Intrinsic electron and hole bands in electron-doped cuprate superconductors

T. Xiang,[1,2] H. G. Luo,[2,3] D. H. Lu,[4] K. M. Shen,[5] and Z. X. Shen[4]
[1]*Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100190, China*
[2]*Institute of Theoretical Physics, Chinese Academy of Sciences, P.O. Box 2735, Beijing 100190, China*
[3]*Center for Interdisciplinary Studies, Lanzhou University, Lanzhou 730000, China*
[4]*Department of Physics, Applied Physics, and Stanford Synchrotron Radiation Laboratory, Stanford University, Stanford, California 94305, USA*
[5]*Department of Physics and Astronomy, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z4*
(Received 10 December 2008; published 30 January 2009)

We propose that the upper Hubbard band (electronlike) and the Zhang-Rice singlet band (holelike) are two essential components in describing low-energy excitations of electron-doped cuprate superconductors. We find that the gap between these two bands is significantly smaller than the charge-transfer gap measured by optics and is further reduced upon doping. This indicates that the charge fluctuation is strong and the system is in the intermediate correlation regime. A two-band model is derived. In the limit that the intraband and interband hopping integrals are equal to each other, this model is equivalent to the unconstrained *t-J* model with on-site Coulomb repulsions.

DOI: 10.1103/PhysRevB.79.014524 PACS number(s): 74.20.−z, 71.10.Fd, 74.72.−h, 79.60.−i

I. INTRODUCTION

Systematical understanding of the doping dependence of electronic structures of cuprate superconductors is fundamentally important in the study of high-T_c mechanism. It was commonly accepted that the low-energy physics is governed by the one-band *t-J* model[1] in hole-doped high-T_c cuprates. However, for electron-doped cuprates, the phase diagram changes substantially and both electronlike and holelike Fermi surfaces were observed slightly below optimal doping by angle-resolved photoemission spectroscopy (ARPES).[2] It has long been realized that a single-band model is not enough and an effective two-band picture[3] should be used to understand ARPES and transport measurement data of electron-doped cuprates. It is still controversial regarding the minimal model for describing this system. A central issue under debate is the microscopic origin of these two bands.

To understand this problem, much of the theoretical studies have been carried out with the one-band Hubbard model.[4–6] In this model, a metallic band is split effectively into the upper and lower Hubbard bands by a correlation energy U that represents the energy cost for a site to be doubly occupied. U could arise either from the on-site Coulomb repulsion between two electrons on Cu $3d$ orbital, which is generally larger than 5 eV, or from the charge-transfer (CT) gap between O $2p$ and Cu $3d$ bands, which is about 1.5–2 eV—a value usually quoted from the optic measurement.[7,8] It seems that in either case U is too large to be relevant to the low-energy electron and hole excitations as observed by ARPES.

A commonly adopted picture is that the two bands result from the band folding[9] induced by the antiferromagnetic interaction in the one-band *t-J* model. This interpretation is consistent with the measurement data in the overdoped regime ($x>0.15$). However, in the low-doping antiferromagnetic phase, it breaks down. The band folding assumes implicitly a band with large Fermi surface exists and it is the antiferromagnetic interactions between the hot spots that split this band into a conduction electron and a shadow hole band. However, in the antiferromagnetic phase at low doping, these bands with the folding gap at the hot spots are not observed. Experimentally, it was clearly indicated that electrons are first doped at the upper Hubbard band (Cu $3d^{10}$ band) near $(\pi,0)$ and its equivalent points. With further doping but still in the antiferromagnetic phase, in-gap spectral weight develops below the Fermi level. These in-gap states move upward and eventually form a holelike Fermi-surface pocket around $(\frac{\pi}{2},\frac{\pi}{2})$.[2] In the heavily overdoped regime, these two Fermi pockets merge together and form a large Fermi surface with a volume satisfying the Luttinger theorem. The doping evolution of electronic structure cannot be interpreted by the band folding mechanism. In addition, the gap induced by the antiferromagnetic interaction is of order J, which is too small to account for the energy splitting between the lower and upper CT bands, at least in the low-doping limit.

In this paper, we will show that both the upper Hubbard band (Cu $3d^{10}$ band) and the Zhang-Rice singlet band play important roles in electron-doped copper oxides. They form the two low-energy bands as observed by ARPES and other experiments. Furthermore, we find that doping is not only to add charge carriers to the system but also to reduce the gap between these two bands. At low doping, electrons are first doped into the upper Hubbard band and the Zhang-Rice singlet band lies well below the Fermi level. Upon further doping, the Zhang-Rice singlet band moves toward the upper Hubbard band and eventually emerges above the Fermi level.[2] In the heavily overdoped sample, these two Fermi surfaces merge together and form a large Fermi surface with a volume satisfying the Luttinger theorem. This picture, as discussed in detail below, is consistent with ARPES as well as other experimental measurements.

This paper is organized as follows. In Sec. II we present a detailed analysis of the measurement data of ARPES and optics, and show that the low-energy physics of electron-doped cuprates can be described by a two-band *t-J* model. In

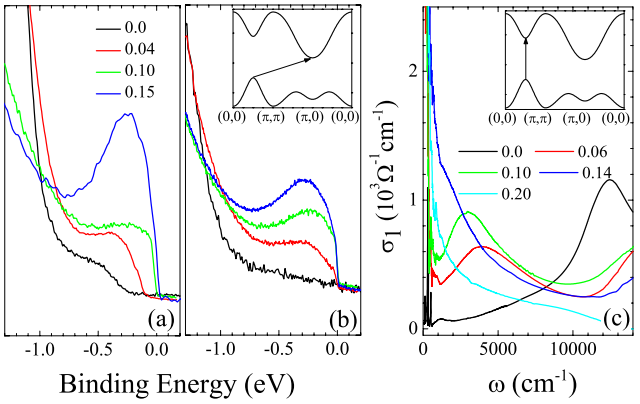

FIG. 1. (Color online) ARPES spectra near (a) the nodal and (b) antinodal regions reproduced from the data published in Ref. 2. (c) The infrared conductivity reproduced from the data published in Ref. 8. The insets of (b) and (c) illustrate the indirect and direct CT gaps.

Sec. III an effective single-band *t-U-J* model is derived from the two-band *t-J* model in the symmetric limit, then we calculate and compare the energy spectra and the staggered magnetization of the *t-U-J* model with experimental results. A brief summary is given in Sec. IV.

II. TWO-BAND PICTURE

Let us start by considering the doping evolution of band structures. In a nominally undoped Nd_2CuO_4, a dispersive band is observed by ARPES at roughly 1.2 eV below the chemical potential. As shown in Ref. 2, the energy-momentum dispersion of this spectral peak behaves almost the same as the lower CT band observed in $Ca_2CuO_2Cl_2$, except that in the latter case the band lies at only ~0.7 eV below the chemical potential. This suggests that these two bands have the same physical origin. The difference is probably due to the intrinsic doping and the chemical potential is pinned near the bottom of conduction band (i.e., Cu $3d^{10}$ band) in Nd_2CuO_4 versus near the top of the valence band (i.e., Zhang-Rice singlet band[1]) in $Ca_2CuO_2Cl_2$.

Doping electrons into Nd_2CuO_4 results in a spectral weight transfer from the main spectral peak at ~1.2 eV to an "in-gap" state. This in-gap state first appears as a weak low-energy "foot" at ~0.5 eV below the Fermi level ε_F along the zone diagonal in the undoped Nd_2CuO_4 [Fig. 1(a)]. It moves toward the Fermi level with doping and becomes a broad hump just below the Fermi level at optimal doping. The hole Fermi pocket observed at high doping originates from these in-gap states. In contrast, the states near $(\pi,0)$ reside at ε_F as they are derived from the bottom of the upper Hubbard band [Fig. 1(b)]. The fact that the broad maximum is slightly below ε_F is caused by the Franck-Condon broadening as discussed below.

It should be pointed out that, same as for the dispersive high-energy band, the in-gap states behave similarly as the low-energy coherent states observed in hole-doped $Ca_2CuO_2Cl_2$ (Ref. 10). Near half filling, the in-gap state in Nd_2CuO_4 lies also at ~0.7 eV above the high-energy spectral peak. This suggests that, similar as in hole-doped materials, the high-energy hump structure in the spectra results from the Franck-Condon broadening and the in-gap states are the true quasiparticle excitations located at the top of the lower CT band.[10] At half filling, the in-gap state is not observed because its quasiparticle weight is vanishingly small.[11]

The spectral weight transfer induced by doping has also been observed in the optical measurements [Fig. 1(c)]. At zero doping, the optical CT gap appears at ~1.5 eV. Upon doping, a midinfrared conductivity peak develops. This midinfrared peak appears at ~0.5 eV at low doping[7,8] and then moves toward zero energy with increasing doping. The doping dependence of the midinfrared peak is consistent with the doping evolution of the in-gap states observed by ARPES. It suggests that the midinfrared peak results mainly from the optical transition between the in-gap states and the upper Hubbard band. The polaron effect may also have some contribution to this midinfrared peak.[12]

The above discussion indicates that the band gap, measured as the minimum excitation energy between the hole and electron bands, is only 0.5 eV at half filling, much lower than the optically measured CT gap, which is usually believed to be about 1.5 eV. This difference between the true quasiparticle gap that determines the transport and thermodynamics and the optically measured CT gap has also been found in hole-doped materials.[13] For La_2CuO_4, Ono *et al.*[14] found recently that the band gap obtained from the high-temperature behavior of the Hall coefficient is only 0.89 eV, while the corresponding optical CT gap is about 2 eV. This means that the optical CT gap, which is generally determined from the peak energy of the optical absorption, does not correspond to the true gap between the two bands in high-T_c oxides. The indirect nature of the gap (insets of Fig. 1) and the Franck-Condon effect lead to the overestimate of the gap by optics. It also means that the charge fluctuation in high-T_c materials is much stronger than usually believed and should be fully considered in the construction of the basic model of high-T_c superconductivity.[3,15,16]

The doping dependence of low-energy peaks observed by both APRES and optics indicates that there is a gap closing with doping. This gap closing may result from the Coulomb repulsion between O $2p$ and Cu $3d$ electrons. Doping electrons increases the occupation number of Cu $3d$ states, which in turn adds an effective potential to the O $2p$ states and raise their energy level. If U_{pd} is the energy of the Coulomb interaction between neighboring O and Cu ions, then the change in the O $2p$ energy level will be $\delta\varepsilon_p \approx +2xU_{pd}$, where x is the doping concentration and the factor 2 appears since each O has two Cu neighbors. U_{pd} is generally estimated to be of order 1–2 eV. Thus a 15% doping of electrons would reduce the CT gap by 0.3–0.6 eV within the range of experimentally observed gap reduction. Furthermore, the electrostatic screening induced by doping can reduce the on-site Coulomb interaction of Cu $3d_{x^2-y^2}$ electrons. This can also reduce the gap between the O $2p$ states and the upper Hubbard bands.

Now let us consider how to characterize the low-energy charge and spin dynamics of the system. For simplicity, we focus on the electronic structure and leave the additional electron-phonon interaction effect for future study. If the

charge fluctuation between the two bands is ignored, then the Zhang-Rice singlet band should be described by an effective one-band t-J model.[1] Similarly, the upper Hubbard band should also be described by an effective one-band t-J model if there is no charge fluctuation. However, in the case where the hybridization or charge transfer between these bands is important, it can be shown from a three-band model that these two t-J models should be combined together and replaced by the following hybridized two-band t-J model:[17]

$$H = \sum_{ij\sigma} t_{ij}^{e} e_i^{\dagger} d_{i\sigma} d_{j\sigma}^{\dagger} e_j + \sum_{ij\sigma} t_{ij}^{h} h_i^{\dagger} d_{i\sigma} d_{j\sigma}^{\dagger} h_j + \sum_{ij\sigma} t_{ij} (\sigma d_{i\sigma}^{\dagger} d_{j\bar{\sigma}}^{\dagger} e_i h_j + \text{H.c.}) + J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_i (\varepsilon_e e_i^{\dagger} e_i + \varepsilon_h h_i^{\dagger} h_i) - V_{pd} \sum_{\langle ij \rangle} e_i^{\dagger} e_i h_j^{\dagger} h_j, \quad (1)$$

where h_i, e_i, and $d_{i\sigma}$ are the annihilation operators of a Zhang-Rice singlet hole, a doubly occupied $d_{x^2-y^2}$ state (doublon), and a pure Cu^{2+} spin, respectively. At each site, these three states cannot coexist and the corresponding number operators should satisfy the constraint

$$e_i^{\dagger} e_i + h_i^{\dagger} h_i + \sum_{\sigma} d_{i\sigma}^{\dagger} d_{i\sigma} = 1. \quad (2)$$

The difference between the number of doubly occupied $d_{x^2-y^2}$ states and Zhang-Rice singlet holes is the doping concentration of electrons, $\langle e_i^{\dagger} e_i - h_i^{\dagger} h_i \rangle = x$.

In Eq. (1), $\mathbf{S}_i = d_i^{\dagger} \sigma d_i / 2$ is the spin operator and σ is the Pauli matrix. ε_e and ε_h are the excitation energies of a doublon and a Zhang-Rice singlet, respectively. t_{ij}^{e} and t_{ij}^{h} are the hopping integrals of the upper Hubbard and Zhang-Rice singlet bands. In Eq. (1), if $\varepsilon_h \gg \varepsilon_e > 0$, then $\langle h_i^{\dagger} h_i \rangle \approx 0$ and H simply reduces to the one-band t-J model of doubly occupied electrons in the doublon-spinon representation. On the other hand, if $\varepsilon_e \gg \varepsilon_h > 0$, then $\langle e_i^{\dagger} e_i \rangle \approx 0$ and H becomes simply the one-band t-J model of Zhang-Rice singlets in the holon-spinon representation. The t_{ij} term describes the hybridization between the upper Hubbard and Zhang-Rice singlets. The last term results from the Coulomb repulsion between a Cu $3d_{x^2-y^2}$ and its neighboring O $2p_{x,y}$ electrons. V_{pd} is proportional to the Coulomb repulsion between Cu and O ions U_{pd}.

III. EFFECTIVE t-U-J MODEL

The model Hamiltonian (1) can be simplified if $t_{ij}^{e} = t_{ij}^{h} = t_{ij}$. In this case, by using the holon-doublon representation of an electron operator

$$c_{i\sigma} = \sigma h_i^{\dagger} d_{i\sigma} + e_i d_{i\bar{\sigma}}^{\dagger},$$

and taking a mean-field approximation for the V_{pd} term,

$$e_i^{\dagger} e_i h_j^{\dagger} h_j \approx \langle e_i^{\dagger} e_i \rangle h_j^{\dagger} h_j + e_i^{\dagger} e_i \langle h_j^{\dagger} h_j \rangle - \langle e_i^{\dagger} e_i \rangle \langle h_j^{\dagger} h_j \rangle,$$

one can then express H as

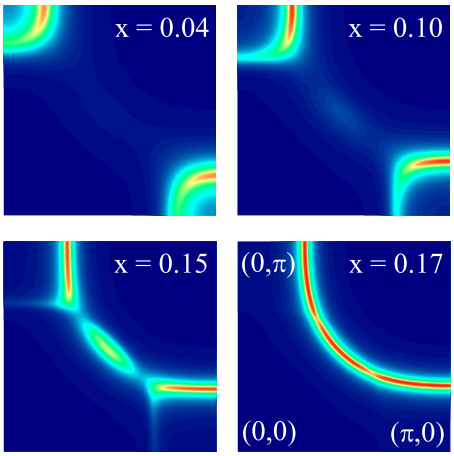

FIG. 2. (Color online) Fermi-surface density map at different dopings x obtained by integrating the spectral function from −40 to 20 meV around the Fermi level for the t-U-J model.

$$H = \sum_{ij\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + J \sum_{\langle ij \rangle} S_i \cdot S_j, \quad (3)$$

where $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$ and $U = \varepsilon_e + \varepsilon_h - 4V_{pd}(\langle e_i^{\dagger} e_i \rangle + \langle h_i^{\dagger} h_i \rangle)$. In electron-doped materials, as the induced hole concentration is very small, $\langle h_i^{\dagger} h_i \rangle \ll \langle e_i^{\dagger} e_i \rangle \approx x$, we have $U \approx \varepsilon_e + \varepsilon_h - 4xV_{pd}$. It should be emphasized that the spin-exchange term in Eq. (3) is not a derivative of the one-band Hubbard model in the strong coupling limit. It actually arises from the antiferromagnetic superexchange interaction between two undoped Cu^{2+} spins via an O $2p$ orbital. This term, as shown in Ref. 18, can enhance strongly the superconducting pairing potential.

The t-U-J model defined by Eq. (3) is obtained by assuming $t_{ij}^{e} = t_{ij}^{h} = t_{ij}$. This is a strong approximation which may not be fully satisfied in real materials. Nevertheless, we believe that this simplified model still catches qualitatively the low-energy physics of high-T_c cuprates. It has already been used, as an extension of either the Hubbard or the t-J model, to explore physical properties of strongly correlated systems, such as the Gossamer superconductivity.[19]

The above Hamiltonian reveals two features about the effective Hubbard interaction. First, U is determined by the CT gap,[15] not the Coulomb interaction between two electrons in a Cu $3d_{x^2-y^2}$ orbital. It is in the intermediate or even weak-coupling regime rather than the strong coupling limit as usually believed. Second, U is doping dependent. It drops with doping. These are in fact the two key features that are needed in order to explain the experimental results with the Hubbard model.[4–6]

We have calculated the single-particle spectral function and the staggered magnetization for the t-U-J model using the mean-field approximation. In the calculation, t_{ij} are parameterized by the first, second, and third nearest-neighbor hopping integrals (t, t', t''). The parameters used are $t = 0.326$ eV, $t' = -0.25t$, $t'' = 0.15t$, $J = 0.3t$ eV, $\varepsilon_e + \varepsilon_h = 4t$, and $V_{pd} = 2.7t$.

Figure 2 shows the intensity plot of the spectral function at the Fermi level. The doping evolution of the Fermi surface

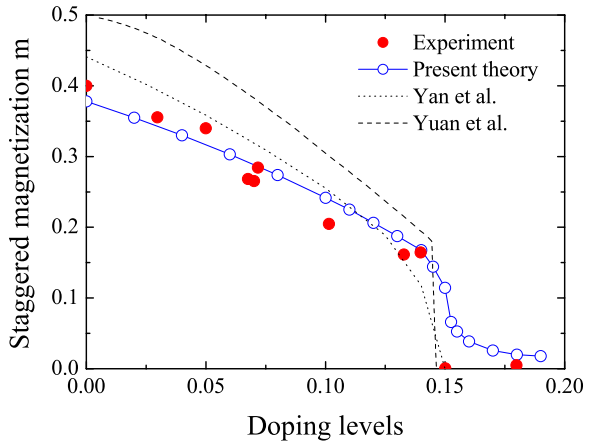

FIG. 3. (Color online) Comparison of the mean-field result (open circles) of the staggered magnetization m as a function of doping with the experimental data (solid circles) (Ref. 23). The theoretical data obtained by Yan *et al.* (Ref. 24) and by Yuan *et al.* (Ref. 25) are also shown for comparison.

agrees with the ARPES measurements.[2] It is also consistent with the mean-field calculation of the Hubbard model by Kusko *et al.*,[4] while our calculation has the same shortcoming of the mean-field calculation in providing too large bandwidth. The difference is that in our calculation, the Hubbard interaction U is not an adjustable parameter of doping. It decreases almost linearly with doping. For the parameters given above, $U \approx (1.3-3.5x)$ eV. Whereas in the calculation of Kusko *et al.*,[4] U is determined by assuming the mean-field energy gap to be equal to the experimentally observed value of the "pseudogap".

Figure 3 shows the theoretical result of the staggered magnetization $m=(\langle n_{i\uparrow}-n_{i\downarrow}\rangle)/2$. The simple mean-field result agrees well with the experimental data,[20–23] especially in the low-doping range. It is also consistent qualitatively with other theoretical calculations.[24,25] m decreases almost linearly at low doping. However, it shows a fast drop above ~ 0.14 when the lower Zhang-Rice singlet holes begin to emerge above the Fermi surface. This abrupt change in m is an indication of a significant reconstruction of the Fermi surface. It may result from the quantum critical fluctuation as suggested in Ref. 26. m does not vanish above the optimal doping; this is probably due to the mean-field approximation.

IV. SUMMARY

In conclusion, based on a thorough analysis of experimental data, we have shown that the band gap between the Zhang-Rice singlet and the upper Hubbard bands is significantly smaller than the optical gap and is further reduced by doping in electron-doped copper oxides. The charge fluctuation modifies substantially the low-lying excitation spectra as well as the phase diagram, in comparison with the hole-doped materials. The low-energy physics of the system is governed by an effective two-band model or approximately by the t-U-J model. This conclusion is drawn based on the analysis of electron-doped materials. However, we believe that it can also be applied to hole-doped cuprate superconductors, especially in the overdoped regime. Our mean-field calculation for the t-U-J model gives a good account for the doping evolution of the Fermi surface as well as the staggered magnetization. It sheds light on the further understanding of high-T_c superconductivity.

ACKNOWLEDGMENTS

We wish to thank N. P. Armitage and N. L. Wang for providing the ARPES and infrared conductivity data shown in Fig. 1. Support from the NSFC and the national program for basic research of China is acknowledged. The Stanford work was supported by Office of Science, Division of Materials Science, DOE under Contract No. DE-AC02-76SF00515.

[1] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).
[2] 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).
[3] H. G. Luo and T. Xiang, Phys. Rev. Lett. **94**, 027001 (2005).
[4] C. Kusko, R. S. Markiewicz, M. Lindroos, and A. Bansil, Phys. Rev. B **66**, 140513(R) (2002).
[5] H. Kusunose and T. M. Rice, Phys. Rev. Lett. **91**, 186407 (2003).
[6] D. Sénéchal and A.-M. S. Tremblay, Phys. Rev. Lett. **92**, 126401 (2004).
[7] Y. Onose, Y. Taguchi, K. Ishizaka, and Y. Tokura, Phys. Rev. Lett. **87**, 217001 (2001).
[8] N. L. Wang, G. Li, D. Wu, X. H. Chen, C. H. Wang, and H. Ding, Phys. Rev. B **73**, 184502 (2006).
[9] H. Matsui, K. Terashima, T. Sato, T. Takahashi, S. C. Wang, H. B. Yang, H. Ding, T. Uefuji, and K. Yamada, Phys. Rev. Lett. **94**, 047005 (2005).
[10] K. M. Shen, F. Ronning, D. H. Lu, W. S. Lee, N. J. C. Ingle, W. Meevasana, F. Baumberger, A. Damascelli, N. P. Armitage, L. L. Miller, Y. Kohsaka, M. Azuma, M. Takano, H. Takagi, and Z. X. Shen, Phys. Rev. Lett. **93**, 267002 (2004).
[11] O. Rösch, O. Gunnarsson, X. J. Zhou, T. Yoshida, T. Sasagawa, A. Fujimori, Z. Hussain, Z.-X. Shen, and S. Uchida, Phys. Rev. Lett. **95**, 227002 (2005).
[12] A. S. Mishchenko, N. Nagaosa, Z.-X. Shen, G. De Filippis, V. Cataudella, T. P. Devereaux, C. Bernhard, K. W. Kim, and J. Zaanen, Phys. Rev. Lett. **100**, 166401 (2008).
[13] Y. Y. Wang, F. C. Zhang, V. P. Dravid, K. K. Ng, M. V. Klein, S. E. Schnatterly, and L. L. Miller, Phys. Rev. Lett. **77**, 1809 (1996).
[14] S. Ono, S. Komiya, and Y. Ando, Phys. Rev. B **75**, 024515 (2007).
[15] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).

[16] C. M. Varma, Phys. Rev. B **73**, 155113 (2006).
[17] A two-specie *t-J* model with equal $+e$ and $-e$ charge carriers but without hybridization was proposed by G. Baskaran, arXiv:cond-mat/0505509 (unpublished).
[18] S. Daul, D. J. Scalapino, and S. R. White, Phys. Rev. Lett. **84**, 4188 (2000).
[19] F. C. Zhang, Phys. Rev. Lett. **90**, 207002 (2003); R. Laughlin, arXiv:cond-mat/0209269 (unpublished).
[20] P. K. Mang, O. P. Vajk, A. Arvanitaki, J. W. Lynn, and M. Greven, Phys. Rev. Lett. **93**, 027002 (2004).
[21] M. J. Rosseinsky, K. Prassides, and P. Day, Inorg. Chem. **30**, 2680 (1991).
[22] M. Matsuda, K. Yamada, K. Kakurai, H. Kadowaki, T. R. Thurston, Y. Endoh, Y. Hidaka, R. J. Birgeneau, M. A. Kastner, P. M. Gehring, A. H. Moudden, and G. Shirane, Phys. Rev. B **42**, 10098 (1990).
[23] The staggered magnetization m is determined by multiplying the value of $m(x)/m(0)$ given in Ref. 20 with the staggered magnetization at zero doping, $m(0)=0.4$, given in Ref. 22.
[24] Q. Yuan, Y. Chen, T. K. Lee, and C. S. Ting, Phys. Rev. B **69**, 214523 (2004).
[25] X. Z. Yan and C. S. Ting, Phys. Rev. Lett. **97**, 067001 (2006).
[26] Y. Dagan, M. M. Qazilbash, C. P. Hill, V. N. Kulkarni, and R. L. Greene, Phys. Rev. Lett. **92**, 167001 (2004).