PHYSICAL REVIEW B **79**, 134522 (2009)

Electronic structure of La_2CuO_4 in the T and T' crystal structures using dynamical mean field theory

Hena Das and Tanusri Saha-Dasgupta

Department of Material Sciences, S. N. Bose National Center for Basic Sciences, JD-III, Salt Lake City, Kolkata 700 098, India

(Received 27 October 2008; revised manuscript received 17 March 2009; published 27 April 2009)

Using Nth order muffin-tin-orbital-based downfolding technique in combination with dynamical mean field theory, we investigate the correlated electronic structure of La_2CuO_4 in the so-called "T" and "T'" crystal structure which serve as the parent compounds for the hole-doped and electron-doped high T_c compounds. La_2CuO_4, which naturally forms in T structure, has been reported to made to form in T' structure by means of special thin-film synthesis technique of replacing La by isovalent RE (RE=Y,Lu,Sm,Gd...) ions [A. Tsukada *et al.*, Solid State Commun. **133**, 427 (2005)]. The experimental studies on T'-structured La_2CuO_4 reveal contrasting properties to that in T structure, which we examine by means of electronic structure calculations. Our dynamical mean field calculations show introduction of correlation effect to the one-electron band structure of T'- and T-structured La_2CuO_4, providing metallic solution in one case (T') and insulating solution to another (T).

DOI: 10.1103/PhysRevB.79.134522 PACS number(s): 74.72.Dn

I. INTRODUCTION

While the high-temperature superconductivity (HTS) in hole-doped cuprates has been studied to a large extent,[1] superconductivity in electron-doped cuprate family is relatively less explored. High-temperature superconductivity has been discovered in hole-doped $La_{2-x}Ba_xCuO_4$, derived from the undoped compound that crystallizes in K_2NiF_4-type T structure.[2] The undoped compound La_2CuO_4 serves also as the parent compound of the electron-doped cuprate superconductors, e.g., $La_{2-x}Ce_xCuO_{4+y}$, which however crystallize in Nd_2CuO_4-type T' structures.[3] For the benefit of understanding the mechanism of high-temperature superconductivity, it would have been interesting to study the properties of the parent compounds in both hole-doped and electron-doped cases. The situation, however, is complicated by the fact that the preparation of undoped T'-structured parent compound is hindered by the structural phase transition to T structure occurring around $x \approx 0.05$.[4]

The preference to formation of T or T' structure in lanthanoid cuprates of general formula Ln_2CuO_4 is generally determined by the ionic radius of Ln^{3+} ion: $T(T')$ structure is favored by large (small) radius of Ln^{3+}. The crossover or the critical radius lies in between La^{3+} and Pr^{3+}.[5] Since the radius of La^{3+} is close to the crossover radius, it seems to be a plausible idea to prepare La_2CuO_4 in T' structure. Following this idea, attempts have been made to synthesis nominally undoped compounds, $La_{2-x}RE_xCuO_4$, by substituting La by RE=Y,Lu,Sm,Gd..., which have the same valence as La^{3+} but have smaller ionic radii.[6] The striking feature that arises out of these studies is that, while La_2CuO_4 in the T structure is strongly insulating, the same in T' structure appears to be conducting with a difference in resistivity of orders of magnitude. While this finding hints toward an interesting implication on mechanism of superconductivity, the experimental situation is faced with difficulties[7] such as the issue of strain effect (since the fabrication was carried out by thin-film synthesis technique), oxygen content of the sample, etc. In this paper, we have therefore taken up the task of investigating electronic structure of La_2CuO_4 in T and T' using first-principles techniques, which is devoid of experimental difficulties concerning synthesis.

It is widely accepted that correlation plays a significant role in the correct description of the electronic structure of cuprates.[8] The density-functional based theories within the local-density approximation (LDA) on the other hand are expected to take into account the structural and chemical intricacies which is needed for the study involving comparison of electronic structure of La_2CuO_4 in two different crystal structures. In the following we have therefore carried out calculations combining these two aspects within the framework of LDA+dynamical mean field theory (DMFT). The choice of DMFT for the many-body part is driven by the fact that the many-body formulation of DMFT takes fully into account the temporal fluctuations, though freezes the spatial fluctuations. This aspect makes it ideally suited to describing correlated metals as well as insulators, as is needed for the present problem.

II. CRYSTAL STRUCTURE

Both T and T' crystal structures of La_2CuO_4 is determined to be in body-centered tetragonal $I4/mmm$ structure.[9] La, Cu, and the plane oxygen (O1) occupy the identical symmetry positions in T and T' given by $4e$ $[(0,0,\pm u_{\mathrm{La}})]$, $2a$ [(0,0,0)], and $4c$ [(0,1/2,0),(1/2,0,0)], respectively. The two structures differ in the position of the out-of-plane oxygen (O2) (see Fig. 1). In case of T structure, O2 occupies the position directly below or above Cu (given by $4e$) while for T' it occupies the position directly below or above O1 (given by $4d$ positions). This results into structures consisting of square CuO_2 planes without any apical oxygen in T' structure instead of two-dimensional (2D) array of CuO_6 octahedra in T structure. The in-plane lattice parameter shows an expansion with a slightly smaller c/a ratio in case of T' structure [$a=4.005$ Å, $c=12.550$ Å] compared to T structure [$a=3.803$ Å, $c=13.150$ Å], resulting into about 6% expansion in volume.[10]

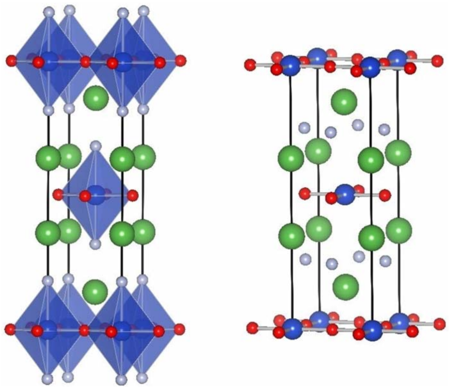

FIG. 1. (Color online) Crystal structure of La_2CuO_4 in T (left panel) and T' (right panel) structures. The La, Cu, and O atoms are represented by the large, mediums and small sized balls, respectively. The in-plane and out-of-plane oxygen atoms are represented by dark and light shades, respectively.

III. ONE-PARTICLE ELECTRONIC STRUCTURE

Figure 2 shows the LDA band structure of La_2CuO_4 in T and T' structures calculated in linear muffin-tin-orbital basis[11,12] projected on to Cu $d_{x^2-y^2}$ character. We find that, while the basic electronic structure is similar between T and T' structures with a single $pd\sigma$ antibonding band arising out of Cu $d_{x^2-y^2}$ and O1 $p\sigma$ crossing the Fermi energy (E_f), the details of the low-energy features are markedly different in two cases in terms of the position and shape of the saddle point.[13] This happens due to change in position of the out-of-plane oxygen, O2. O2, which is positioned directly below O1 for T' structure, develops a strong hybridization with O1 resulting into O1 p_z-O2 p_z band lying close to E_f. The O2 p_x-p_y originating from square $O2_2$ layer in T' structure also is energetically positioned close to E_f. In case of T structure on the other hand the conduction band is significantly mixed with Cu $3z^2$ and O2 p_z character due to short Cu-O2 distance, with O2 serving the purpose of apical oxygen in CuO_6 octahedra. The resulting difference in case of T' structure pushes down the energy of the saddle point and changes the shape of the 2D Fermi surface from square oriented in (π,π) direction in T structure to a rounded square oriented in $(\pi,0)$ direction in T' structure (see inset of Fig. 2).

As discussed above, the low-energy-band structures are described by a single $pd\sigma$ antibonding band. This gives rise to a single sheet in the Fermi surface which is also seen in the photoemission experiment.[14] It is therefore natural that most theories of HTS cuprates[15] are based on single-band t-t'-t''-U-like or t-t'-t''-J-like model with an effective Cu $d_{x^2-y^2}$-like orbital per CuO2 layer. $t,t',t'',\ldots$ denote the nearest-neighbor, second-nearest-neighbor, third nearest-neighbor, and further nearest-neighbor hopping integrals, respectively, on a square lattice with Cu ions. In order to derive a single-band one-particle Hamiltonian, we have performed Nth order muffin-tin-orbital-based (NMTO) downfolding calculations[16] which is capable of providing the low-energy one-band Hamiltonian starting from the full LDA basis by integrating out all the degrees of freedom other than Cu $d_{x^2-y^2}$. The integrated-out degrees of freedom renormalize the basis kept active in the calculation. Such an approach for single-band modeling of hole-doped cuprates[17] has been found to be highly successful. The resulting single band for La_2CuO_4 in T and T' structures, in comparison to full LDA band structure, is also shown in Fig. 2.

NMTO-downfolding technique not only provides the single-band describing accurately the antibonding $pd\sigma$ band but also provides the underlying Wannier-type basis. In Figs. 3(a) and 3(b), we show the plot of such Wannier-type functions for both T and T' structure projected on to the CuO_2 plane and perpendicular to the CuO_2 plane, respectively. The Wannier-type functions have the central Cu $d_{x^2-y^2}$ symmetry, which antibonds to O1 $p\sigma$ in its immediate neighborhood—a general feature of the electronic structure of HTS cuprates. The tails extending to further neighbors reflect the structure specific trend between T and T'. The immediate feature to notice is that the Wannier-type functions of T' structure appears to be more delocalized in plane and more compact out of plane compared to that of T structure. If one interprets the hopping integrals as overlap integrals for such Wannier-type functions, one may realize that this larger amplitudes at the further neighbor oxygen results into larger further neighbor in-plane hoppings in a one-band model. The plot of the functions seen from side [c.f. Fig. 3(b)] shows the out-of-plane orbital characters of the conduction-band Wannier-type functions. Considering the case of T structure, starting from the central Cu atom and going in the a direction, we see Cu $d_{x^2-y^2}$ antibond to neighboring O1 p_x, which itself anti-

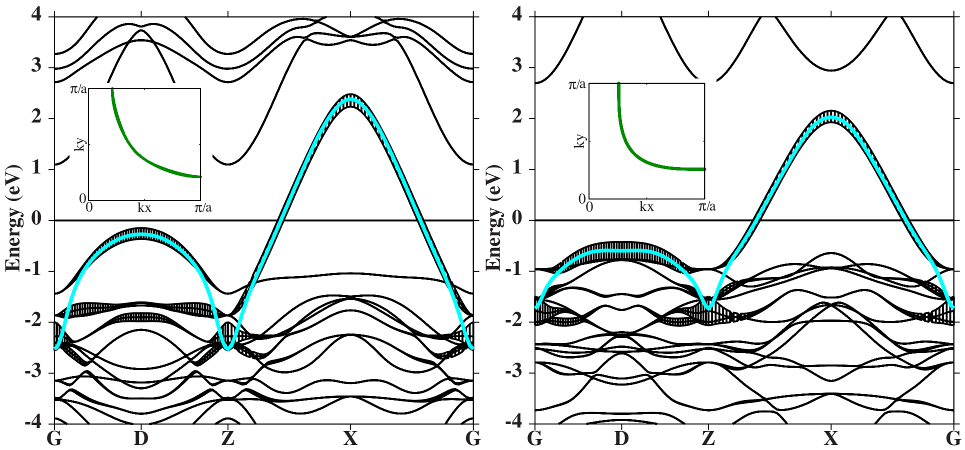

FIG. 2. (Color online) Band structure of La_2CuO_4 in T (left panel) and T' (right panel) structures plotted along the high-symmetry points of the body-centered tetragonal BZ. The fatness associated with each band is proportional to the orbital character of Cu $d_{x^2-y^2}$. The single band shown as thick line is the effective one band obtained by NMTO-downfolding technique. The inset shows the corresponding Fermi surfaces.

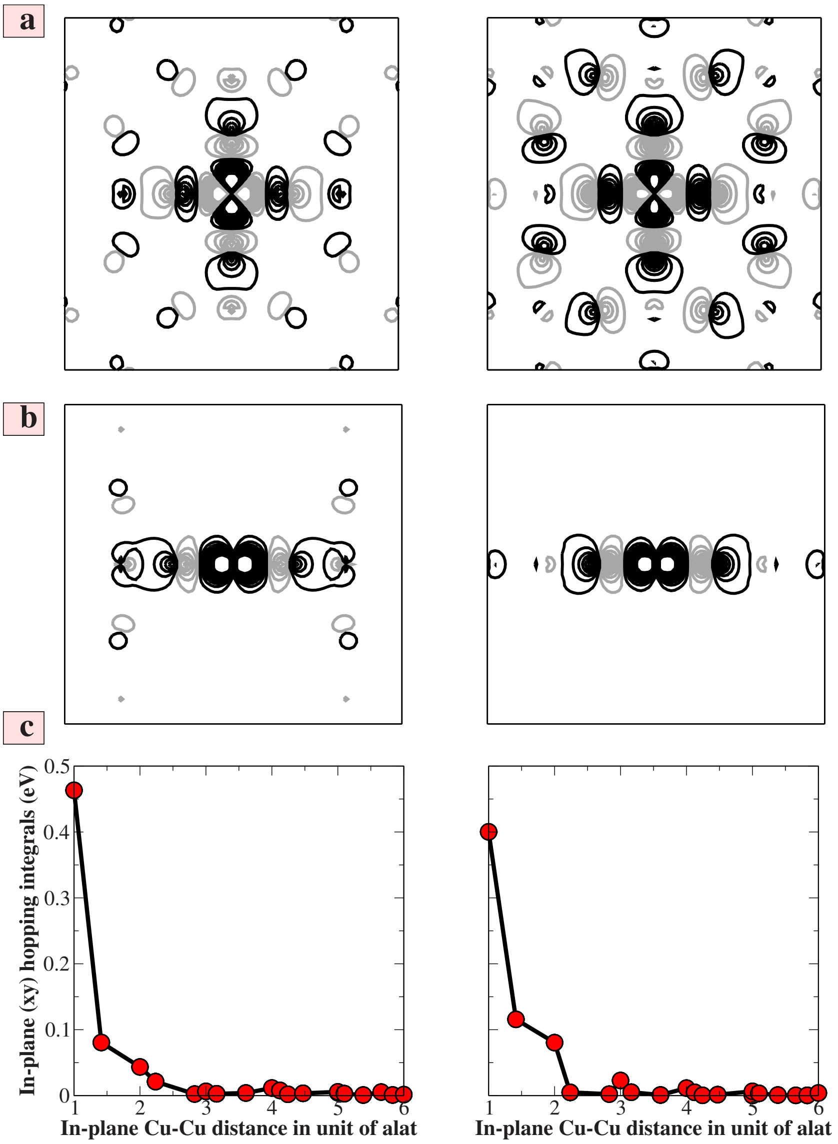

FIG. 3. (Color online) Effective Cu $d_{x^2-y^2}$ Wannier-type functions and the hopping integrals of a single-band model of La_2CuO_4 in T (left panels) and T' (right panels) structures. (a) Wannier-type functions projected on to CuO_2 plane (*ab* plane) and (b) Wannier-type functions projected on to plane perpendicular to CuO_2 plane (*ac* plane). Lobes of opposite signs are colored as black and gray. (c) In-plane hopping integrals in the basis of effective Wannier-type functions, plotted as a function of Cu-Cu distances, measured in unit of lattice constant (alat).

bonds to $3z^2$ on the next Cu. From here and moving along the c direction, we see also $3z^2$ antibond to O2 p_z, which itself bonds to further neighbor La orbitals. For T' structure we find about the same amount of Cu $d_{x^2-y^2}$ and nearly same amount of O1 character but negligible Cu $3z^2$ and certainly no O2 p_z since due to symmetry O2 p_z cannot bind to Cu $d_{x^2-y^2}$ any more. We on other hand find with diffused Cu s character that causes inflation of the black lobe of O1-like tail compared to the gray lobe. Constructing the real-space Hamiltonians in the basis of the above discussed Wannier-type functions for the conduction band, as shown in Fig. 3(c), exhibit a reduction in nearest-neighbor hopping interaction t in T' structure compared to T structure, which is governed by the increase in Cu-O1 bond length in case of T' structure compared to T structure. We however, notice an enhancement of the next-nearest-neighbor hopping, t', and other longer-ranged hoppings, t'', and so on in T' structure compared to T structure in agreement with conclusions drawn on basis on the plot of Wannier-type functions. The spread of the single-band Wannier function and the resulting tight-binding Hamiltonian may be expressed in terms of the so-called range parameter, r, as introduced in Ref. 17. The r-parameter is found to be 0.14 for T structure and 0.4 for T' structure. As has been found in Ref. 17, the range is intimately connected to the energy of axial orbital, a hybrid between Cu s, $3z^2$, and apical oxygen p_z, which is governed by the distance of apical oxygen to CuO_2 plane. In cases of short distances of apical oxygen to CuO_2 plane, finite mixing of Cu s with Cu $3z^2$ and apical oxygen p_z character causes the energy of the hybrid axial orbital to be pushed up in energy which in turn reduces the range of the in-plane hoppings. While such a scenario is valid for T-structured La_2CuO4, in absence of the apical oxygen in T' structure such mechanism is not operative for T'-structured La_2CuO4, giving rise to the long range of the in-plane hoppings.

IV. LDA+DMFT RESULTS AND DISCUSSION

In the next step, we carried out DMFT calculations on the 2D single-band Hubbard Hamiltonian given by

$$H = \sum_{i,j,\sigma} t_{i,j} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} - \mu \sum_{i} n_{i},$$

where $t_{i,j}$'s are the single-particle hopping interaction between the effective Cu $d_{x^2-y^2}$ as obtained in downfolded NMTO-Wannier-type function basis. $n_{i\sigma}=c^{\dagger}_{i\sigma}c_{i\sigma}$, where $c^{\dagger}_{i\sigma}$ creates a σ-spin electron at site i and U, is the Hubbard interaction. The double-counting correction is absorbed in the chemical-potential shift μ.

The DMFT (Ref. 18) maps the many-body crystal problem defined by the Hubbard Hamiltonian introduced above onto an effective self-consistent quantum impurity problem. The corresponding local Green's function matrix is calculated via the Brillouin-zone (BZ) integration,

$$G(\omega_n) = \sum_{k} [(\omega_n + \mu)I - H^{\mathrm{LDA}}(k) - \Sigma(\omega_n)]^{-1}. \tag{1}$$

$H^{\mathrm{LDA}}(k)$, defined in the above, is the one-band dispersion given by the Fourier transform of the real-space Hamiltonian formed by hopping interactions, $t_{i,j}$'s. The chemical potential μ is defined self-consistently through the total number of electrons; $\omega_n=(2n+1)\pi/\beta$ are the Matsubara frequencies with β as the inverse temperature ($\beta=1/\mathrm{T}$). Σ is the self-energy matrix.

The self-consistency condition within DMFT implies the local Green's function to be the same as the corresponding solution of the quantum impurity problem $G_{\sigma}(\tau-\tau')=1/Z\int D[\mathbf{c},\mathbf{c}^{\dagger}]e^{-S_{\mathrm{eff}}}\mathbf{c}(\tau)\mathbf{c}^{\dagger}(\tau')$, where the effective action S_{eff} is defined in terms of the so-called bath Green's function $\mathcal{G}^{-1}_{\sigma}(\omega_n)=G^{-1}_{\sigma}(\omega_n)+\Sigma_{\sigma}(\omega_n)$, which describes the energy, orbital, spin, and temperature-dependent interaction of a particular site with the rest of the medium.

The crux of the DMFT problem lies in the solution of the quantum impurity problem. The quantum impurity problem in our calculations is solved by the numerically exact quantum Monte Carlo (QMC) scheme.[19] The computational effort becomes prohibitive rather quickly as one lowers the temperature since in order to maintain the accuracy of the calculation one needs to increase the imaginary time slices as one increases β. The results reported in the following are done for $\beta=30$ (in unit of eV^{-1}) with 290 slices in imaginary time and 100 000 QMC sweeps. The maximum entropy method[20] has been used for analytical continuation of the diagonal part of the Green's function matrix to the real energy axis to get the DMFT spectral density.

The choice of Hubbard U is a delicate issue in the whole calculation scheme. The choice of U for a given compound depends on the choice of representation basis and therefore depends on the model used for the description of the compound. The U is expected to be significantly screened in case of a single-band model due to the much delocalized character of the effective single-band Wannier-type function. The Slater integral computed in the basis of the computed Wannier-type functions[21] show significant reduction compared to that calculated using constraint density-functional calculations[22] for cuprates. This is also in accordance with the recent proposal by Comanac *et al.*[23] obtained combining DMFT studies and analysis of optical spectra of cuprates that the correlation strength in the cuprates is actually smaller than the critical U for a Mott transition in the nonmagnetic sector. In the calculations reported in the following, we have fixed the value of U to 4.5 eV. We have kept the same value of U between the T and T' structures although the T' structure is expected to have a lower U value compared to T structure due to the more delocalized nature in case of T' structure.

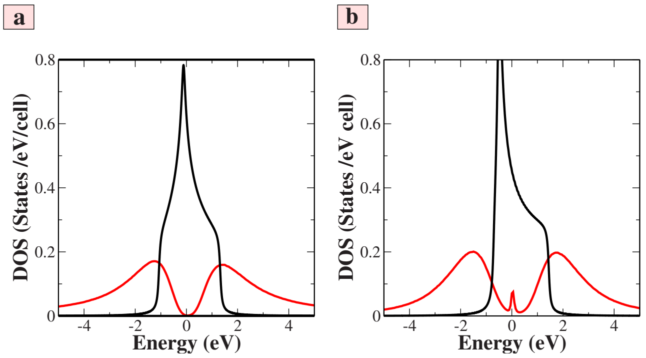

FIG. 4. (Color online) DMFT spectral function at $T=580$ K (thick line) and the LDA DOS (thin line) La_2CuO_4 in T (left panel) and T' (right panel) structures. The zero of the energy is set at μ.

The calculated spectrum as presented in Fig. 4 show formation of lower and upper Hubbard bands, signaling the correlated nature of the compounds. Interestingly, for T' structure we find simultaneous presence of Hubbard subbands and a coherent quasiparticle peak, compared to that of an insulator as found in the case of T-structured La_2CuO_4. We note that the conclusions drawn are based on the finite temperature calculations, carried out at a temperature of 580 K. Since the overall bandwidths of the single-electron spectra for both T and T' are about 4 eV and the U value used in the DMFT calculations is 4.5 eV, which may be about or slightly less than the critical U value for the Mott transition, the $T=0$ state might be metallic even for the T-structured La_2CuO_4, as hinted in Ref. 23. It will be therefore fair to claim that the T-structured La_2CuO_4 has a lower coherence temperature (lower than 580 K) compared to that of the T'-structured La_2CuO_4, indicating the *more metallic* character of the T'-structured La_2CuO_4 compared to T structure.

We further note that the bandwidth of the single-particle density of states (DOS) for T' structure is somewhat smaller compared T structure. Nevertheless our finite temperature calculations find the metallic solution of the T' structure and the insulating solution of the T structure. This apparently counterintuitive result may be explained in terms of the fact that, instead of the bandwidth alone, what matters is the shape of the single-particle density of states, a good measure being the second moment of the density of states. The band energy is therefore measured[24] by $(\frac{\mu_2}{\mu_0})^{1/2}$, where μ_2 and μ_0 are the second and zeroth moments of the density of states. We found the second moment is determined by the interplay between the bandwidth, governed by the nearest-neighbor hopping parameter t, and the range parameter r. For T' structure although the bandwidth is smaller than T structure, the r value is larger compared to T structure, which makes the second moment to be larger and hence the band energy to be larger.

V. SUMMARY

To conclude, using combination of LDA to take into account the composition and structural aspect, and DMFT to take into account the correlation aspect, we have studied the electronic structure of T- and T'-structured La_2CuO_4. Our calculation shows the change in position of the out-of-plane oxygen between T and T' structures, resulting into significant changes in the one-particle electronic structure. Upon incorporation of correlation effect, these differences translate into insulating solution in case of T structure and correlated metallic situation in case of T' structure for calculations carried out at a temperature of 580 K. This indicates higher coherence temperature and therefore more metallic character for T' structure compared to T structure. Our study suggest that both T- and T'-structured cuprates are close to or even below the critical U for Mott transition, and therefore far from a very strong-coupling regime, a fact which has been also suggested in Ref. 23. As a result, the delicate band-structure differences between T- and T'-structured La_2CuO_4 cause the interesting effect of the *more metallic* character in one case over the other. Our findings seem to support the initial experimental studies made by Tsukada *et al.* in this context. This should be explored more carefully in the future. Finally, our calculations do not take into account the presence of antiferromagnetic fluctuations.[25] Therefore, the obtained results may be considered as the effect of correlation on the single-particle band structure arising out of presence and absence of apical oxygen in T and T' structures. Our study nevertheless provides useful hint to future studies.

ACKNOWLEDGMENT

T.S.D. acknowledges the support of Advanced Materials Research Unit and Swarnajaynti grant. H.D. and T.S.D. acknowledge useful discussion with O.K. Andersen during the visit to MPI, Stuttgart under the partner group program and with I. Dasgupta.

---

[1] E. Dagotto, Rev. Mod. Phys. **66**, 763 (1994).

[2] J. G. Bednorz and K. A. Müller, Z. Phys. B: Condens. Matter **64**, 189 (1986).

[3] A. Sawa, M. Kawasaki, H. Takagi, and Y. Tokura, Phys. Rev. B **66**, 014531 (2002).

[4] M. Naito and M. Hepp, Jpn. J. Appl. Phys., Part 1 **39**, L485 (2000).

[5] Y. Tokura, H. Takagi, and S. Uchida, Nature (London) **337**, 345 (1989); J. T. Markert, E. A. Early, T. Bjornholm, S. Ghamaty, B. W. Lee, J. J. Neumeier, R. D. Price, C. L. Seaman, and M. B. Maple, Physica C **158**, 178 (1989).

[6] A. Tsukada, Y. Krockenberger, M. Noda, H. Yamamoto, D. Manske, L. Alff, and M. Naito, Solid State Commun. **133**, 427 (2005).

[7] P. G. Radaelli, J. D. Jorgensen, A. J. Schultz, B. A. Hunter, J. L. Wagner, F. C. Chou, and D. C. Johnston, Phys. Rev. B **48**, 499 (1993); H. Sato and M. Naito, Physica C **274**, 221 (1997).

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

[9] Y. Tokura, H. Takagi, and S. Uchida, Nature (London) **337**, 345 (1989).

[10] A. Tsukada, T. Greibe, and M. Naito, Phys. Rev. B **66**, 184515 (2002).

[11] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[12] Three different empty spheres have been used to achieve the space filling with a choice of sphere radii at La, Cu, and O sites as 1.7, 1.2, and 1.1 Å, respectively.

[13] The obtained band structure in T' structure is found to be similar to that of reported band structure of isostructural Nd_2CuO_4 by S. Massidda, N. Hamada, Jaejun Yu, and A. J. Freeman, Physica C **157**, 571 (1989).

[14] N. P. Armitage, F. Ronning, D. H. Lu, C. Kim, A. Damascelli, K. M. Shen, D. L. Feng, H. Eisaki, Z.-X. Shen, P. K. Mang, N. Kaneko, M. Greven, Y. Onose, Y. Taguchi, and Y. Tokura, Phys. Rev. Lett. **88**, 257001 (2002).

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

[16] O. K. Andersen and T. Saha-Dasgupta, Phys. Rev. B **62**, R16219 (2000), and references therein.

[17] E. Pavarini, I. Dasgupta, T. Saha-Dasgupta, O. Jepsen, and O. K. Andersen, Phys. Rev. Lett. **87**, 047003 (2001).

[18] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).

[19] J. E. Hirsch and R. M. Fye, Phys. Rev. Lett. **56**, 2521 (1986).

[20] M. Jarrell and J. E. Gubernatis, Phys. Rep. **269**, 133 (1996).

[21] W. Heitler and F. London, Z. Phys. **44**, 455 (1927).

[22] O. Gunnarsson, O. K. Andersen, O. Jepsen, and J. Zaanen, Phys. Rev. B **39**, 1708 (1989).

[23] A. Comanac, L. D. Medici, M. Capone, and A. J. Millis, Nat. Phys. **4**, 287 (2008).

[24] F. Ducastelle, *Order and Phase Stability in Alloys*, Cohesion and Structure, edited by F. R. de Boer and D. G. Pettifor (North-Holland, Amsterdam, 1991), Vol. 3.

[25] Antiferromagnetic LDA+U calculations for T'-structured La_2CuO_4 gave rise to a small energy gap of ≈ 0.1 eV, compared to energy gap of 1.8 eV for T-structured La_2CuO_4. LDA+U approach which does not take into account the dynamical fluctuation effect tend to overestimate the insulating solution.