electron doped systems.[2] Coming back to the positive charges added to our embedding, they would correspond to the situation where every second pair of ZRPs in Fig. 1(a) is removed, i.e., $x=1/12$ doping. In addition, we retain only the NN pairs around the "quantum" cluster. For symmetry reasons, the extra positive charges on the left-hand side are shifted by one plaquette to the right.

With the extra positive charge around the cluster, the two O holes are pushed from the outermost plaquettes toward the inner region. To study electron-lattice couplings, we first determined the cluster geometry configuration that minimizes the total energy. However, only the positions of those ions are relaxed that have each neighbor represented at the all-electron level. These are the Cu ions and the intervening ligands O_b. Under the assumption of charge segregation into hole-rich and hole-poor regions and filamentary conduction[11,17,26,28] the vibrations of these ions should be the most relevant. The CASSCF calculations were carried out with a minimal active space. That is one orbital per hole, in our case nine electrons in nine orbitals. It was shown[13] that the overall picture does not change when using larger active spaces.[29] All calculations were performed with the MOLCAS 6 package.[30] *All-electron* atomic natural-orbital basis sets from the MOLCAS library were employed, with the following contractions: Cu $21s15p10d/5s4p3d$, O $14s9p/4s3p$. As already mentioned, the apical oxygens are not included in the "quantum" cluster, but modeled by formal PCs.

The CASSCF calculations always converge to states where the $2p$ holes are separated by more than two lattice constants. However, depending on geometry and the initial guess for the orbitals, these states may have different character. Two symmetry-equivalent *minimum-energy* geometries were identified. These are configurations where two ZRP states are formed on CuO_4 plaquettes that are separated by two other Cu ions, see Fig. 1(b). The spins on these intervening cations are antiferromagnetically (AFM) coupled. For the ZR plaquettes, the Cu-O_b distances are shorter by 5%. Mulliken populations (MPs) of the relevant Cu $3d$ and O $2p$ atomic orbitals (AOs) on these plaquettes are listed in Table I (second column). The composition of the bonding (B) and antibonding (AB) $d_{x^2-y^2}$-$p_{x,y}$ σ-orbitals is depicted in Fig. 2. Due to correlation effects, the occupation numbers (ONs) of the AB orbitals are relatively large. Since the charge distribution on the two ZR plaquettes is nearly identical, only the orbitals on one of these plaquettes are shown in the figure.

When the bridging O_b ions are shifted back to the middle positions, each of the $2p$ holes is partially transferred onto a single ligand. This is illustrated in Table I and Fig. 2. The results were obtained by static total energy calculations

TABLE I. MPs illustrating the distribution of the doped holes (Ref. 15). The lowest-energy configuration corresponds to distorted, ZR plaquettes separated by two other Cu $3d^1_{x^2-y^2}$ ions (second column). The ZR plaquettes are labeled with indices 1 and 2. Other notations are as in Fig. 1. When the O_b ions are shifted to the middle positions, each hole is partially transferred onto a single ligand (third column). In parentheses, the same quantities are shown for a single doped hole, see text. Relative energies (REs) are given in the last entry.

Configuration/ relevant atomic orbitals	Shorter (5%) Cu−O_b bonds	Undistorted structure
Cu_1 $3d_{x^2-y^2}$	1.03 (1.03)	1.09 (1.08)
O^l_{1b} $2p_y$	1.64 (1.62)	1.77 (1.76)
O_{1a} $2p_x$ (×2)	1.61 (1.62)	1.69 (1.68)
O^r_{1b} $2p_y$	1.61 (1.62)	1.29 (1.31)
Cu_2 $3d_{x^2-y^2}$	1.03	1.09
O^l_{2b} $2p_y$	1.65	1.77
O_{2a} $2p_x$ (×2)	1.61	1.68
O^r_{2b} $2p_y$	1.60	1.30
REs (meV)	0.00 (0.00)	650 (380)

(adiabatic approximation).[12] It can be seen in Fig. 2 that in the undistorted structure the doped-hole orbitals have much weight onto one of the adjacent plaquettes as well. O-ion half-breathing displacements that shorten the Cu-O_b bonds on these *adjacent* plaquettes induce propagation of the ZR singlet(s) along the Cu-O_b-··· chain. We found that the $2p$ hole is already moved to the other plaquette for distortions of these adjacent Cu-O_b bonds of less than 0.5% of the high-symmetry distance. The adiabatic energy barrier is in the two-hole cluster 325 meV per hole, see Table I. Separate calculations were performed with a single doped hole and no extra positive charge in the PC embedding. The energy barrier is in this case 380 meV.[31] The energy difference between the two situations, 55 meV per hole, is considerable. In the presence of other *mobile* $2p$ hole polarons in the CuO_2 plane(s), the effect would be further enhanced and should lead to a strong reduction of the polaron effective mass. We arrive thus at Hirsch's paradigm:[22,32] carriers are not happy being together, but they are happy *moving together*. This was described as a kinetic-energy-driven mechanism for SC and a change of color was predicted when entering the superconducting state.[22] That the onset of SC is indeed accompanied by a transfer of spectral weight from the visible region to the infrared range was recently confirmed by Molegraaf *et al.*[33]

We would like to note at this point that for no distortions and a single O hole, ZR-like solutions can also be obtained. Such a state, with the $2p$ hole symmetrically distributed over the four ligands on a given plaquette, is only a few meV above the symmetry-broken d^9-p^5 -like state, which shows that for the isolated hole the relaxation effects associated with the symmetry-broken configuration are rather small.[34] Nevertheless, due to the mutual interaction, symmetric ZR-like solutions cannot be obtained for an undistorted cluster and two O holes.

In comparison to the study from Ref. 22 and other model Hamiltonian studies, we can identify much more precisely

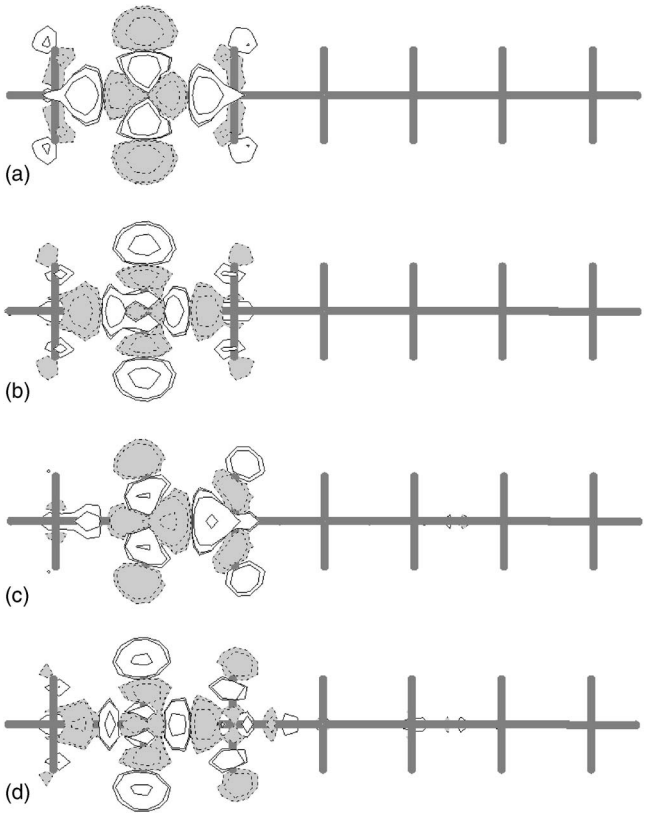

FIG. 2. (a) B and (b) AB orbitals defining a ZRP on a distorted plaquette. Their ONs are 1.86 and 0.14. (c) B and (d) AB orbitals in the undistorted structure. The ONs are 1.74 and 0.26. The $2p$ hole has now the largest weight onto a single O_b oxygen, see also Table I. The same 7-plaquette cluster from Fig. 1(b) is sketched. Positive and negative lobes of the p and d WFs are shown in white and gray, respectively. For the B combinations the p and d AOs are strongly overlapping. There is a change of phase of the p AOs in the AB combinations.

the crucial interactions in the doped plane. However, at this stage we are not able to provide a clear explanation for the pairing mechanism. It is obvious in any case that this is related to both long-range Coulomb interactions and shorter-range interactions. Our results may be associated with the 4-plaquette correlation bag of Goodenough.[28] The ZR singlet polarons in such a correlation bag are separated by AFM coupled $d_{x^2-y^2}$ spins that bear some resemblance to the spin-singlet pairs of the resonating-valence-bond state.[36] Cu-O bond-length fluctuations may induce charge transfer along a chain of plaquettes. In the intermediate, undistorted geometry the quasilocalized $2p$ holes tend to polarize FM the NN $3d$ spins. In other words, the $3d$ spin on the adjacent plaquette is already "prepared" for the transfer of the $2p$ hole. Also, strong antiferromagnetic correlations exist between the d^9-p^5-d^9 units and the "bipolaronic" WF has a complex structure. Our data suggest that two ZR-like quasiparticles could form a 4-plaquette bipolaronic singlet state only above a certain hole concentration. The distribution of "doped" holes displayed in Fig. 1(b) corresponds (at the scale of the figure) to 8% to 9% doping, only slightly higher than the concentration where SC actually occurs. We also

note that the effect described above, i.e., a lowering of the effective energy barrier due to longer-range interactions, is still obtained and has the same order of magnitude when the positions of the extra positive embedding PCs are changed, individually or collectively, by distances as large as one lattice constant. In addition, our results are essentially the same when modifying the values of the charges placed at the La sites in our embedding. We have performed calculations where an average charge of 2.9+ was used at the La sites, simulating a random distribution of Sr ions at 10% doping. We found no changes for the charge distribution on the ZR-like plaquettes and changes of not more than 2% for the local effective potential barriers.

More investigation is needed for a better understanding of these effects and quantitative estimates. First, a more rigorous treatment of the dynamical electron correlation[23] is required.[37] Second, the electronic and lattice degrees of freedom should be described on equal footing, beyond the adiabatic approximation. Another nontrivial task is a self-consistent procedure to determine the (dynamic) in-plane distribution of the charge carriers, perhaps in the spirit of the dynamical mean-field theory. Nevertheless, the purpose of the present study is not to provide highly accurate numbers, but to gain better insight into the very nature of the many-body in-plane interactions. It is our belief that realistic effective models can only be constructed with the help of this type of first-principles investigations.

III. CONCLUSIONS

To conclude, using a WF-based *ab initio* approach, we investigate microscopic electron-lattice, magnetic, and non-local Coulomb interactions characterizing the hole dynamics in (under)doped cuprates. The dressed carriers display features which are reminiscent of both ZR spin-singlet states and Jahn-Teller polarons. We find that at doping levels that are large enough, the adiabatic energy barrier associated to each polaronic state is significantly lower for the synchronized, coherent "hopping" of two ZRPs than in the case of an isolated ZRP. This is due to unscreened intercarrier Coulomb interactions and requires phase coherence among the O-ion half-breathing vibrations. Tunneling effects cannot be neglected for a relatively flat, multiwell energy landscape.[11,20] Following the discussion from Ref. 20, we suggest that the coherent, superconducting phase is the result of such coherent quantum lattice fluctuations involving the in-plane O ions. Coherent, collective tunneling effects in the CuO_2 planes should lead to extended, "resonant" states[10,20] and a lowering of the in-plane kinetic energy, see also Refs. 22, 32, and 38. Polaronic behavior and local double-well potentials were also found in the electron doped case,[13] which suggests some common "global" features for the two types of doping: quantum polarons coupled through spin and longer-range unscreened Coulomb interactions.

ACKNOWLEDGMENT

We thank I. Eremin, J. Röhler, M. Grilli, J. Ranninger, and P. Fulde for fruitful discussions.

[1] D. Reznik, L. Pintschovius, M. Ito, S. Iikubo, M. Sato, H. Goka, M. Fujita, K. Yamada, G. D. Gu, and J. M. Tranquada, Nature (London) **440**, 1170 (2006).
[2] M. Braden, L. Pintschovius, T. Uefuji, and K. Yamada, Phys. Rev. B **72**, 184517 (2005).
[3] A. Lanzara, P. V. Bogdanov, X. J. Zhou, S. A. Kellar, D. L. Feng, E. D. Lu, T. Yoshida, H. Eisaki, A. Fujimori, K. Kishio, J.-I. Shimoyama, T. Noda, S. Uchida, Z. Hussain, and Z.-X. Shen, Nature (London) **412**, 510 (2001).
[4] G.-H. Gweon, T. Sasagawa, S. Y. Zhou, J. Graf, H. Takagi, D.-H. Lee, and A. Lanzara, Nature (London) **430**, 187 (2004).
[5] M. Acosta-Alejandro, J. Mustre de León, S. D. Conradson, and A. R. Bishop, J. Supercond. **15**, 355 (2002).
[6] B. I. Kochelaev, J. Sichelschmidt, B. Elschner, W. Lemor, and A. Loidl, Phys. Rev. Lett. **79**, 4274 (1997).
[7] M. Capone, G. Sangiovanni, C. Castellani, C. Di Castro, and M. Grilli, Phys. Rev. Lett. **92**, 106401 (2004).
[8] O. Rösch and O. Gunnarsson, Phys. Rev. Lett. **92**, 146403 (2004).
[9] S. Ishihara and N. Nagaosa, Phys. Rev. B **69**, 144520 (2004).
[10] E. V. L. de Mello and J. Ranninger, Phys. Rev. B **55**, 14872 (1997).
[11] A. R. Bishop, D. Mihailovic, and J. Mustre de León, J. Phys.: Condens. Matter **15**, L169 (2003).
[12] L. Hozoi, S. Nishimoto, and A. Yamasaki, Phys. Rev. B **72**, 144510 (2005).
[13] L. Hozoi and S. Nishimoto, Phys. Rev. B **73**, 245101 (2006).
[14] C. J. Calzado and J.-P. Malrieu, Phys. Rev. B **63**, 214520 (2001).
[15] The undoped configuration implies Cu $3d^9$ and O $2p^6$ formal valence states (each $2p$ orbital is doubly occupied).
[16] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).
[17] V. Hizhnyakov and E. Sigmund, Physica C **156**, 655 (1988).
[18] V. J. Emery and G. Reiter, Phys. Rev. B **38**, 4547 (1988).
[19] V. J. Emery and G. Reiter, Phys. Rev. B **38**, 11938 (1988).
[20] L. Proville and S. Aubry, Eur. Phys. J. B **11**, 41 (1999); **15**, 405 (2000).
[21] A. S. Alexandrov and N. Mott, *Polarons and Bipolarons* (World Scientific, Singapore, 1995).
[22] J. E. Hirsch, Physica C **201**, 347 (1992); J. E. Hirsch and F. Marsiglio, Phys. Rev. B **62**, 15131 (2000).
[23] T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory* (Wiley, Chichester, 2000).
[24] R. J. Cava, A. Santoro, D. W. Johnson, and W. W. Rhodes, Phys. Rev. B **35**, 6716 (1987).
[25] F. Illas, J. Rubio, and J. C. Barthelat, Chem. Phys. Lett. **119**, 397 (1985); W. R. Wadt and P. J. Hay, J. Chem. Phys. **82**, 284 (1985).
[26] S. A. Kivelson, I. P. Bindloss, E. Fradkin, V. Oganesyan, J. M.

Tranquada, A. Kapitulnik, and C. Howald, Rev. Mod. Phys. **75**, 1201 (2003).

[27] A. M. Gabovich, A. I. Voitenko, J. F. Annett, and M. Ausloos, Supercond. Sci. Technol. **14**, R1 (2001).

[28] J. B. Goodenough, J. Phys.: Condens. Matter **15**, R257 (2003).

[29] Extra orbitals added to the active space turn out to have occupation numbers either very close to 2.00 or to 0 (Ref. 13). Also, when enlarging the active space, it is not obvious how many extra orbitals are required for a balanced description of the different configurations.

[30] MOLCAS 6, Department of Theoretical Chemistry, University of Lund, Sweden.

[31] This value is somewhat larger than in Ref. 12 because the polarization of the apical-oxygen valence shells is neglected.

[32] J. E. Hirsch, Science **295**, 2226 (2002).

[33] H. J. A. Molegraaf, C. Presura, D. van der Marel, P. H. Kes, and M. Li, Science **295**, 2239 (2002).

[34] O-hole broken-symmetry configurations in transition metal oxides were previously discussed in Refs. 35, for example.

[35] C. de Graaf, R. Broer, W. C. Nieuwpoort, and P. S. Bagus, Chem. Phys. Lett. **272**, 341 (1997); A. H. de Vries, L. Hozoi, R. Broer, and P. S. Bagus, Phys. Rev. B **66**, 035108 (2002).

[36] P. W. Anderson, Science **235**, 1196 (1987).

[37] Dynamical electron correlation effects are not expected to affect the type of long-range couplings investigated here. Still, these effects are essential for highly accurate estimates of local quantities, such as the stabilization energy due to the local deformations.

[38] V. J. Emery and S. A. Kivelson, J. Phys. Chem. Solids **61**, 467 (2000).