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Spin glass behaviors compatible with a Zhang–Rice singlet within an effective model for cuprate superconductors

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Abstract

To address the incompatibility of Zhang–Rice singlet formation and the observed spin glass behavior, an effective model is proposed for the electronic behavior of cuprate materials. The model includes an antiferromagnetic interaction between the spin of the hole in a Zhang–Rice orbital and the spin of the hole on the corresponding copper site. While in the large interaction limit this recovers the t–J model, in the low energy limit the Zhang–Rice singlets are deformed. It is also shown that such deformation can induce random defect ferromagnetic (FM) bonds between adjacent local spins, an effect herein referred to as unusual double exchange, and then spin glass behavior shall result in the case of localized holes. A derivation of the model is also presented.

1. Introduction

An interesting problem in understanding hole-doped cuprate superconductors such as $La_{2-x}Sr_xCuO_4$ is that of the intervening phase, namely the spin glass (SG) between antiferromagnetism (AFM) and superconductivity (SC) in the phase diagrams, with regard to temperature T and doping level x [1]. One impetus for studying SGs is to discover the meaning of the similarity and differences between the phase diagram of hole-doped compounds and that of electron-doped compounds such as $Nd_{2-x}Ce_xCuO_4$ [2]. Perhaps the most remarkable difference just comes from SG, which occur exclusively for hole-doped materials [2]. If all differences have the same origin, then decoding the SG behavior will provide very useful information that may put stringent constraints on the architecture of the microscopic model, which remains controversial. In view of recent experiments aimed at investigating the properties within the low-doping regime [3–5] where SG occurs, it becomes even more urgent to understand the nature of this phase.

Shortly after the original discovery of cuprates, the SG phase transition from AFM was theoretically proposed to happen at low doping levels [6]. Indeed, this transition was later observed experimentally, and it has been used to explain the rapid destruction of AFM upon doping [7]. This proposal assumes that every excess hole is totally localized on a single O site situated between two Cu sites, that is a Cu–O–Cu configuration. Then the spin of such a hole could couple to its neighboring Cu spins simultaneously, and, regardless of the sign of this coupling, an effective ferromagnetic (FM) correlation should develop between these Cu spins [6]. Thus, given randomly distributed localized holes, those effective defect FM bonds should also be randomly spread amid the original host AFM bonds, implying SG transition at certain critical doping levels [6].

The above proposed Cu–O–Cu configurations were once suggested as the correct basis states for describing quasi-particle states of an O hole moving in some FM background [8]. However, this suggestion must be abandoned for several reasons, as stressed by Zhang and Rice in [9]. The most compelling of those reasons is based on an important symmetry that is primarily due to the signs of Cu and O atomic wavefunctions [9]. As a result of this symmetry, only symmetric O states, $P_{i\sigma}$ (see below), which make up half the number of the total O states, couple to Cu spins, while the other half of the O states are non-bonding and hence irrelevant to low energy physics. Therefore, despite its potential in explaining the SG transition, the O-centered Cu–O–Cu basis, which contains all O states and does not differentiate between bonding and non-bonding O states, is inconsistent with such

symmetry considerations [9]. By virtue of this symmetry, only symmetric O states should be present in effective microscopic models. So, an O hole should never be absolutely localized on a single O site within low energy physics[1].

Highlighting this symmetry, Zhang and Rice in their famous work [10] were able to map the triple-band Emery model onto a single-band t–J model. They kept only symmetric O states and found strong AFM interaction between the hole on a symmetric O state and the Cu spin in the same CuO_4 plaquette. They argued that this interaction should drive the O hole to form a singlet with the Cu spin, which is spinless and should behave in the same manner as a doubly occupied Cu site. Thus, as they concluded, a single-band t–J model would suffice for the low energy physics. Such singlets have already been verified experimentally [11].

However, as noticed by some authors [6, 12], in terms of perfect Zhang–Rice singlets (ZRS) the t–J model seems not to be able to reproduce SG behaviors. Actually, had this model been able to do so, SG would also have occurred in electron-doped materials [2] because the t–J model seems even more suitable for electron-doped materials than for hole-doped ones, since in the former the O sites are less complex. Now people tend to believe that the destruction of AFM upon doping occurs in essentially different ways in the two families of cuprates. In the hole-doped family the destruction is accompanied by SG transition, whereas in the electron-doped one it is directly associated with gradual dilution of Cu spins [13]. This dilution can be well understood with the t–J model, assuming holes are localized, which corresponds to infinite $|J/t|$. At the other extreme, with infinite $|t/J|$, one gets freely moving holes. But one can hardly get SG within this context [14].

We are then left with a dilemma: although both SG and ZRS are well established, they seem incompatible. To address this incompatibility, in this paper we claim that ZRS are in fact not perfect but somewhat deformed, primarily due to the requirement of reducing the kinetic energy of doped holes. We show that such deformation can create considerable FM correlations between close Cu spins, and in the case of localized holes SG transition should emerge. Following the widely accepted ideas, we assume that the fundamental physics is obeyed by CuO_2 planes and that every planar Cu site is singly occupied by holes (see figure 1). We work with the hole representation, in which the vacuum is denoted by $|0\rangle \equiv |2p^6 3d^{10}\rangle$. In obtaining a model for our purpose we have been scrupulously guided by the above discussions implying incompatibility between SG and ZRS. Firstly, due to the mentioned symmetry, only symmetric O states should be included to accommodate holes. Secondly, the AFM interaction discovered by Zhang and Rice must be present, and is indispensable in the formation of ZRS. Thirdly, one has to add two terms to account for the motion of excess holes and the AFM order, respectively. Summarizing these conditions,

[1] In fact, for the system studied in [8], a localized state necessitates the presence of all momentum quasi-particle states. However, only the zero momentum state, which obviously respects the said symmetry, can be written as a superposition of all Cu–O–Cu configurations; this is a complete coincidence, because none of the other states can be. Therefore, a localized state cannot be a superposition of Cu–O–Cu configurations. Such superposition cannot even give the correct density of states [9].

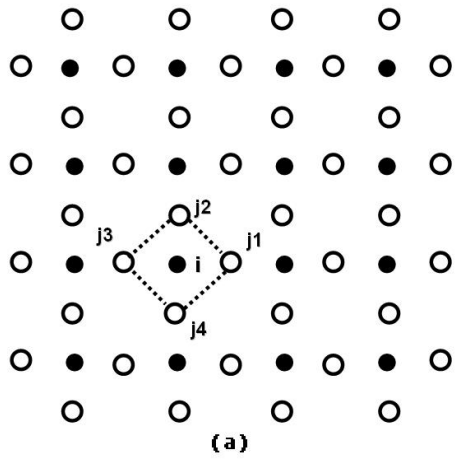

Figure 1. Schematic illustration of the CuO_2 plane: the dotted line encloses a plaquette, filled circles being Cu sites and open ones being O sites, $M_{i;j_1} = M_{i;j_4} = 1$ and $M_{i;j_2} = M_{i;j_3} = 2$. The spacing between two neighboring Cu sites is set to unity. The horizontal unit vector is $\vec{x}$ and the vertical one is $\vec{y}$.

the minimum model may be put as a sum of three terms, that is,

$$H = H_K + H_t + H_J. \tag{1}$$

Explicitly,

$$H_K = K \sum_i S_i \cdot s_i \tag{2}$$

where S_i is the Cu spin on site $\vec{R}_i$ and s_i is the spin operator of O holes. Also,

$$H_t = \sum_{i,i'} t_{ii'} \phi^\dagger_{i\sigma} \phi_{i'\sigma} \tag{3}$$

where $t_{ii'}$ are hopping constants, which, as shown in what follows, are negative for nearest neighbor (nn) pairs and negligible but maybe positive otherwise, and $\phi_{i\sigma}$ are orthogonal symmetric O orbitals (see below). Finally,

$$H_J = J \sum_{\langle i,j \rangle} S_i \cdot S_j \tag{4}$$

where the sum is taken over all nn pairs. In these expressions both K and $J \ll K$ are positive and $s_i = \frac{1}{2} \sum_{\sigma\sigma'} \phi^\dagger_{i\sigma} \tau_{\sigma\sigma'} \phi_{i\sigma'}$, τ being the Pauli matrices. We see that H_K is responsible for ZRS, H_t for the motion of holes and H_J for AFM order. A pictorial illustration of H is given in figure 2.

It is noted that H is double band rather than single band. There is evidence calling for double-band descriptions [15]. This model emerges naturally from the existing facts. Let us also see that this model is actually the same model as was implicitly used by Zhang and Rice to derive the t–J model. They thought that as H_K dominates over other terms, the t–J model could bear all the low energy physics. However, as we have emphasized, the t–J model cannot admit SG. Nonetheless, as the main result of this paper we can show that SG does ensue from H, suggesting that H contains more physics than the t–J model.

Let us try to understand this qualitatively. To this end it is useful to look at an extreme of H. This extreme is taken as

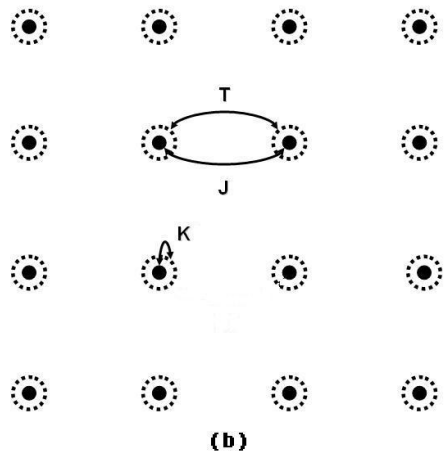

Figure 2. Schematic illustration of the model proposed in the text as H. On each site there is a local spin (filled circle) as well as a ϕ-orbital (dotted circle encircling the filled circle).

$|t/K|$ vanishes. The physics in this limit should be completely determined by H_K, whose eigenstates are just perfect ZRS and corresponding triplets. These triplets are higher in energy than ZRS by K and can be ignored at low temperatures. Therefore, this extreme is equivalent to the Zhang–Rice t–J model. However, at small but finite $|t/K|$, ZRS should no longer be perfect due to perturbation from H_t, which can deform ZRS. It is just this deformation that makes the difference. Roughly, this occurs by a mechanism that is analogous to double exchange (DE) [16–18]. Because of hopping, an O hole can simultaneously couple to several Cu spins, resulting in effective FM alignment of Cu spins. However, in the usual DE the carrier–spin coupling is FM, while in the present case it is AFM. As will be shown below, quantum effects are robust in this case and must be considered. To draw the distinction, we shall use unusual DE (UDE) instead of DE for the present case.

Although we have emphasized the empirical aspects of H, a systematic derivation will be given in section 2. Section 3 is devoted to SG, wherein we shall first show how the problem in the case of localized holes can be reduced to a double-site model, and then we solve this model to clarify UDE. Some discussions shall also be given in this section. In section 4 we give a summary.

2. Deriving the model

In section 1 we argued that the structure of H has been tightly restricted by empirical facts. Here we hope to perform a formal derivation to make H even sounder.

The starting point is the Emery model [19], in which only orbitals that participate in planar σ-bonds are present. This model may be given as

$$\mathcal{H} = \Delta N_p + U\sum_i n_{i\uparrow}n_{i\downarrow} + \sum_{\sigma,i;j}(V_{i;j}d^\dagger_{i\sigma}p_{j\sigma} + \text{h.c.}) \quad (5)$$

where i and j refer to the ith Cu site and the jth O site that is nearest to this Cu site, respectively; p- and d-class operators annihilate O and Cu holes, respectively; and $N_p = \sum_{j\sigma} p^\dagger_{j\sigma}p_{j\sigma}$ and $n_{i\sigma} = d^\dagger_{i\sigma}d_{i\sigma}$. Coefficients in the equation are the charge-transfer gap, Δ, which is the energy cost of moving a hole from Cu to O, the Cu on-site repulsion U and the hopping integral $V_{ij} = V_{ji} = (-1)^{M_{i;j}}V$, V being a constant and $(-1)^{M_{i;j}}$ the pre-factor indicating the phase (figure 1). An energy reference has been chosen in which the on-site Cu energy vanishes. As said, we shall work in a subspace whose states have every Cu site singly occupied. One may deduct the chemical potential μ from Δ to fix the average total number of doped holes. If applied to electron-doped cuprates the Emery model will simply reduce to the t–J model within the said subspace [20]. We shall assume holes sit on Zhang–Rice orbitals. To build these orbitals we have to at first construct for every copper site $\vec{R}_i$ the following two orbitals

$$P^{s/A}_i = (1/2)\left(\left|i;i+\frac{\vec{y}}{2}\right\rangle \pm \left|i;i-\frac{\vec{y}}{2}\right\rangle + \left|i;i-\frac{\vec{x}}{2}\right\rangle \pm \left|i;i+\frac{\vec{x}}{2}\right\rangle\right)$$

where $\vec{x}$ and $\vec{y}$ are basis vectors of the Cu sub-lattice. We see that these two kinds of orbitals, although not orthogonal, can be readily used to span a complete Hilbert space to accommodate O holes, because each O site has only one effective p-orbital (either p_x or p_y) and the total number of planar O orbitals is twice the number of planar Cu sites. The inclusion of spin indices yields $P^{s/A}_{i\sigma} \equiv P^{s/A}_i \otimes |\sigma\rangle$. These orbitals are not mutually orthogonal. However, following Anderson [21], one can construct from them a complete set of normalized orthogonal basis states. To this end, we shall first define the following ϕ^s_i orbitals [10]

$$\phi^s_{i\sigma} = \sum_{i'} \lambda(i'-i)P_{i'\sigma}$$

where

$$\lambda(i'-i) = \frac{1}{N}\sum_k \left[1 - \frac{1}{2}(\cos k_x + \cos k_y)\right]^{-1/2} e^{ik\cdot(R_{i'}-R_i)}$$

is a normalization factor. It is easy to verify their orthogonality. Next, a similar set for P^A can also be obtained as $\phi^A_{i\sigma} = \sum_{i'}\bar{\lambda}(i-i')P^A_{i'\sigma}$, where

$$\bar{\lambda}(i-i') = \frac{1}{N}\sum_k \left[1 + \frac{1}{2}(\cos k_x + \cos k_y)\right]^{-1/2} e^{ik\cdot(R_{i'}-R_i)}.$$

In the above, N is the number of total Cu sites or CuO_2 units, for example. It is useful to note that, as displayed in figure 3, although both $\lambda(y)$ and $\bar{\lambda}(y)$ are decaying functions peaked at the origin only $\bar{\lambda}$ is oscillatory (that is to say, $\bar{\lambda}(i'-i)\bar{\lambda}(i'-i-\vec{e}) < 0$). Whereas both the s-set and A-set are individually orthonormalized, their direct sum is not, because ϕ^s is not always orthogonal to ϕ^A. Actually, we can prove $\langle\phi^A_{i\sigma}|\phi^s_{i'\sigma}\rangle \approx g(\vec{e})\delta_{i-i',\vec{e}}$, with $|g| \approx \frac{1}{4}$ and $\vec{e}$ being $\vec{x}$ or $\vec{y}$. Nevertheless, the standard Gram–Schmidt procedure allows one to construct the following ϕ^a orbitals:

$$\phi^a_i = \frac{1}{\sqrt{4|g|^2+1}}[\phi^A + |g|(\phi^s_{i+\vec{x}} - \phi^s_{i-\vec{x}} + \phi^s_{i-\vec{y}} - \phi^s_{i+\vec{y}})]$$

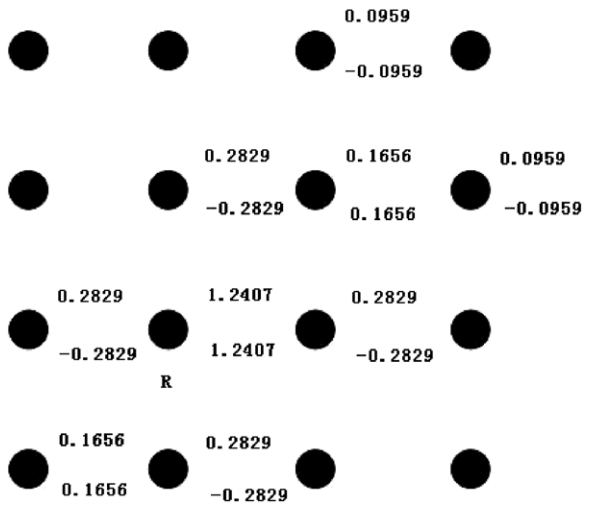

Figure 3. Numerical values of λ (the upper number) and $\bar{\lambda}$ (the lower number) computed on a 40×40 lattice. The reference point is labeled by R.

which, to the order of g, are mutually orthogonal and also orthogonal to all ϕ^s orbitals.

Now expressing the original p-orbitals as a linear combination of ϕ-orbitals, the Emery model can be recast as

$$\mathcal{H} = U\sum_i n_{i\uparrow}n_{i\downarrow} + \sum_{\nu,\nu',i,i',\sigma}\tilde{\Delta}^{\nu\nu'}_{ii'}\phi^{\nu\dagger}_{i\sigma}\phi^{\nu'}_{i'\sigma} + \sum_{i,i',\sigma,\nu}(\tilde{V}^{\nu}_{ii'}d^{\dagger}_{i\sigma}\phi^{\nu}_{i'\sigma} + \text{h.c.}) \tag{6}$$

where $\nu = s/a$ and

$$\tilde{V}^{\nu}_{ii'} = \sum_j V_{ij}\omega^{\nu}_{ji'}; \qquad \tilde{\Delta}^{\nu\nu'}_{ii'} = \Delta\sum_j \omega^{\nu *}_{ji}\omega^{\nu'}_{ji'}$$

with $\omega^{\nu}_{ji} = \langle\phi^{\nu}_{i\sigma}|p_{j\sigma}\rangle$ being the expansion coefficients. Let us note that $\tilde{\Delta}^{\nu\nu}_{ii} = \Delta$, a result of the fact that $\tilde{\Delta}^{\nu\nu}_{ii}$ and Δ mean the same charge-transfer gap. To proceed, we need to confine ourselves to the subspace where all Cu sites are singly occupied by holes. This can be formally implemented using the canonical perturbation method that was utilized by Zaanen [22]. Following Zaanen exactly and noticing that all projection operators involved in this method concern only d-orbitals and all other orbitals are left intact, we could up to a trivial renormalization constant obtain the following Hamiltonian defined in the subspace under consideration

$$\mathcal{H}' = \sum_{ii'i''\nu\nu'} J^{\nu\nu'}_{ii'i''}S_i\cdot\sum_{\sigma\sigma'}\phi^{\nu\dagger}_{i'\sigma}\vec{\tau}_{\sigma\sigma'}\phi^{\nu'}_{i''\sigma'} + \sum_{ii'\nu\nu'\sigma} t^{\nu\nu'}_{ii'}\phi^{\nu\dagger}_{i\sigma}\phi^{\nu'}_{i'\sigma} + J\sum_{\langle i,i'\rangle}S_i\cdot S_{i'} \tag{7}$$

where $J = \frac{2V^4}{\Delta^2}[\frac{4}{\Delta} + \frac{3U-4\Delta}{(U-\Delta)^2}]$ and

$$J^{\nu\nu'}_{ii'i''} = \left(\frac{1}{\Delta} + \frac{1}{U-\Delta}\right)\tilde{V}^{\nu}_{i'i}\tilde{V}^{\nu'}_{ii''}$$

while

$$t^{\nu\nu'}_{ii'} = \tilde{\Delta}^{\nu\nu'}_{ii'} + \frac{1}{2}\sum_{i''}\left(\frac{1}{\Delta} - \frac{1}{U-\Delta}\right)\tilde{V}^{\nu}_{ii''}\tilde{V}^{\nu'}_{i''i'}.$$

For later discussions, let us specify the expressions for all the relevant parameters. First of all, those concerning expansion coefficients are not hard to get and can be given as

$$\omega^A_{ji} \equiv \langle\phi^A_{i\sigma}|p_{j\sigma}\rangle = \tfrac{1}{2}(\bar{\lambda}(i-j_w) + \bar{\lambda}(i-j_{\bar{w}}))$$

$$\omega^s_{ji} = \tfrac{1}{2}(\lambda(i-j_w) - \lambda(i-j_{\bar{w}}))$$

where, if j indicates the O site at $\vec{R}_j$, the $j_{w/\bar{w}}$ denotes the position of its nearest Cu site that is either below (above) it or to the right (left) of it, or say, w = down/right and $\bar{w}$ = up/left. From the properties of functions λ and $\bar{\lambda}$, one could infer that those ω are generally very small except when i coincides with either j_w or $j_{\bar{w}}$. This reminds us that we may drop the last four terms of ϕ^a to simplify the computation. Although there are four such terms in total, in effect only one of them will contribute at a time under any situation. For example, the four Cu sites that correspond to the last four terms of $\omega^a_{ji} \approx \omega^A_{ji} + |g|(\sum_{\vec{e}}\text{sgn}(\vec{e})\omega^s_{j,i+\vec{e}})$ can never be adjacent to j simultaneously and, for a given j, there is one site which can be next to it. Therefore, in comparison with the leading term, the last four terms can be left out for simplicity. And all later calculations will refer to this approximation. Another helpful property is $\sum_{j\in\{i\}}\omega^A_{ji}\omega^A_{ji'} = \sum_{j\in\{i\}}\omega^s_{ji}\omega^s_{ji'}$, where $\{i\}$ is the set of positions of O sites belonging to the ith plaquette. This property illustrates the fact that, were it not for terms other than hopping ones, neither ϕ^s nor ϕ^a would be singled out as the temperature decreases. Indeed, as we shall show in what follows, it is the first term in $\mathcal{H}'$ that discriminates between them. To make this clear, explicit expressions for $\tilde{V}$ are needed. They read

$$\tilde{V}^a_{ii'} = \frac{V}{2}\{\bar{\lambda}(i'-i-\vec{y}) - \bar{\lambda}(i'-i+\vec{y}) + \bar{\lambda}(i'-i+\vec{x}) - \bar{\lambda}(i'-i-\vec{x})\}$$

$$\tilde{V}^s_{ii'} = \frac{V}{2}\left\{4\lambda(i'-i) - \sum_{\vec{e}}\lambda(i'-i-\vec{e})\right\}.$$

Now it is straightforward to realize that $\tilde{V}^a$ is zero for $i = i'$ and extraordinarily small for other cases, whereas $\tilde{V}^s$ is fairly large for $i = i'$ and similarly minute for other cases. Therefore it is reasonable to ignore products involving $\tilde{V}^a$. Thus, in the first sum of $\mathcal{H}'$ we need only keep the term headed by $J^{ss}_{ii'i''}$, which in fact is significant only for $i = i' = i''$. In other words, Kondo-like scattering is negligible (however, these scattering terms were once used to dismiss the t–J model [8]) and only Heisenberg coupling of strength $K_0 \equiv J^{ss}_{iii}$ should be retained. This is self-evident, since such scattering involves a couple of sites and must occur only with difficulty. This analysis shows ϕ^a form a non-bonding band, while ϕ^s give rise to a bonding and an anti-bonding band, a result quite consistent with the analysis of Zhang and Rice [9, 10]. The non-bonding band is irrelevant and can be traced out. We assume that such tracing out will not lead to new structures differing from the structure of H and that it will at most result in renormalization factors to parameters such as K_0 and $t^{ii'}_0 \equiv \tilde{t}^{ss}_{ii'}$. As can be demonstrated numerically, $t^{ii'}_0$ is a rapidly decaying function that's negative for nn hopping but positive for nnn pairs.

Using K and t to denote the renormalized parameters eventually confirms the effective Hamiltonian H (equation (1))

3. Spin glass

In this section we shall demonstrate how a SG can result from the interplay between H_K and H_t. This section, for the sake of clarity, will be divided into three subsections. In the first of them it is shown that the whole problem eventually boils down to a double-site problem if doped holes are localized and sparse. Thereafter, in section 3.2, this two-site problem is solved to display deformation of ZRS and how this deformation creates FM correlations between Cu spins. Section 3.3 contains additional remarks meant for the completeness of the argument presented in this paper.

3.1. SG at low doping

Suppose we inject only a few excess holes into a CuO_2 plane. These holes will be well localized, as observed in experiments at low doping [23]. Now that these holes are very sparse and hence well separated on average, there should be negligible spatial correlation between them, that is each of them can be dealt with independently. So, let us focus on one such localized hole. Primarily due to H_t, which tends to delocalize this hole so as to lower its kinetic energy, the localized state this hole finds itself in should in general have a spread of several plaquettes, which means that, because of H_K, this hole couples simultaneously to several Cu spins belonging to these plaquettes. As a consequence, we expect effective FM correlations among these spins. This effect will be referred to as UDE. Now, in the spirit of section 3.2, one can be convinced that, the UDE strength should decline as the localized state size increases, although the possible lowest kinetic energy the hole can take remains unchanged (it is always $-|t|$). Therefore, when taking into account the originally existing AFM coupling (H_J) between Cu spins, the best strategy to minimize the total energy (including both the spin energy and the kinetic energy) is to let the localized state extend over only two plaquettes. This argument is similar to the argument once used to estimate the size of a spin bag [24]. We note that the configuration suggested here may be verified by a variational method within the semi-classical frame, as in [25]. In summary, a localized hole should take an orbital state of this form, which may be called a rectangle state as depicted in figure 3,

$$|\vec{R}_i, \vec{e}\rangle = \frac{1}{\sqrt{2}}(|\phi_{\vec{R}_i}\rangle + |\phi_{\vec{R}_i+\vec{e}}\rangle) \tag{8}$$

which induces an FM bond, $|i;\vec{e}\rangle$, whose strength will be shown to be much larger than J, connecting two spins, $S_{\vec{R}_i}$ and $S_{\vec{R}_i+\vec{e}}$. Note that the hole's spin can be either up or down (see section 3.2) but it cannot have both components present simultaneously in the thermodynamic ground state, due to spontaneous time reversal symmetry (TRS) breaking that usually occurs in infinite spin systems. Therefore, the total spin of the entire system should not be zero on average, in agreement with experiments [26, 27]. This symmetry will certainly be restored for the isolated double-site system to be discussed. Along the above line of thought, we naturally arrive at this conclusion: every localized hole makes a FM bond between adjacent Cu spins, and in the case of randomly quenched holes, these FM bonds will be distributed randomly; then, according to general theory [28–30], a bond-disordered SG should result.

3.2. UDE

In section 3.1 we argued that a localized hole should have a spatial extension of around two plaquettes and, due to DE, FM coupling should be initiated between the Cu spins on these plaquettes. However, it should be noted that previous work on DE is largely concerned with situations where the carrier–spin coupling (in the present context, $K < 0$) is FM and the spins are large so that they can be treated as classical vectors [16–18]. These works showed that the DE strength is first order in the hopping constant t, independent of K. This result should not apply to the present case, where one is concerned with small one-half spins and AFM carrier–spin coupling. It is expected that quantum effects are important in this case. Indeed, the UDE strength we found is only second order in t and hinges on K, usually much larger than J, which is of order t^4. But as K goes to infinity, its strength vanishes. To explore UDE, we shall perform perturbation analysis accompanied by exact numerical calculations on a double-site model.

This double-site system contains one hole and two Cu spins (local spins), one spin for each site. Anticipating that the J-term has little to do with UDE, we will not mention it for the moment. Now H becomes

$$H_{12} = t\sum_{\sigma}(\phi^{\dagger}_{1\sigma}\phi_{2\sigma} + \text{h.c.}) + K(s_1 \cdot S_1 + s_2 \cdot S_2) \tag{9}$$

where $t < 0$ and $K > 0$. Here the on-site energy has been set to zero, which should not affect our results.

It is instructive to consider two limits of H, in one of which $|t/K| \gg 1$ while in the other $|t/K| \ll 1$. The latter case is our main concern. It will be shown that in both limits we end up with effective FM coupling between S_1 and S_2. Let's begin with the former, in which hole hopping dominates and localization of the hole shall lift the energy drastically. Thus, an itinerant hole is favored and a FM combination of S_1 and S_2 should result. To elucidate this, it is better to work with a delocalized representation. We then introduce the plus- and minus-orbitals expressed by

$$\phi_{\pm\sigma} = \frac{1}{\sqrt{2}}(\phi_{1\sigma} \pm \phi_{2\sigma})$$

which bring the first term of H_{12} into a diagonal form. In terms of these two orbitals, H_{12} could be recast as

$$H_{12} = H_+ + H_- + \mathcal{V}$$

where H_- can be obtained from H_+ by replacing $\phi_{+\sigma}$ ($\phi^{\dagger}_{+\sigma}$) with $\phi_{-\sigma}$ ($\phi^{\dagger}_{-\sigma}$) and

$$\begin{aligned} H_+ &= t\phi^{\dagger}_{+\sigma}\phi_{+\sigma} + \frac{K}{2}(S_1 + S_2)\cdot s_+ \\ \mathcal{V} &= \frac{K}{4}(S_1 - S_2)\cdot\sum_{\sigma\sigma'}(\phi^{\dagger}_{+\sigma}\vec{\tau}_{\sigma\sigma'}\phi_{-\sigma'} + \text{h.c.}). \end{aligned} \tag{10}$$

Obviously, $\mathcal{V}$ means Kondo-like scattering, which necessarily involves both the plus state and the minus state. Since this scattering relates to the difference of S_1 and S_2, it favors AFM alignment of these two spins and FM configuration will lessen its effect.

However, this scattering should be essentially suppressed at low temperatures in the case of large $|t|$, because the minus state is energetically unfavored due to its higher energy $(-t)$. Henceforth, the low energy physics is essentially set by H_+, with minute modifications from scattering. Since the first term of H_+ commutes with the hole's spin operator s_+, the eigenstates of H_+ are identical with that of its second term, whose eigenstates are well known and can be written as $|\Lambda\Lambda_z L\rangle$, which is labeled with three q-numbers [6]. Here $\Lambda = S_1 + S_2 + s_+$ and $L = S_1 + S_2$. As can be exactly shown [6], regardless of the sign of K, the ground state $|GND\rangle$ always has $L = 1$, which implies parallel alignment of S_1 and S_2. Actually, if we use $\langle S_1 \cdot S_2\rangle$ as an indicator, we could find $\langle GND|S_1 \cdot S_2|GND\rangle > 0$. For example, if $K > 0$, $|GND\rangle = |\frac{1}{2}\frac{\pm 1}{2}1\rangle$ and $\langle S_1 \cdot S_2\rangle = \frac{1}{6}$, thus concluding an effective FM coupling. Were two spins AFM correlated in a state, the indicator would be negative in this state. For example, $\langle\frac{1}{2}\frac{1}{2}0|S_1 \cdot S_2|\frac{1}{2}\frac{1}{2}0\rangle = -\frac{3}{4}$.

Let us note that in this extreme one does not get a Zhang–Rice singlet at all, which suggests crossover within H_{12}.

Going to the other extreme, where $|t/K| \ll 1$ and the hopping term may be taken as a perturbation, one still envisages FM coupling between S_1 and S_2. Pictorially, hopping, be it small or large, between two sites will make the hole couple simultaneously to spins on the sites and hence entails FM interaction. Thus, the hole can be taken as some gluon that is running between the spins and then glues them. Evidently, H_{12} at $t = 0$ has 16 eigenstates in total, of which 4 are composed of Zhang–Rice singlets and the other 12 consist of triplets. As a guide to the labeling of these states, a state in which there is a singlet on site 1 and a spin with σ ($\uparrow$ or $\downarrow$) on site 2 shall be written as $|1ZR; 2\sigma\rangle$. Generally, these states may be written as $|1ZR/\alpha/\beta/\gamma; 2\sigma\rangle$ and $|2ZR/\alpha/\beta/\gamma; 1\sigma\rangle$, the meanings of which shall become clear later. However, one may also use another representation with a basis state written as $|1/2\sigma; S_{1z}S_{2z}\rangle \equiv |1/2\sigma\rangle \otimes |S_{1z}S_{2z}\rangle$, which has a hole with spin σ on site $1/2$. The relations between these representations are as follows:

$$\begin{aligned}
|1ZR; 2\sigma\rangle &= \frac{1}{\sqrt{2}}(|1\uparrow; \downarrow\sigma\rangle - |1\downarrow; \uparrow\sigma\rangle)\\
|1\alpha; 2\sigma\rangle &= |1\uparrow; \uparrow\sigma\rangle;\\
|1\gamma; 2\sigma\rangle &= \frac{1}{\sqrt{2}}(|1\uparrow; \downarrow\sigma\rangle + |1\downarrow; \uparrow\sigma\rangle)\\
|1\beta; 2\sigma\rangle &= |1\downarrow; \downarrow\sigma\rangle.
\end{aligned} \tag{11}$$

Similar expressions for $|2ZR/\alpha/\beta/\gamma; 1\sigma\rangle$ can also be easily obtained. As mentioned, there are four degenerate singlets that form a subspace of energy $-\frac{3K}{4}$ while the remaining degenerate states belong to another subspace of higher energy $\frac{K}{4}$. At low temperatures, the latter is much less important and we thus focus on the former.

Now let us add the small hopping term as a perturbation. Conventional degenerate perturbation theory shall, to zeroth order, mix $|1ZR; 2\uparrow/\downarrow\rangle$ with $|2ZR; 1\uparrow/\downarrow\rangle$ to form

$$|\pm; \uparrow/\downarrow\rangle \equiv \tfrac{1}{2}(|1ZR; 2\uparrow/\downarrow\rangle \pm |2ZR; 1\uparrow/\downarrow\rangle). \tag{12}$$

And their energies are $\mathcal{E}_{\pm}^{\uparrow/\downarrow} = -\frac{3K}{4} \pm \frac{t}{2}$, which implies that a singlet hops with strength $\frac{t}{2}$. To get the effective coupling, we find it is necessary to include the first order correction to the above states, which implies that the UDE strength is of order t^2. After some calculation we arrive at the following corrected states:

$$\begin{aligned}
|+; \uparrow\rangle_c &= |+; \uparrow\rangle - \frac{t}{2K - t}\left\{[|1\alpha; 2\downarrow\rangle + |2\alpha; 1\downarrow\rangle]\right.\\
&\quad \left. - \frac{1}{\sqrt{2}}[1\gamma; 2\uparrow\rangle + |2\gamma; 1\uparrow]\right\}\\
|-; \uparrow\rangle_c &= |-; \uparrow\rangle - \frac{t}{2K + t}\left\{[|2\alpha; 1\downarrow\rangle - |1\alpha; 2\downarrow\rangle]\right.\\
&\quad \left. + \frac{1}{\sqrt{2}}[1\gamma; 2\uparrow\rangle - |2\gamma; 1\uparrow]\right\}\\
|+; \downarrow\rangle_c &= |+; \downarrow\rangle + \frac{t}{2K - t}\left\{[|1\beta; 2\uparrow\rangle + |2\beta; 1\uparrow\rangle]\right.\\
&\quad \left. - \frac{1}{\sqrt{2}}[1\gamma; 2\downarrow\rangle + |2\gamma; 1\downarrow]\right\}\\
|-; \downarrow\rangle_c &= |-; \downarrow\rangle + \frac{t}{2K + t}\left\{[|2\beta; 1\uparrow\rangle - |1\beta; 2\uparrow\rangle]\right.\\
&\quad \left. + \frac{1}{\sqrt{2}}[1\gamma; 2\downarrow\rangle - |2\gamma; 1\downarrow]\right\}.
\end{aligned} \tag{13}$$

Let us note that these expressions respect time reversal symmetry (TRS).

Clearly the corrected states have essentially the same energy orders as before, that is plus states are lower than minus states by nearly $|t|$. It is straightforward to evaluate the indicators over them. We found

$$\langle S_1 \cdot S_2\rangle_{+\uparrow/\downarrow} = -\frac{3}{2}\frac{t}{2K - t}\left(1 + \frac{t}{2K - t}\right)$$

and

$$\langle S_1 \cdot S_2\rangle_{-\uparrow/\downarrow} = \frac{3}{2}\frac{t}{2K + t}\left(1 - \frac{t}{2K - t}\right).$$

Therefore, as long as $t < 0$ and $K > 0$, the plus state will have lower energy and should be favored at low temperatures and its indicator will be always positive, invariably indicating an effective FM coupling. According to Zhang and Rice [10], for $U = 2\Delta$ one gets $t \sim -3\frac{V^2}{\Delta}$ and $K \sim 15\frac{V^2}{\Delta}$. With these estimations, $\langle S_1 \cdot S_2\rangle_+ \sim 0.15$. As t/K vanishes, the FM coupling, the strength of which should scale as $\sim t^2/K$, will vanish as well. This property thus supplies one further piece of evidence against t–J model in addressing problems about spin glass.

To gain further insight into the structure of the corrected states, it is useful to rearrange them into another form. For

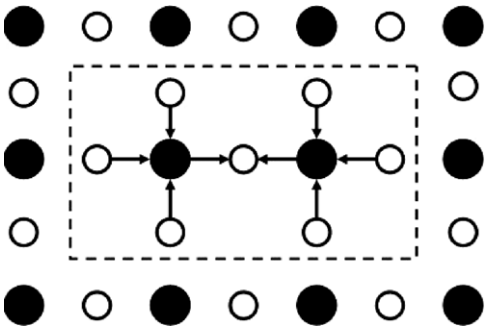

Figure 4. Schematic illustration of a rectangle (the area enclosed by dashed line) and an example of how the rectangle may be relatively isolated due to lattice distortion. The arrows indicate how each atom is displaced. The phonon shown has a mixing character. Lattice distortion shall increase lattice energy, which, however, may be compensated by a decrease in other energy components. This is possible due to increase of hopping constant within the rectangle. Increase of t shall increase K and J and thus may reduce spin energy. Further work is needed to find out whether these energies can be balanced.

example,

$$|+;\uparrow\rangle_c = \frac{1-3|\eta|}{2}(|1\uparrow;\downarrow\uparrow\rangle + |2\uparrow;\uparrow\downarrow\rangle) + 2|\eta||\phi_{+\uparrow}\rangle \otimes \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}} - \frac{|\eta|+1}{\sqrt{2}}|\phi_{+\downarrow}\rangle \otimes |\uparrow\uparrow\rangle$$

where $\eta = \frac{t}{2K-t}$. One may say that the first line represents an incoherent AFM component which will not lead to coherence between $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$ but has negative $\langle S_1 \cdot S_2\rangle$. However, the last two lines are coherent FM components. At $\eta = 0$, the AFM component cancels out FM components. As $|\eta|$ increases, the FM components grow whereas the AFM component wanes. Any one FM component can be roughly obtained by rotating the other component. A similar analysis is also applicable to other states.

To supplement the above analytical consideration, we have performed numerical calculation to further investigate the nature of the system's ground state. We used a computer to directly diagonalize H_{12} in the representation $\{|i\sigma; S_1S_2\rangle, i = 1, 2\}$. And the ground state is found to be doubly degenerate due to TRS. Thus, without losing any generality we only consider one of the two ground states. Further, t was set to -1 so that only one parameter K had to be varied. Numerical results exhibit that the ground state under consideration could always be approximated as

$$\begin{aligned}|\alpha\beta\gamma\rangle &\equiv \alpha(|1\uparrow;\downarrow\downarrow\rangle + |2\uparrow;\downarrow\downarrow\rangle) \\ &\quad + \beta(|1\downarrow;\uparrow\downarrow\rangle + |2\downarrow;\downarrow\uparrow\rangle) \\ &\quad + \gamma(|1\downarrow;\downarrow\uparrow\rangle + |2\downarrow;\uparrow\downarrow\rangle) \\ &\equiv \alpha|a\rangle + \beta|b\rangle + \gamma|c\rangle\end{aligned}$$

where the last line defines three states $|a/b/c\rangle$ and $|\alpha| > |\beta| > |\gamma|$. All coefficients are real. Meanwhile, we found $|\alpha|$ was always around 0.5, and $|\beta|$ increased to 0.5 as K went to infinity but at the same time $|\gamma|$ disappeared gradually. Besides, $\alpha\beta < 0$ and $\beta\gamma > 0$. This information indicates to us

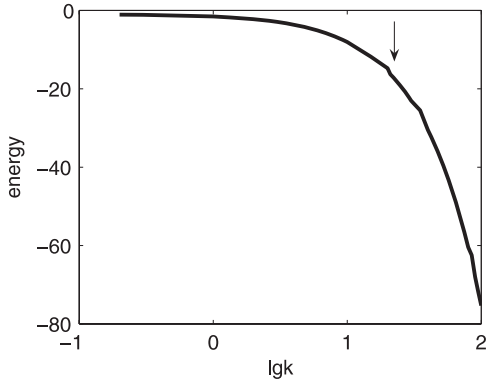

Figure 5. Energy plotted against $\log_{10}^{K}$. See the annotation in figure 6 for the region indicated by the arrow.

that it may be more convenient to rewrite $|\alpha\beta\gamma\rangle$ as

$$\begin{aligned}|\alpha\beta\gamma\rangle &= \{(\gamma-\beta)(|a\rangle - |b\rangle)\} \\ &\quad + \{(\alpha+\beta-\gamma)|a\rangle + \gamma(|b\rangle + |c\rangle)\}.\end{aligned}$$

One could easily verify the following equations:

$$|a\rangle - |b\rangle = |ZR1\rangle|2\downarrow\rangle + |ZR2\rangle|1\downarrow\rangle$$

$$|c\rangle + |b\rangle = (|1\downarrow\rangle + |2\downarrow\rangle) \otimes (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$$

$$|a\rangle = (|1\uparrow\rangle + |2\uparrow\rangle) \otimes |\downarrow\downarrow\rangle.$$

Now we see that $(|a\rangle - |b\rangle)$ is just a pure ZRS state while both $|a\rangle$ and $(|b\rangle + |c\rangle)$ are pure states with $L = 1$. Therefore, as K goes to infinity, the amplitude of the ZRS state is elevated to its highest (0.5) whereas the $L = 1$ state gets chronically out of order. Henceforth, there's an evident crossover from ZRS to the $L = 1$ state within the simple H_{12}.

We have also obtained the energy in terms of those coefficients. It reads

$$E = 2t(\alpha^2 + 2\beta\gamma) + \frac{K}{2}(4\alpha\beta - \alpha^2 - \beta^2 + \gamma^2). \qquad (14)$$

Evidently, the terms in the first bracket come from the kinetic energy while those in the second from the magnetic potential energy. Even from this expression, one could infer the competition between ZRS and the $L = 1$ state. For example, if K is much smaller than $|t|$ kinetic energy dominates, so for E to be ground state energy one should let $\beta\gamma$ be maximized under the constraint that $\alpha^2 + \beta^2 + \gamma^2 \approx \frac{1}{2}$, which means $\beta \approx \gamma$, whence ZRS is of little importance in this example. Generally, one could use the variational principle to establish the expressions of all coefficients in terms of K and t. However, we would rather plot the energy in figure 4 and other quantities in figure 5. Clearly the indicator, using the expression of $|\alpha\beta\gamma\rangle$, can be written as

$$\langle S_1 \cdot S_2\rangle = \frac{\alpha^2 - \beta^2 - \gamma^2}{2} + 2\beta\gamma$$

and is positive all the way up to $K = \infty$, a result consistent with earlier analytical considerations.

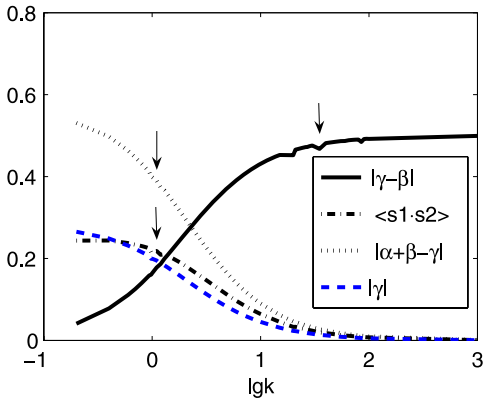

Figure 6. The absolute values of all coefficients and the indicator plotted versus $\log_{10}^{K}$. Let us point out that the non-analytic features as indicated by the arrows should not be regarded as singularities intrinsic to the system, rather they should be seen as flaws of the approximate expression of the ground state.

(This figure is in colour only in the electronic version)

3.3. Additional remarks

For completeness of this paper we add a couple of remarks as follows.

(1) Obviously, the above described SG phase breaks TRS and local translational symmetry, and it also reduces the 90° rotation C_4 symmetry down to 180° rotation C_2 symmetry. Further, every rectangle state is O-centered rather than Cu-centered. All these features are in agreement with experiments [3–5]. Although these features are shared by Cu–O–Cu configurations, it is still possible to distinguish them from our rectangle states because the latter are stabilized by UDE, which is special in some respects. For example, UDE can lead to an unusual temperature dependence of magnetic susceptibility [17]. Besides, there must exist some relations between SG transition temperature and electrical conductivity, since both quantities are linked with t. In fact, similar relations have already been found between Curie temperature and electrical conductivity [16]. The establishment of these relations, which are unique to UDE-caused SG, will be published elsewhere.

(2) The SG phase is glassy not only in spin but also in charge, namely the charges associated with doped holes are also irregularly dispensed.

(3) We note that (a) DE (or UDE) coupling cannot be written as a sum of terms relating Cu spins by pairs [17]; (b) the UDE strength is second order in t, but DE strength is linear in t [16]; (c) DE (or UDE) is much more effective than a direct FM bond in destroying the original AFM order [25].

(4) An indispensable element of the present SG theory is the localization of doped holes. Whether this localization is intrinsic or not to CuO_2 planes is an interesting question. Some authors ascribe it to external factors such as impurity potential from out-of-plane dopant atoms [31]. However, intra-plane factors may be more relevant. Firstly, it has been demonstrated that, for carriers doped in a classical AFM background, there should be a transition from being self-trapped to being free at some critical doping [25]. Below this critical doping, doped carriers are self-trapped and cause local distortion of the background. As doping increases, they become free and uniform canting gets stable. This transition should manifest itself as a turn in electrical conductivity. Measurements do reveal this trait [32]. Secondly, coupling to a phonon may greatly assist localization. Usually the phonon is assumed to be of pure O character. This coupling is essential in some models of cuprates, such as the bi-polaron model. It is also necessary in explaining isotope effects [33]. Perhaps the simplest example illustrating how phonon interaction may strengthen localization is shown in figure 4. More work is required to discover the details.

(5) It is noted that the term H_K tends to prevent double hole occupation of any plaquette or any rectangle. This is because (a) under both situations there is only one effective orbital, which is the Zhang–Rice orbital for the former but a rectangle state for the latter, and (b) every orbital can admit only one singlet.

4. Summary

In summary, we have analyzed the incompatibility between ZRS formation and SG behavior that arises within the usual theoretical jargon. Having recourse to a different model, which has the t–J model as one of its extremes, we are able to resolve this incompatibility by observing that the actual ZRS should be deformed due to the motion of doped holes. This deformation, which is first order in t, can provoke FM coupling, which is second order in t, between adjacent Cu spins, a phenomenon referred to as UDE. And if holes are localized randomly, bond-disordered SG should obtain.

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For other reasons in favor of the Zhang–Rice orbital please see Halperin B I and Varma C M 1976 *Phys. Rev.* B **14** 4030 Gooding R J and Mailhot A 1993 *Phys. Rev.* B **48** 6132
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