# SPIN-ORBITAL MODELS AND d-d EXCITONS IN DOPED MOTT–HUBBARD INSULATORS*

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*(Received January 29, 1993)*

Using the example of high temperature superconductors, we show that in the strongly correlated multiband Hubbard model the low energy excitations may be described by an effective spin-orbital model. The Hund's rule exchange interaction leads to a competition between different possible magnetic order in the ground state. In a doped material this competion is additionally enhanced by the differences in the kinetic energies which leads to the formation of three-particle bound states. Superconducting ground state may be then stabilized by the exchange of $d$–$d$ excitons.

PACS numbers: 74.72. -h, 64.60. -i, 05.90. +m, 71.27. +a

## 1. Introduction

In spite of the fact that the High Temperature Superconducting Oxides (HTSO) have been discovered already over six years ago [1], there is still no consensus concerning the minimal theoretical model which describes the essential physics. It is well known that the $CuO_2$ planes are the common structural element of all Cu-based HTSO and thus one is interested in

* Presented at the V Symposium on Statistical Physics, Zakopane, Poland, September 21-30, 1992.

describing the electronic structure of these planes. The band structure calculations [2] suggest that the three-band Hubbard model [3] reproduces correctly the relevant part of the band structure in the insulating compounds, like $La_2CuO_4$ and $YBa_2Cu_3O_6$. As the holes are strongly correlated at the Cu sites [4, 5], the low-energy excitations in a doped insulator may be described by the effective spin-fermion model [6], where the conventional hole doping of the above compounds to $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{6+x}$, respectively, leads to the formation of the local states, the so-called Zhang–Rice singlets [7]. Therefore, the situation resembles the strongly correlated Hubbard model near half-filling and may be described by the $t$–$J$ model [8]. The propagation of holes in such a model happens due to their coupling to quantum fluctuations which results in a new energy scale of the order of the exchange interaction, $J$, for the hole quasiparticles [9].

The above scenario sounds very simple and attractive, but there are serious and accumulating theoretical arguments that the real situation within the $CuO_2$ planes of HTSO is more complex. Calculations aiming at a realistic description of the electronic structure indicate that more orbitals are involved in accommodating the holes than those considered in the three--band model of Varma, Schmitt-Rink and Abrahams [3]. The analysis of the experimental data in terms of the ionic model [10] allowed to establish the existing correlation between the maximal values of the transition temperatures in the HTSO, $T_c^{\max}$, and the positions of the atomic levels of the oxygen ions in apical positions. This naturally suggests that the $Cu(3d_{3z^2-r^2})$ states should play as well an important role in the doped systems, as the sizable number of doped holes is accommodated in the $a_1$ symmetry [11]. Indeed, polarized X-ray absorption spectroscopy (XAS) [12] and electron-energy-loss spectroscopy (EELS) [13] show that hole occupancy of the $3d_{3z^2-r^2}$ orbitals amounts to $\sim 10\%$ in the doped materials. These experimental results are in good agreement with the direct analysis of the ground states obtained from the multiband Hubbard models which include explicitly the $Cu(3d_{3z^2-r^2})$ orbitals by using mean-field approaches to the strongly-correlated periodic models (local ansatz [5] and slave boson [14]), by correcting the Hartree–Fock state by the configuration interaction method [15], and by the exact diagonalization of finite clusters [16].

Excitonic mechanism of pairing due to the intersite Coulomb interaction between Cu and O ions in HTSO has been proposed already by Varma, Schmitt-Rink and Abrahams [3]. According to this idea, the doped holes, which occupy mainly the oxygen orbitals in $CuO_2$ planes for realistic parameters [2, 5–7, 14–16], attract each other for sufficiently strong intersite Coulomb interaction, $U_{dp}$ [17]. However, the realistic value of the intersite repulsion, $U_{dp} \simeq 1$eV [18, 19], is too low to explain the observed superconductivity by this mechanism. Potential importance of the $3d_{3z^2-r^2}$ orbitals

for the miscroscopic mechanism of paring in the HTSO has been emphasized by Weber [20], who proposed that the difference in intersite Coulomb interactions between the holes within Cu($3d_{x^2-y^2}$) and O($2p_{x(y)}$), and the holes within Cu($3d_{3z^2-3^2}$) and O($2p_{x(y)}$) orbitals may promote local *d-d* excitations and lead to the pairing of doped holes. The analysis of the *d-d* excitonic model performed by using weak-coupling Bardeen–Cooper–Schrieffer (BCS) formalism showed that, in agreement with experiment, superconductivity of *s*-wave symmetry is indeed stable for low doping, while *d*-wave symmetry is favoured for higher dopings [21]. This model has been next reformulated in terms of localized quadrupolar fluctuations on the copper sites, promoting the pairing of *d*-wave symmetry already at low doping [22].

All the above excitonic mechanisms have concentrated on the Coulomb interactions being an immediate reason for the effective pairing interaction. In what follows we want to concentrate on another, not yet discussed possibility, that *d-d* excitons, and possibly also attractive interactions in HTSO, may originate from purely kinetic energy terms. Therefore, we consider below (in Sec. 2) an effective spin-orbital model derived earlier from the four-band model for the undoped system [23]. The motion of doped holes in $CuO_2$ planes may be then studied by considering their coupling to the spins in an effective model of *t–J* variety. As discussed elsewhere [24], the possibility of local triplet states leads in such a model to a more complex analytic structure of the one-particle Green function. Instead of solving directly this complicated problem, we focus ourselves in Sec. 3 on the energetics of charge order in an effective model which neglects spins and show that *d–d* excitons occur in the doped systems due to the increase of kinetic energy. They may lead either to phase separation or to superconductivity in the intermediate regime of parameters. In Sec. 4 we point out that the presented model and its analysis are representative for a whole class of doped Mott–Hubbard insulators.

## 2. Spin-orbital model for $d^9$ configuration in $CuO_2$ plane

The commonly used three-band model for $CuO_2$ planes of HTSO [3] includes the Cu($3d_{x^2-y^2}$) and O($2p_{x(y)}$) orbitals. Here we extend this model by the Cu($3d_{3z^2-r^2}$) orbitals, in agreement with the evidence discussed above that these states are important in HTSO given above [10–16]. Thus, we start from the four-band model, analyzed first in Ref. [4],

$$H = H_0 + H_{\rm int}\,, \tag{1}$$

where $H_0$ describes the one-particle part,

$$H_0 = \sum_{m\alpha\sigma} \varepsilon_\alpha n_{m\alpha,\sigma} + \sum_{i\sigma} \varepsilon_p n_{i,\sigma} + \sum_{mi\alpha\sigma} V_{mi,\alpha}(d^\dagger_{m\alpha,\sigma} a_{i,\sigma} + \text{H.c.})\,, \tag{2}$$

and $H_{\rm int}$ describes the on-site electron-electron interactions on Cu ions in the form being rotationally invariant in the orbital space [25],

$$H_{\rm int} = (U + 2J_H) \sum_{m\alpha} n_{m\alpha,\uparrow} n_{m\alpha,\downarrow} + U \sum_{m\sigma} n_{mx,\sigma} n_{mz,-\sigma}$$
$$+(U - J_H) \sum_{m\sigma} n_{mx,\sigma} n_{mz,\sigma} - \tfrac{1}{2} J_H \sum_{\sigma} d^{\dagger}_{ix,\sigma} d_{ix,-\sigma} d^{\dagger}_{iz,-\sigma} d_{iz,\sigma} \,. \quad (3)$$

Here $d^{\dagger}_{m\alpha,\sigma}$ and $a^{\dagger}_{i,\sigma}$ are creation operators of a hole within a $3d_{x^2-y^2}$ for $\alpha = x$ ($3d_{3z^2-r^2}$ for $\alpha = z$) and $2p_{x(y)}$ orbital, respectively. The atomic energies, $\varepsilon_x$ and $\varepsilon_p$ define the charge transfer energy, $\Delta = \varepsilon_p - \varepsilon_x$, while the energy difference between the two $3d$ orbitals defines the energy of a local $d$-$d$ excitation (crystal-field energy), $E_z = \varepsilon_z - \varepsilon_x$. The hopping between the Cu and O orbitals is described by the hybridization elements, $V_{mi,\alpha}$, for $\alpha = x, z$. The values of these elements depend on the chosen phase convention and their absolute values fulfill for the atomic functions the Slater–Koster relation, $|V_{mi,x}| = |V_{mi,x}|/\sqrt{\alpha_0}$, where for the atomic $3d$ wave functions one has $\alpha_0 = 3$ [26]. The one-particle parameters which define the Hamiltonian $H_0$ are shown schematically in Fig. 1, with $t_0 = |V_{mi,x}|$. We describe the electron-electron interactions by two parameters at Cu sites: the on-site Coulomb interaction, $U$, and the exchange interaction, $J_H$. The value of the intraorbital Coulomb repulsion, $U + 2J_H$, is related to the intersite Coulomb and exchange elements due to the rotational invariance of $H_{\rm int}$ in the orbital space [25]. For simplicity we have ignored in the Hamiltonian (1)–(3) the interoxygen hopping ($t_{pp}$), as well as the Coulomb interactions on the oxygen ions ($U_p$) and between the holes on Cu and O sites ($U_{dp}$) [14, 19]. These elements could in principle be included, but they complicate the analytic treatment and do not influence the qualitative analysis of the model in the strong coupling limit presented below.

Physical properties of a charge-transfer system described by the Hamiltonian (1)–(3) and filled by one hole per unit cell, as $CuO_2$ plane, depend on the parameters. One expects that if one of the characteristic parameters for transition metal oxides: either Coulomb interaction, $U$, or the charge transfer energy, $\Delta$, is small, the system is metallic and otherwise is an insulator [27]. The realistic parameters which describe the $CuO_2$ planes in HTSO: $\Delta = 3.6$eV, $U = 10$eV, $t_0 = 1.3$eV [18, 19], suggest that the holes localize to a large extent at Cu sites in the undoped system. Indeed, the direct calculation of the charge distribution gives that $\sim 60 - 70\%$ of the holes in the undoped systems is within the $3d_{x^2-y^2}$ orbitals, while the remaining $\sim 30 - 40\%$ distribute over the $2p_{x(y)}$ and, to some extent as well over the $3d_{3z^2-r^2}$ orbitals [5, 14–16]. One finds as well that the undoped systems are antiferromagnetic insulators of the charge-transfer type [28], using the

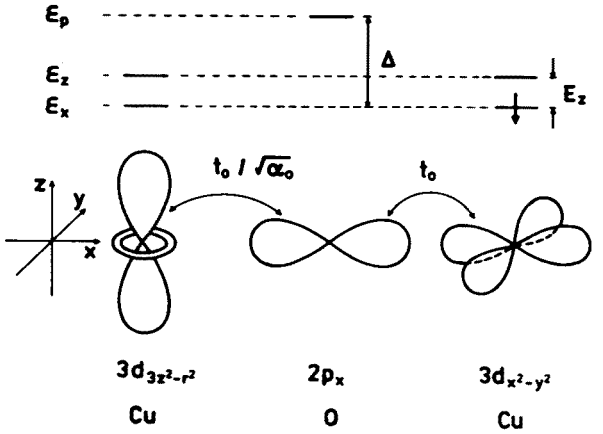


Fig. 1. Schematic representation of the electronic structure parameters which describe atomic orbitals: Cu($d_{x^2-y^2}$), Cu($d_{3z^2-r^2}$), and O($2p_{x(y)}$), in the four-band model given in Eqs (1)–(3) for a $CuO_2$ plane in HTSO. The hopping between the $d_{3z^2-r^2}$ and $2p_{x(y)}$ atomic functions is reduced by a factor $\sqrt{\alpha_0}$ with respect to the hopping parameter between the $d_{x^2-y^2}$ and $2p_{x(y)}$ ones, $t_0$. The charge transfer energy and the $d$–$d$ excitation energy are defined as $\Delta$ and $E_z$.

classification of Zaanen, Sawatzky and Allen [27]. It is therefore justified to consider a strongly correlated system described by the Hamiltonian (1)–(3) with $t_0 \ll \Delta$ and $t_0 \ll U$ as representative for the situation within the $CuO_2$ planes of HTSO.

Let us consider a strongly correlated system described by the Hamiltonian (1)–(3), with $t_0 \ll \Delta$ and $t_0 \ll U$, filled by one hole per $CuO_2$ unit. Under these circumstances one may derive the effective Hamiltonian by considering the virtual transitions to the excited states, similarly as it was originally done for the Hubbard [8] and for the three-band model [6]. Although the actual calculation in the realistic situation for $CuO_2$ plane is more complicated, one may imagine this transformation as performed in two steps: (*i*) first the hopping between the Cu orbitals and the oxygen orbitals in intermediate position is transformed away to generate the effective hopping elements between the $3d$ orbitals at Cu sites, and (*ii*) next the transitions to the doubly occupied configurations at Cu sites are considered to derive the effective magnetic interaction. This allows to use strong coupling perturbation theory [29], starting from the two-band Hubbard Hamiltonian. The superexchange magnetic couplings, as well as the interorbital transitions are obtained by transforming away virtual fluctuations to intermediate state: $d_i^9 d_j^9 \rightleftharpoons d_i^8 d_j^{10}$. These transitions are realized by different possible hopping processes between the $d$ orbitals of two neighbouring sites, described by the parameters $t_{xx}$, $t_{xz} = t_{xx}/\sqrt{\alpha_0}$ and $t_{zz} = t_{xx}/\alpha_0$, for

the $x$-$x$, $x$-$z$ and $z$-$z$ hopping, respectively. In this way one finds a rather lengthy effective Hamiltonian, being a generalization of the Hamiltonian derived earlier by Kugel and Khomskii [30] by the terms which result from the difference in the intraorbital and interorbital Coulomb repulsion for the electrons with opposite spins,

$$
\begin{aligned}
H_J =& (2J - J_2) \sum_{<ij>} \Big[ \Big( \vec{S}_{i,xx} + \frac{1}{\alpha_0} \vec{S}_{i,zz} + \frac{(-1)^{\vec{y}\cdot\vec{\delta}}}{\sqrt{\alpha_0}} \vec{S}_{i,xz} \Big) \\
& \cdot \Big( \vec{S}_{j,xx} + \frac{1}{\alpha_0} \vec{S}_{j,zz} + \frac{(-1)^{\vec{y}\cdot\vec{\delta}}}{\sqrt{\alpha_0}} \vec{S}_{j,xz} \Big) \\
& + \frac{1}{\alpha_0^2} (n_{i,-} + (-1)^{\vec{y}\cdot\vec{\delta}} \sqrt{\alpha_0} T_{i,xz})(n_{j,-} + (-1)^{\vec{y}\cdot\vec{\delta}} \sqrt{\alpha_0} T_{j,xz}) \Big] \\
& + \Big[ E_z + z(2J - J_2) \frac{1}{\alpha_0^2} \Big] \sum_i n_{i,-} \\
& + \frac{2J_1}{\alpha_0^2} \sum_{<ij>} \Big[ \Big( \vec{S}_{i,xx} - \vec{S}_{i,zz} + (-1)^{\vec{y}\cdot\vec{\delta}} \sqrt{\alpha_0} \vec{S}_{i,xz} \Big) \\
& \cdot \Big( \vec{S}_{j,xx} - \vec{S}_{j,zz} + (-1)^{\vec{y}\cdot\vec{\delta}} \sqrt{\alpha_0} \vec{S}_{j,xz} \Big) \\
& - 4 \Big( \vec{S}_{i,xx} + \vec{S}_{i,zz} \Big) \cdot \Big( \vec{S}_{j,xx} + \vec{S}_{j,zz} \Big) \\
& + \alpha_0 \Big( n_{i,-} + (-1)^{\vec{y}\cdot\vec{\delta}} \sqrt{\alpha_0} T_{i,xz} \Big) \Big( n_{j,-} + (-1)^{\vec{y}\cdot\vec{\delta}} \sqrt{\alpha_0} T_{j,xz} \Big) \Big] , \qquad (4)
\end{aligned}
$$

where $\delta$ and $\vec{y}$ are the unit vectors which point in the $\vec{i} - \vec{j}$ and $y$-direction, respectively, and $z$ is the number of neighbours ($z = 4$ in D=2). The phase factor $(-1)^{\vec{y}\cdot\vec{\delta}}$ follows from the different signs of the hopping between the $x^2 - y^2$ and $3z^2 - r^2$ orbitals in the $x$ and $y$ direction. $\vec{S}_{i,\alpha\beta}$ are intraorbital and interorbital spin operators, respectively, defined as follows by the fermion operators,

$$S^+_{i,xx} = d^\dagger_{ix\uparrow} d_{ix\downarrow} , \qquad (5a)$$

$$S^+_{i,zz} = d^\dagger_{iz\uparrow} d_{iz\downarrow} , \qquad (5b)$$

$$S^+_{i,xz} = d^\dagger_{ix\uparrow} d_{iz\downarrow} + d^\dagger_{iz\uparrow} d_{ix\downarrow} , \qquad (5c)$$

$$S^z_{i,xx} = \tfrac{1}{2} (n_{ix\uparrow} - n_{ix\downarrow}) , \qquad (6a)$$

$$S^z_{i,zz} = \tfrac{1}{2} (n_{iz\uparrow} - n_{iz\downarrow}) , \qquad (6b)$$

$$S^z_{i,xz} = \tfrac{1}{2} (d^\dagger_{ix\uparrow} d_{iz\uparrow} + d^\dagger_{iz\uparrow} d_{ix\uparrow} - d^\dagger_{ix\downarrow} d_{iz\downarrow} - d^\dagger_{iz\downarrow} d_{ix\downarrow}) . \qquad (6c)$$

They fulfill the usual spin commutation relations,

$$[S_i^\mu, S_j^\nu] = i\,\delta_{ij}\epsilon_{\mu\nu\xi}S_i^\xi\,. \tag{7}$$

The remaining operators are spin-independent and express the asymmetry in the hole distribution over $x$ and $z$ orbitals, and the mixing between the two orbitals, respectively,

$$n_{i,-} = \tfrac{1}{2}\left(d^\dagger_{ix\uparrow}d_{ix\uparrow} + d^\dagger_{ix\downarrow}d_{ix\downarrow} - d^\dagger_{iz\uparrow}d_{iz\uparrow} - d^\dagger_{iz\downarrow}d_{iz\downarrow}\right), \tag{8a}$$

$$T_{i,xz} = \tfrac{1}{2}\left(d^\dagger_{ix\uparrow}d_{iz\uparrow} + d^\dagger_{ix\downarrow}d_{iz\downarrow} + d^\dagger_{iz\uparrow}d_{ix\uparrow} + d^\dagger_{iz\downarrow}d_{ix\downarrow}\right). \tag{8b}$$

The superexchange interaction, $J$, and the coefficients in the correction terms, $J_1$ and $J_2$, are given as follows,

$$J = \frac{t_{xx}^2}{U}\,, \tag{9a}$$

$$J_1 = \tfrac{1}{2}\frac{J_H}{U}(1 - \frac{J_H}{U})^{-1}\,, \tag{9b}$$

$$J_2 = \tfrac{1}{2}\frac{J_H}{U}(1 + \frac{2J_H}{U})^{-1}\,. \tag{9c}$$

The correction terms arise from the splitting between the triplet and singlet states in the intermediate $d^8$ configuration and are linear in $J_H/U$ for large Coulomb interaction, $U$. We note that the Hamiltonian (4) contains in the leading order, $\sim J$, two terms: the superexchange interaction and the orbital interaction. For convenience, the energy origin has been chosen at $E_z/2$ which gives the energies of $\mp E_z/2$ for a hole occupying the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ level, respectively.

A qualitative information about the possible ground states of the model Hamiltonian (4) may be obtained by solving the classical problem in the mean-field approximation (MFA), where we neglect the terms which contain the $S^+_{i,\alpha\beta}$ operators (5a)–(5c). As the spin and orbital degrees of freedom decouple in the MFA, it is convenient to introduce the mixed representation,

$$c^\dagger_{i\sigma} = \cos(\theta_i)d^\dagger_{ix,\sigma} + \sin(\theta_i)d^\dagger_{iz,\sigma}\,. \tag{10}$$

The most general two-sublattice solution is obtained by assuming the same angles in Eq. (10) for the two sublattices, $\theta_i = \theta_A$ if $i \in A$, and $\theta_i = \theta_B$ if $i \in B$. From the form of the Hamiltonian (4) (with $J > 0$) one expects the antiferromagnetic (AF) Néel order. It may be easily shown that the AF states are of pure $d_{x^2-y^2}$ or $d_{3z^2-r^2}$ character with the energies normalized per site:

$$E_{\rm AF}(x) = -\tfrac{1}{2}E_z - \frac{2}{\alpha_0}(2J - J_2) + \frac{2}{\alpha_0}J_1\,, \tag{11}$$

$$E_{\rm AF}(z) = \tfrac{1}{2}E_z + \frac{2}{\alpha_0^2}(2J - J_2) + \frac{2}{\alpha_0}J_1\,. \tag{12}$$

As a consequence of the reduced hopping between the $d_{3z^2-r^2}$ orbitals with respect to the $d_{x^2-y^2}$ ones (see Fig. 1), the AF order of $x^2-y^2$ symmetry is stable even for $E_z < 0$. A transition from the $x^2-y^2$ to $3z^2-r^2$ AF state occurs for $J_H = 0$ only at $E_z = -16J/\alpha_0^2$. One finds therefore that the AF order suppresses the orbital ordering [23]. The reason is the term with alternating phases in the $x$ and $y$ directions which cancels the coupling between the average orbital and spin fields in the MFA. The situation is reversed, however, for the ferromagnetic (F) spin order. Here one finds that the AF orbital order with the alternating phases for the two sublattices in Eq. (10), $\theta_A = -\theta_B$, is the most stable phase for $J_H > 0$ and close to the transition line between the AF states in the $x^2-y^2$ and $3z^2-r^2$ orbitals. The optimal mixing of the two orbitals in the F phase is determined by the condition

$$\cos(2\theta_A) = \frac{\alpha_0^2 \frac{E_z}{K} + 2 - \frac{1}{4}(\alpha_0^2-1)}{\frac{1}{4}(\alpha_0+1)^2 + (\alpha_0+1) + (\alpha_0^2+\alpha_0+2)\frac{K_1}{K}}, \tag{13}$$

where $K = 2(2J - J_2)$ and $K_1 = 4J_1$ for the square lattice. The energy (normalized per one site) of the F phase with AF orbital order is given by,

$$\begin{aligned} E_{\rm F}(AFO) = &-\left(\frac{1}{2}E_z + \frac{1}{\alpha_0^2}K\right)\cos(2\theta_A) \\ &+ \tfrac{1}{16}K\left\{\left[\left(1-\frac{1}{\alpha_0}\right) + \left(1+\frac{1}{\alpha_0}\right)\cos(2\theta_A)\right]^2\right. \\ &\left. + 4\frac{1}{\alpha_0^2}\left[(1+\alpha_0)\cos^2(2\theta_A) - \alpha_0\right]\right\} \\ &+ \tfrac{1}{4}K_1\left[\frac{1}{\alpha_0^2}(2\cos^2(2\theta_A)-5) + \left(1+\frac{1}{\alpha_0}\right)\cos^2(2\theta_A) - 1\right]. \end{aligned} \tag{14}$$

For $\alpha_0 = 3$, $J_H = 0$ and $E_z = -16J/9$ one finds that the energy of the F phase is degenerate with that of the AF phases and $\cos(2\theta_A) = -0.5$. Thus, at this point one gains the same amount of energy by the mixing of orbitals due to the alternating phases as the loss of the magnetic energy due to reversing the spins from the AF to F configuration. The phase diagram of the spin-orbital model (4) is presented in Fig. 2. The region of stability of the F phase increases with the increasing value of $J_H/U$. Due to the alternating phases on the two sublattices, one finds larger lobes and, consequently, stronger bonds, in the $x$ and $y$ directions for the transition metal ions on $A$ and $B$ sublattice, respectively [24]. Therefore, a quadrupolar distortion is stabilized in this phase. In fact, similar arguments were used on a more qualitative level by Kugel and Khomskii [31] who predicted the existence of

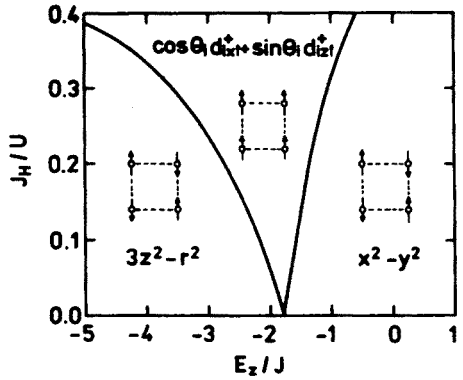


Fig. 2. Phase diagram of the model Hamiltonian (4) found in the mean-field approximation, as a function of the $d$–$d$ excitation energy, $E_z/J$, and the Hund's rule exchange interaction, $J_H/U$. The ferromagnetic quadrupolar phase with the local occupancies of $\cos(\theta_i)d^\dagger_{ix,\uparrow} + \sin(\theta_i)d^\dagger_{iz,\uparrow}$, is stable between the pure $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ antiferromagnetic Néel states.

such a structural distortion in the quasi-2D F compound, $K_2CuF_4$. Later such a phase was indeed detected experimentally [32].

The elementary excitations of the different classical ground states may be investigated by making a Random Phase Approximation (RPA) in the respective equations of motion for the transverse Green functions [33] $<< S^+_{i,\alpha\beta} | S^-_{j,xx} >>$. Such a calculation allows to demonstrate that the *magnons* for the spin-orbital model (4) have a mixed spin-orbital character. The increased number of degrees of freedom causes larger quantum corrections to the energy of the ground state that those found for the standard Heisenberg Hamiltonian in D=2 dimensions. More details may be found in Refs [23] and [33].

## 3. Triplet $t$–$J$ model and $d$–$d$ excitons in doped $CuO_2$ plane

Theoretical understanding of the doped Mott–Hubbard insulators is a challenging problem. The simplest and generic way of approaching its solution is by considering the well known $t$–$J$ model [8], intensely studied in recent years. The essential limitation of the $t$–$J$ model is the use of the single nondegenerate band. Therefore, the motion of doped holes is confined to a single $d$ orbital and each moving hole may be dressed only by low-energy spin excitations. In reality, however, the holes moving in the transition metal oxides may be as well excited to the higher energy $d$-orbital states. Consider as an example the case of a high temperature superconductor. As the energy of the $d$–$d$ excitation, $E_z = 0.5$eV [19], is lower than the typical

bandwidth at finite doping, such excitations are likely to be excited by the hopping of doped holes. It is straightforward to see from Fig. 1 that the kinetic energy is larger for the holes within the $d_{x^2-y^2}$ orbitals and the hopping Hamiltonian may be written in the generic form,

$$H_t^0 = t_x \sum_{<ij>,\sigma} \left[ d^\dagger_{ix,\sigma} d_{jx,\sigma} + \frac{1}{\sqrt{\alpha_0}} (d^\dagger_{ix,\sigma} d_{jz,\sigma} + d^\dagger_{iz,\sigma} d_{jx,\sigma}) + \frac{1}{\alpha_0} d^\dagger_{iz,\sigma} d_{jz,\sigma} \right], \tag{15}$$

where $t_{xx} = t_x$. This expression, however, does not include the dependence of the actual hopping process on the symmetry of the initial and final states formed locally before and after the considered hopping which makes the dynamics of holes more even complex, as we present below.

We want to consider the case where the hole doping of the Mott–Hubbard, or charge-transfer insulator in the $d^9$ limit leads locally to the formation of triplet states, stabilized by the Hund's rule exchange interaction, $J_H$. These triplet states may propagate by virtual transitions via the oxygen orbitals in intermetallic positions in the $CuO_2$ planes. The hopping elements for the $d_{x^2-y^2} - p_{x(y)}$ and $d_{3z^2-r^2} - p_{x(y)}$ terms differ by a factor of $\sqrt{\alpha_0}$ discussed above. Let us assume that Cu site, $i$, is occupied by a triplet $|s + 1/2, m_1\rangle$, while the neighboring site, $j$, is occupied by one of the $d^9$ states, $|s, m_2\rangle$. As a result of two consecutive hoppings via the intermediate oxygen orbital, the configuration changes to $|s, m_1 - 1/2\rangle$ ($|s, m_1 + 1/2\rangle$) and $|s + 1/2, m_2 + 1/2\rangle$ ($|s + 1/2, m_2 - 1/2\rangle$) at sites $i$ and $j$, respectively. Thus, compared to the singlet hole in the $t$–$J$ model, there are more possibilities for the hopping which reflect the new internal degree of freedom of the triplet hole. The hopping amplitudes may be easily constructed from the overlaps of the states at sites $i$ and $j$ before and after the hopping and are given by Clebsch–Gordan coefficients. It is convenient to represent the triplet holes as products of SU(3) Schwinger bosons, $a^\dagger_{im}$, and auxiliary fermions, $h^\dagger_i$. They represent the internal spin degree of freedom, $m_i = 1, 0, -1$, and the charge of doped hole, respectively, in analogy to the singlet holes in the $t$–$J$ model [34]. The $s = 1/2$ spin background may be realized in two ways, if either $d_{x^2-y^2}$ or $d_{3z^2-r^2}$ orbitals are occupied. This may be represented by the SU(2) Schwinger bosons which occur now in two flavours, $b^\dagger_{ix,m}$ and $b^\dagger_{iz,m}$. Altogether, we may write the following hopping Hamiltonian for triplet holes in the $d^9$ background,

$$H_t = \frac{t}{2} \sum_{\vec{i},\vec{\delta}} \sum_{m,n=-1/2}^{1/2} \left\{ \left( b^\dagger_{\vec{i}+\vec{\delta},z,n} + \frac{(-1)^{\vec{\delta}\cdot\vec{y}}}{\sqrt{\alpha_0}} b^\dagger_{\vec{i}+\vec{\delta},x,n} \right) \right.$$
$$\left. \times \left[ \sum_{\pm} \sqrt{(3/2 \pm m)(3/2 \pm n)}\, a^\dagger_{\vec{i},m\pm 1/2}\, a_{\vec{i}+\vec{\delta},n\pm 1/2} \right] \right.$$

$$\times \left( b_{\vec{i},z,n} + \frac{(-1)^{\vec{\delta}\cdot\vec{y}}}{\sqrt{\alpha_0}} b_{\vec{i},x,n} \right) h_{\vec{i}} h^{\dagger}_{\vec{i}+\vec{\delta}} + \text{H.c.} \Big\} . \tag{16}$$

By adding this Hamiltonian to the spin-orbital model Hamiltonian derived in Sec. 2, one obtains the generalized $t$–$J$ model for the triplet hole, including the crystal field excitation [24],

$$H_{t-J} = H_t + H_J . \tag{17}$$

This forms a complicated many body problem and so far only the limiting case of the motion of a single triplet hole in the AF background stable within the $d_{x^2-y^2}$ orbitals, *i.e.* the projection of the full problem to the lowest energy manifold, has been studied [24]. The main qualitative difference between the present problem (17) and the singlet $t$–$J$ model, which may be formally obtained by projecting the effective magnetic Hamiltonian of Sec. 2, $H_J$ of Eq. (4), and the generic hopping Hamiltonian, $H_t^0$ of Eq. (15), to the $d_{x^2-y^2}$ subspace, lies in the possibility of free triplet hole propagation, without disturbing the magnetic order. This free dispersion is reduced by the factor of $1/\sqrt{2}$ with respect to the free fermion dispersion, $\sim \varepsilon_{\vec{k}}$, which results from the overlap factor between initial and final states before and after the hopping of the triplet hole. We have found that this dispersion is strongly renormalized by the coupling of holes to the spin-waves in the AF background of $x^2 - y^2$ symmetry which gives finite lifetime to the quasiparticle poles. As a result of this coupling, the spectral function found in the selfconsistent Born approximation [34] has distinct peaks which resemble the original dispersion, but even the lowest energy quasiparticle has finite lifetime, *i.e.* Fermi liquid behaviour breaks down [24]. Therefore, perturbation theory is divergent for the triplet hole problem.

The above $t$–$J$ model (17) is exceedingly complicated. Although the single-hole problem in the quantum antiferromagnet, described by the standard (singlet) $t$–$J$ model, may be successfully treated by solving the linear spin-wave theory and finding the spectral density by the selfconsistent Born approximation for the hole-magnon couplings [35], there are no standard methods of treating the finite hole density problem, and, as discussed above, for the single triplet hole even the perturbation theory breaks down. Therefore, it is instructive to look at a simplified model which deals only with the charge degrees of freedom and ignores entirely the spin dependences in the hopping problem. The possible hopping processes in such a model are shown in Fig. 3 (a). They correspond to the respective hoppings in the full model which includes the spin variables, as presented in Fig. 3 (b). Since $J \ll E_z$ and $J \ll t$ for the typical situation, as for the holes in $CuO_2$ planes of HTSO with $J \simeq 0.12$eV, $E_z \simeq 0.5$eV, and $t \simeq 0.4$eV [18–20], one may expect that such a simplified model will still capture the essential dependence

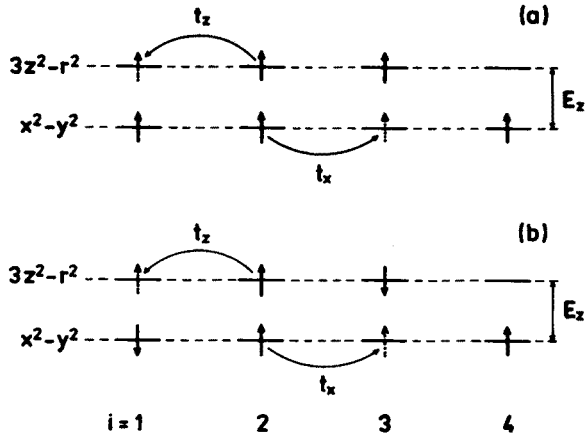


Fig. 3. Schematic representation of the spinless model given by Eq. (18) which represents the dynamics of a doped hole in $CuO_2$ plane (a): the local triplet on the site $i = 2$ may hop either to site $i = 3$ with a preexisting $d$–$d$ exciton with amplitude $t_x$, or to site $i = 1$ with amplitude $t_z = t_x/\alpha_0$. The same transitions are possible as well in the realistic antiferromagnetic state in $d_{x^2-y^2}$ (b), but the presence of low-energy spin excitations complicates the mathematical analysis.

of the determined ground state on the orbital degrees of freedom, while the lower-energy spin excitations could change this picture only quantitatively. The spinless model which corresponds to the full generalized $t$–$J$ model (17) is,

$$H = t\sum_{i\vec{\delta}}\left(b_{iz} + \frac{(-1)^{\vec{\delta}\cdot\vec{y}}}{\sqrt{\alpha_0}}b_{ix}\right) f_i^\dagger f_{i+\vec{\delta}}\left(b^\dagger_{i+\vec{\delta},z} + \frac{(-1)^{\vec{\delta}\cdot\vec{y}}}{\sqrt{\alpha_0}}b^\dagger_{i+\vec{\delta},x}\right)$$
$$+E_z\sum_i b^\dagger_{iz}b_{iz} + \sum_i \lambda_i\Big(\sum_{\xi=x,z} b^\dagger_{i\xi}b_{i\xi} + f_i^\dagger f_i - 1\Big), \qquad (18)$$

where $b^\dagger_{ix}$ and $b^\dagger_{iz}$ are Schwinger bosons which represent the orbital degrees of freedom and $\lambda_i$ are Langrange multipliers to enforce the local constraint. Hence, we neglect all spin dependences in the hopping and consider only the orbital dependence. Further, we assume that the spectrum of orbital excitations can be modelled by a single oscillator. Hamiltonian presented in Eq. (18) may be solved in the MFA for a strongly correlated system by applying the slave-boson MFA of the Newns and Read variety [36]. It is obtained by replacing the Schwinger boson operators, $b^\dagger_{i\xi}$ and $b_{i\xi}$ by scalars $\langle b\rangle$, and taking a global ($\lambda$) instead of a local constraint ($\lambda_i$). For this

uniform distribution of the average boson fields we obtain a MF free energy,

$$\mathcal{F}_{\rm MF} = \eta^2 b^2 E_z + \lambda(b^2(1+\eta^2)-1) - \frac{1}{\beta}\int \frac{d^2k}{(2\pi)^2}\ln(1+{\rm e}^{-\beta E_{\vec{k}}}), \quad (19)$$

where $E_{\vec{k}}$ are the excitation energies,

$$E_{\vec{k}} = \lambda + zt^2 b^2 \left[(\eta^2 + \frac{1}{\alpha_0})\gamma_{\vec{k}} + \frac{2\eta}{\sqrt{\alpha_0}}\gamma^-_{\vec{k}}\right]. \quad (20)$$

In Eqs (19) and (20) we used the parametrization: $\langle b_x\rangle = b$, $\langle b_z\rangle = \eta b$, and $\gamma_{\vec{k}} = \frac{1}{z}\sum_{\vec{\delta}}\exp(-i\vec{k}\cdot\vec{\delta})$ and $\gamma^-_{\vec{k}} = (1/z)\sum_{\vec{\delta}}(-1)^{\vec{y}\cdot\vec{\delta}}\exp(-i\vec{k}\cdot\vec{\delta})$ are the structure factor for the 2D lattice, and the structure factor for the hopping with the alternating phase factor, respectively ($z$ is the coordination number). There are three possible saddle points of $\mathcal{F}_{\rm MF}$. Either the holes in the $d^9$ background localize within the $d_{x^2-y^2}$ orbitals, with the free energy at $T=0$

$$\mathcal{F}_{\rm MF} = \frac{1}{\alpha_0}(1-n)E_+, \quad (21)$$

where $n$ is carrier density and $E_+ = (zt/N)\sum^{occ.}_{\vec{k}}\gamma_{\vec{k}}$, or they localize within the $d_{3z^2-r^2}$ orbitals, with the free energy at $T=0$

$$\mathcal{F}_{\rm MF} = (1-n)(E_+ + E_z), \quad (22)$$

or, finally, a mixed state with non-trivial orbital ordering is stabilized. The saddle point equations yield $b^2 = (1-n)/(1+\eta^2)$ and

$$\eta = \frac{-E_-}{\sqrt{\alpha_0}(E_z+\lambda+E_-)}, \quad (23)$$

$$\lambda = -\tfrac{1}{2}\left(\frac{(\alpha_0+1)E_+}{\alpha_0} + E_z + \sqrt{\left(\frac{(\alpha_0+1)E_+}{\alpha_0}+E_z\right)^2 - \frac{4}{\alpha_0}(E_+^2 + E_+E_z - E_-^2)}\right), \quad (24)$$

where $E_- = (zt/N)\sum^{occ.}_{\vec{k}}\gamma^-_{\vec{k}}$ is the new kinetic energy resulting from the orbital mixing. The mechanism of this new kinetic energy contribution is as follows. If the $d^9$ states are mixtures of $x$ and $z$, the hole will hop easier in, *e.g.*, the $x$-direction than in the $y$-direction, if the phasing is uniform. The system now gains energy because the $x \leftrightarrow z$ term in Eq. (18) contributes on average. The Fermi surface gets orthorombically distorted and therefore $E_- \neq 0$ in Eqs (23)–(24). On the other hand, this new state costs kinetic

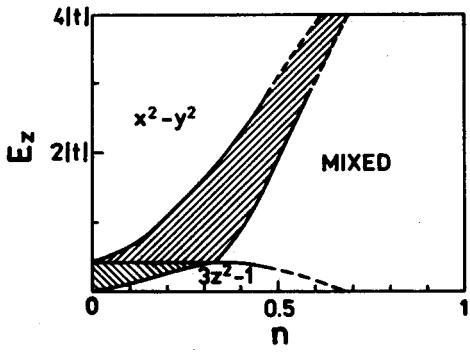


Fig. 4. Mean-field phase diagram for the spinless $d^9$ triplet hole model (18) as a function of the crystal field energy $E_z/|t_x|$ ($t = t_x$), and hole concentration, $n$. The shaded areas indicate regions of phase separation between the pure and mixed phases.

energy in the $x \leftrightarrow x$ and $z \leftrightarrow z$ channels ($E_+$) and, therefore, the orbital mixing can only pay off at some substantial hole concentration.

In Fig. 4 we sketch the phase-diagram as a function of doping, $n$, and crystal-field energy, $E_z/|t|$, using the single band value for $\alpha_0$. This phase diagram has a similar appearance as the one expected for the charge-transfer mechanism of Varma *et al.* [37]. At low doping we find the pure $x^2 - y^2$ phase (but, of course, fluctuations will mix in some finite amount of $3z^2 - r^2$ character). Depending on the actual value of $E_z$, a first-order transition would follow to the mixed-phase (dashed line), but according to the Maxwell construction this is masked by a region of phase separation (shaded area). Obviously, if $E_z/t$ gets smaller, the stability of the mixed phase increases and the opposite holds if $\alpha_0$ gets smaller. We note that the $3z^2-r^2$ character of the background increases relatively little for increasing doping in the region where the mixed-phase is the ground state.

The above effects hint at a possible mechanism for superconductivity. The attractive interaction is now driven by the real increase in kinetic energy of the composite holes if they exchange crystal-field excitations. It may be formally derived from the model Hamiltonian (18) by a canonical transformation which transforms away the orbital excitation. As a result, one finds the familiar BCS (Bardeen–Cooper–Schrieffer) attractive interaction, induced by $d$–$d$ excitons. The interaction is large because it is set by the bandwidth $\sim (\alpha_0 - 1)t/\alpha_0$, and together with the density of states $\sim \alpha_0/t$, we find

$$\lambda = \frac{(\alpha_0 - 1)^2}{\alpha_0} \frac{t}{E_z}, \tag{25}$$

which results in

$$T_c \sim E_z \exp(-1/\lambda)\,, \tag{26}$$

but only for sufficiently high hole doping, *i.e.* if $E_F > E_z$, where $E_F$ is the Fermi energy measured from the bottom of the doped band. This would suggest very high transition temperatures indeed and there could be several reasons to influence the final value of $T_c$ in a particular compound (small polaron effects and structural stability, the effects of the spins, vertex corrections, *etc.*). We would like to emphasize that our mechanism is distinct from those originally suggested for *d–d* excitons, as here the difference in the hopping is the driving force of the pairing, rather than different Coulomb interactions [20, 21], or the interaction between the electric quadrupole moments [22]. Unfortunately, it seems however that there is now firm experimental evidence [38] that the three particle bound states formed by the moving hole an a *d–d* exciton bear no relevance to high $T_c$ superconductivity.

The electronic instability detected in the above spinless model should have pronounced structural consequences. The orbital polarization in the mixed-phase should couple strongly with the lattice [39]. At half-filling, the electron-phonon distortion is of the form,

$$H_{EP} = \sum_{\vec{q}} \left[ K_n(\vec{q}) n_{\vec{q},-}\, n_{-\vec{q},-} + K_t(\vec{q}) T_{\vec{q},xz} T_{-\vec{q},xz} \right], \tag{27}$$

where $K_t(\vec{q} = (\pi, \pi))$ dominates for $CuO_2$ planes in HTSO [39]. Here $n_{\vec{q},-}$ and $T_{-\vec{q},xz}$ are the Fourier transforms of $n_{i,-}$ and $T_{i,xz}$ defined in Eqs (8a) and (8b). Such electron-phonon coupling also tends to favour an orbital mixed phase with the staggered phases, as obtained above for the F state at intermediate *d–d* exciton energy $E_z$. As a result, the purely electronic and electron-phonon interactions act together, causing an orthorombic instability. Thus the electron-phonon coupling amplifies the lattice instability in $K_2CuF_4$. On the contrary, within the $CuO_2$ planes of HTSO one expects a competition between the nondistortive AF states the distortive hole-induced instabilities. Thus, the doping can lead to *quadrupolar* local distortions, where two oxygens move towards, and two away from the Cu atom. With our uniform phasing, these local distortions line up and the crystal as a whole gets orthorombically distorted. It cannot be excluded that the competition with the superexchange and phonon induced couplings (which favour staggered configurations [39]) might give rise to more complicated ordering patterns, involving larger length scales. We wonder if such a theory might underlie the recent structural model proposed for oxygen deficient $YBa_2Cu_3O_{7-x}$ [40]. In fact, the recent neutron scattering data [41] of a variety of HTSO seem to indicate such an instability.

## 4. Discussion and summary

The triplet $t$–$J$ model presented in the previous Section is by no means the only possible model to describe the doped carriers in a Mott–Hubbard insulator. A similar model Hamiltonian may be as well constructed for the doping of Mott–Hubbard insulator in $d^8$ configuration, corresponding to the undoped NiO, or $La_2NiO_4$. As the undoped nickelates are usually high-spin materials, the underlying spin model favours again an AF ordering of the spins $S = 1$ at each site, if the triplets described in Sec. 3 are locally stable against the low-spin singlet configurations, $|x\uparrow, x\downarrow\rangle$. The corresponding superexchange Hamiltonian in the $d^8$ limit is [33],

$$H_J(d^8) = 2J' \sum_{<ij>} \Big[ \left(\vec{S}_i + (-1)^{\vec{\delta}\cdot\vec{y}} \sqrt{\alpha_1}\vec{Z}_i\right) \cdot \left(\vec{S}_j + (-1)^{\vec{\delta}\cdot\vec{y}} \sqrt{\alpha_1}\vec{Z}_j\right) + \alpha_2 n_{i,S} n_{j,S} \Big] + E_S \sum_i n_{i,S} \,, \tag{28}$$

where $\alpha_1$ and $\alpha_2$ are the parameters depending on the geometry of the wave functions forming the bonds. If $\alpha_0 = 3$, as in Fig. 1, $\alpha_1 = {}^3/_8$ and $\alpha_2 = {}^1/_4$, while $J' = 8t^2/9U$. The spin and pseudospin operators, $\vec{S}_i$ and $\vec{Z}_i$, may be written as follows,

$$S_i^+ = \sqrt{2}(B_{i,1}^\dagger B_{i,0} + B_{i,0}^\dagger B_{i,-1}) \,, \tag{29a}$$

$$Z_i^+ = \sqrt{2}(B_{i,1}^\dagger A_i + A_i^\dagger B_{i,-1}) \,, \tag{29b}$$

$$S_i^z = B_{i,1}^\dagger B_{i,1} - B_{i,-1}^\dagger B_{i,-1} \,, \tag{29c}$$

$$Z_i^z = -(A_i^\dagger B_{i,0} + B_{i,0}^\dagger A_i) \,, \tag{29d}$$

where the operators $B_{i,m}^\dagger$ and $A_i^\dagger$ are the creation operators of the $m$-component of the triplet and of the singlet at site $i$, respectively,

$$B_{i,1}^\dagger = d_{ix,\uparrow}^\dagger d_{iz,\uparrow}^\dagger \,, \tag{30a}$$

$$B_{i,0}^\dagger = \frac{1}{\sqrt{2}} \left( d_{ix,\uparrow}^\dagger d_{iz,\downarrow}^\dagger + d_{ix,\downarrow}^\dagger d_{iz,\uparrow}^\dagger \right) \,, \tag{30b}$$

$$B_{i,-1}^\dagger = d_{ix,\downarrow}^\dagger d_{iz,\downarrow}^\dagger \,, \tag{30c}$$

$$A_i^\dagger = d_{ix,\uparrow}^\dagger d_{iz,\downarrow}^\dagger \,. \tag{30d}$$

The triplet-singlet excitation energy is $E_S = J_H - E_z$, using the notation introduced in Sec. 2. The new Hamiltonian (28) gives by itself a very interesting quantum-mechanical problem which may be again studied on the

mean-field level. The obtained phase diagram indicates that a mixed phase of different kind is stable as well in the intermediate parameter regime [33]. Hole doping of such an insulator (to $d^7$ configurations) gives again interesting possibilities and promotes locally the orbital mixing, on the costs of magnetic energy [42]. We believe that local excitonic excitations might be responsible for the virtual disappearance of the Mott–Hubbard gap from the inverse photoemission of doped nickelates, according to more detailed calculations by van Elp *et al.* [43].

The purpose of this paper is to point out that carrier-exciton bound states are in fact quite common in transition metal oxides. In contrast to the charge-transfer three-body bound states [44], the relevant excitons are of the crystal-field variety, while the interaction responsible for the exciton-carrier binding is the atomic Hund's rule interaction, $J_H$. Such states may be considered to be more the rule than the exception in doped Mott–Hubbard insulators. A challenging problem for each realization of the doped Mott–Hubbard insulator is the question how these three-particle bound states may delocalize. We have demonstrated on the example of the cuprates that the delocalization of the carrier-exciton composites leads to additional couplings with the crystal field excitations. A better understanding of these complicated phenomena requires further studies of realistic and complex $t$–$J$ models, which, in our opinion, should provide as well better answers concerning the spectral functions observed in photoemission and inverse photoemission spectroscopies in doped transition metal oxides.

In summary, we have identified previously unknown effects related to the binding of $d$–$d$ excitons to holes in doped Mott–Hubbard insulators. The delocalization of these composite carriers might give rise to a novel kind of Jahn–Teller like structural distortion. Although we concentrated for pedagogical purposes mostly on the cuprates, we argue that these effects should be quite common in doped Mott–Hubbard systems in general.

We thank G.A. Sawatzky, L.F. Feiner, P. Horsch, P.B. Littlewood, S. Schmitt-Rink and J. van Elp for helpful discussions. JZ acknowledges financial support by the Foundation of Fundamental Research on Matter (FOM), which is sponsored by the Netherlands Organization for the Advancement of Pure Research (NWO) and AMO the support by the Committee of Scientific Research (KBN) of Poland, Project No. 2 0386 91 01.

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