Possible three-dimensional superconducting properties of strongly correlated honeycomb compound In$_3$Cu$_2$VO$_9$

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Abstract. We present the zero- and finite-temperature superconducting properties of a modified $t-J-J_c$ model on three-dimensional honeycomb lattice by employing the strongly correlated Slave Boson mean-field theory, focusing on the low energy physics in In$_3$Cu$_2$VO$_9$. We find that the highest superconducting transition temperature $T_c \approx 4$ K occurs at doping hole concentration $\delta = 0.03$. The superconducting phase disappears at doping concentration of $\delta = 0.06$. The superconducting ground state in doped In$_3$Cu$_2$VO$_9$ supports a $d_{x^2-y^2}$ pairing symmetry when the interlayer coupling $J_c$ increases from 1.2 to 5.2 meV. Our theoretical results suggest that doped In$_3$Cu$_2$VO$_9$ is a possible superconducting honeycomb system.

1. Introduction

Unconventional high-temperature superconductivity (SC) in two-dimensional honeycomb lattice has attracted great attention in recent years, since its low-energy quasi-particles in normal state are Dirac particles with relativistic linear spectrum. However, such candidate compounds are rather rare, especially in strongly correlated systems with strong spin fluctuations. Layered honeycomb copper oxide In$_3$Cu$_2$VO$_9$ synthesized by Möller et al. behaves very similar electronic states to those in high-$T_c$ cuprates. It lies in strongly correlated limit with $(U/t \gg 1)$, the Cu-3d electron is half filling with 3d$^9$ and $S = 1/2$, and Cu-O-Cu forms a superexchange antiferromagnetic (AFM) coupling [1]. A recent work by Liu et al. presented the tight-bonding parameters $t_{ij}$ and the spin coupling strengths $J_{ij}$ of undoped In$_3$Cu$_2$VO$_9$ [2], demonstrating that it is a strongly correlated system. We also showed that the ground state of such a layered honeycomb compound is spin disordered [3], implying a considerable spin fluctuations. This arises a great interesting problem: whether could doped In$_3$Cu$_2$VO$_9$ exhibit high-$T_c$ SC like doped cuprates?

Until now, there has not been any experimental evidence for SC phase upon doping in In$_3$Cu$_2$VO$_9$, since the electron or hole carriers are difficult to be doped into the compound, no insulator-metal transition occurs [4], not to mention the metal-SC transition. Recently, the development of liquid or solid gating technology makes it possible to tune the carrier concentration in strongly correlated compounds, appealing for the exploration of the SC
properties of In$_3$Cu$_2$VO$_9$. Meanwhile, the SC properties in monolayer honeycomb lattice, such as in graphene, were extensively studied by many theorists, for example, see Ref.[5, 6]. However, strongly correlated In$_3$Cu$_2$VO$_9$ is considerably different from weakly interacting graphene and strongly correlated cuprates. On the one hand, no AFM long-range order (LRO) and AFM transition were observed in the specific heat of undoped In$_3$Cu$_2$VO$_9$ down to 2 K [1]. Instead, its magnetic susceptibility and specific heat exhibit a very broad bump over a wide temperature range from 50 K to 300 K [4], implying a possibility of the spin disorder or liquid insulating ground state. On the other hand, according to Ref.[2], there are two kinds of magnetic frustrations in In$_3$Cu$_2$VO$_9$: one is from the intralayer next-nearest-neighbour (NNN) AFM spin coupling, the other comes from the interlayer nearest-neighbour (NN) spin coupling. The interlayer magnetic frustration might stabilize the exotic spin disorder phase and contribute to the SC phase in finite doping.

Thus, it is essential to explore the role of interlayer frustration on the SC ground state and the SC symmetry of the effective $t$-$J_1$-$J_2$-$J_c$ model in a three-dimensional (3D) system, so as to mimic the low-energy physics of doped In$_3$Cu$_2$VO$_9$. In addition, very few work has come to the doped hole concentration $\delta$ dependence of the transition temperature $T_c$ in frustrated honeycomb lattice. In the rest of this paper, we first outline the model Hamiltonian and the Slave boson mean-field theory (SBMFT) in Sec.2, and then present the parameter and doping dependences and pairing symmetry of the SC properties in Sec.3, and the final section is devoted to the summary.

2. Model Hamiltonian and Slave Boson Method

In accordance with Ref.[2], the low-energy physics of doped In$_3$Cu$_2$VO$_9$ is dominated by the kinetic energy and the AFM spin interactions in the honeycomb planes of copper ions, i.e. a generalized $t$ – $J$ model. The model Hamiltonian thus reads as:

$$ H = -\sum_{ij,\sigma} t_{ij} \left( \hat{f}_{i\sigma}^{\dagger} \hat{f}_{j\sigma} + h.c. \right) + \sum_{ij} J_{ij} \left( S_i \cdot S_j - \frac{1}{4} n_i n_j \right) $$

(1)

where nonzero $t_{ij}$ are the intralayer NN, NNN and interlayer NN hopping integrals $t_1$, $t_2$, and $t_c$; and finite $J_{ij}$ are the intralayer NN, NNN and interlayer NN AFM spin interactions $J_1$, $J_2$ and $J_c$, respectively. Due to the large-U limit, the high-energy double occupation state should be projected out in the electron projection operator $\hat{f}_{i\sigma}$, so the Coleman-Barnes’ SBMFT [7] is a suitable technique to treat such a strongly correlated Hamiltonian.

The essence of the SBMFT is to project the electron operator $\hat{f}_{i\sigma}$ as a product of holon boson $h_{i\sigma}$ of the charge and spinon fermion $g_i$ of the spin,

$$ \hat{f}_{i\sigma}^{\dagger} = g_i h_{i\sigma}^{\dagger}, \quad \hat{f}_{i\sigma} = h_{i\sigma} g_i^{\dagger} $$

(2)

with the constraint condition

$$ g_i^{\dagger} g_i + \sum_{\sigma} h_{i\sigma}^{\dagger} h_{i\sigma} = 1. $$

(3)

on each sublattice site. The holons and spinons satisfy commutation and anticommutation relation, respectively. Within the slave boson framework, the projected generalized $t$ – $J$ model Hamiltonian is rewritten as,

$$ H = -\sum_{ij,\sigma} t_{ij} \left( g_i^{\dagger} j_{i\sigma}^{\dagger} h_{j\sigma} h_{i\sigma} + h.c. \right) - \mu \sum_{i\sigma} h_{i\sigma}^{\dagger} h_{i\sigma} + \sum_{i} \lambda_i \left( g_i^{\dagger} g_i + \sum_{\sigma} h_{i\sigma}^{\dagger} h_{i\sigma} - 1 \right) $$

$$ + \frac{(1+\delta)^2}{2} \sum_{ij} J_{ij} \left( h_{i\sigma}^{\dagger} h_{j\sigma}^{\dagger} h_{j\alpha} h_{i\alpha} + h_{i\sigma}^{\dagger} h_{j\alpha}^{\dagger} h_{i\sigma} h_{j\alpha} \right) $$

(4)

2
where $\mu$ is the chemical potential and $\lambda$ is the Lagrangian multiplier. In accordance with the results of the first-principles electronic structures calculations, we take $t_1$, $t_2$, $t_c$, $J_1$, and $J_2$ are $-180$, $-24.1$, $-48.9$, $16.2$, and $0.3 \text{ meV}$, respectively [2]. Note that the interlayer NN coupling $J_c$ was estimated from the AFM ordered phases, we expect that it was well underestimated. In this paper we take $J_c = 4.2 \text{ meV}$ [3].

To deal with such a 3D strongly correlated and frustrated model Hamiltonian Eq.(4), we first adopt the SBMFT to explore the pairing symmetry of SC phases. Within the SBMFT technique, we define the order parameters representing the resonating valence bond (RVB) spinon singlet $\Delta$ and the coherent motion of spinons $P_{\alpha\beta}$ and motion of holons $Q_{\alpha\beta}$, respectively. Here $\alpha, \beta$ represent the four sublattices in 3D $\text{In}_3\text{Cu}_2\text{VO}_9$.

$$
\Delta_{\alpha\beta r} = -\frac{J_1(c)}{2} \langle h_{\beta i+r}^\dagger h_{\alpha i}^\dagger - h_{\beta i+r} h_{\alpha i} \rangle,
\Delta_{\alpha\alpha r} = -\frac{J_2}{2} \langle h_{\alpha i+r}^\dagger h_{\alpha i}^\dagger - h_{\alpha i+r} h_{\alpha i} \rangle,
P_{\alpha\beta} = \sum_{\sigma} \langle h_{\alpha\sigma i}^\dagger h_{\beta i+r\sigma} \rangle, \quad Q_{\alpha\beta} = \langle g_{\alpha i}^\dagger g_{\beta i+r} \rangle.
$$

(5)

here $r$ is the NN or NNN direction vector, the corresponding coordination numbers $z_1$, $z_2$, and $z_c$ are 3, 6, and 2 for intralayer NN, intralayer NNN and interlayer NN, respectively. The Fourier transformation of these RVB gap functions are then: $\Delta_{\alpha\beta}(k) = \sum_r \Delta_{\alpha\beta r} e^{ik \cdot r}$, and $\Delta_{\alpha\alpha}(k) = \sum_r \Delta_{\alpha\alpha r} \cos(k \cdot r)$.

At $T = 0 \text{ K}$, the holon hopping order parameters $Q_{\alpha\beta} \approx \delta$. Thus we could rewrite the Hamiltonian Eq.(4) in the SBMFT approach in the momentum space.

$$
H^{MF} = -\sum_{\alpha\beta m, k \sigma} z_m \gamma_{\alpha\beta} \left( t_m \delta + \frac{1}{4} J_m P_{\alpha\beta}^\dagger \right) h_{\alpha k \sigma}^\dagger h_{\beta k \sigma}^\dagger
+ \sum_{\alpha\beta, k} \left( \Delta_{\alpha\beta}(k) h_{\alpha k \dagger}^\dagger h_{\beta -k \dagger}^\dagger + \Delta_{\alpha\beta}^*(k) h_{\beta k \dagger}^\dagger h_{\alpha -k \dagger}^\dagger \right)
+ \sum_{\alpha k} \left[ \lambda - \mu - z_2 \gamma_{\alpha\alpha} \left( t_2 \delta + \frac{1}{4} J_2 P_{\alpha\alpha} \right) - \frac{n}{4} \sum_{\nu} J_{\nu} z_{\nu} \right] h_{\alpha k \sigma}^\dagger h_{\alpha k \sigma}^\dagger
+ \sum_{\alpha k} \Delta_{\alpha\alpha}(k) h_{\alpha k \dagger}^\dagger h_{\alpha -k \dagger}^\dagger + H.c. + E_0
$$

(6)

with the constant energy $E_0$ defined as

$$
E_0 = 2N \sum_{\alpha\beta \nu} \frac{\left| \Delta_{\alpha\beta r} \right|^2}{J_{\nu}^r} + N \sum_{\alpha \beta \nu} \frac{z_{\nu} J_{\nu}^r}{4} \left( n^2 + \left| P_{\alpha\beta} \right|^2 \right) - 4N(\lambda - \mu)n
$$

(7)

where the subscript $m$ runs over 1 and $c$, and $\nu$ over 1, 2, and $c$; $J_{\nu}^r = J_{\nu}(1 + \delta)^2$. $\gamma_{\alpha\beta}$ are the geometrical structure factors of the intralayer NN, interlayer NN and intralayer NNN spins.

Diagonalize the SBMFT Hamiltonian $H^{MF}$ by employing a complex $8 \times 8$ Bogoliubov transformation [7], we obtain eight energy dispersion relations $\omega_{k\sigma}$ of the fermion excitations. Thus we achieve the free energy $F = -k_B T \ln \text{Tr} \left( e^{-\beta H^{MF}} \right)$ as follows:

$$
F = -k_B T \sum_{k \sigma} \ln \left[ 1 + \exp \left( -\beta \omega_{k\sigma} \right) \right] + E_0
$$

(8)

Then minimizing the free energy with respect to the RVB order parameters $\Delta_{\alpha\beta r}$, spinon motion order parameters $P_{\alpha\beta}$, the chemical potential $\mu$ and the Lagrangian multiplier $\lambda$, one arrives the
saddle points of free energy minimum. The saddle point satisfies the following self-consistent
equations,

$$
\delta = \frac{1}{4N} \sum_{k,u} \frac{\partial \omega_{kua}}{\partial \mu} \frac{1}{1 + \exp \left( \beta \omega_{kua} \right)}
$$

$$
\Delta_{\alpha \beta r} = -\frac{J_{1(c)}}{2N} \sum_{k,u} \frac{\partial \omega_{kua}}{\partial \Delta_{\alpha \beta r}} \frac{1}{1 + \exp \left( \beta \omega_{kua} \right)}
$$

$$
\Delta_{\alpha \alpha r} = -\frac{J_{2}}{2N} \sum_{k,u} \frac{\partial \omega_{kua}}{\partial \Delta_{\alpha \alpha r}} \frac{1}{1 + \exp \left( \beta \omega_{kua} \right)}
$$

$$
P_{\alpha \beta} = -\frac{4}{3N} \sum_{k,u} \frac{\partial \omega_{kua}}{\partial P_{\alpha \beta}} \frac{1}{1 + \exp \left( \beta \omega_{kua} \right)}
$$

$$
P_{\alpha \alpha} = -\frac{4}{3J_{2}N} \sum_{k,u} \frac{\partial \omega_{kua}}{\partial P_{\alpha \alpha}} \frac{1}{1 + \exp \left( \beta \omega_{kua} \right)}
$$

(9)

Solving these self-consistent equations, we could obtain the doping hole concentration $\delta$ and
interlayer NN $J_c$ dependences of moduli of the order parameters and the SC phases’ symmetry
in the ground state. We set the moduli of the intralayer NN, intralayer NNN and interlayer NN
RVB order parameters as $|\Delta_{\alpha \beta r}| = \Delta_1$, $|\Delta_{\alpha \alpha r}| = \Delta_2$, and $|\Delta_{\alpha \beta r}| = \Delta_3 \text{ or } \Delta_4$, respectively.

3. Numerical Results and Phase Diagrams

Performing the numerical calculation to Eq.(9), we could explore the SC groundstate properties
of the 3D In$_3$Cu$_2$VO$_9$ in the framework of the SBMFT.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** (Color online) Dependence of the transition temperature $T_{RVB}$ on hole doping
concentration $\delta$ obtained by SBMFT and mean-field solution $T_c$ in 3D In$_3$Cu$_2$VO$_9$.

Fig.1 displays the hole doping concentration dependence of the SC transition temperature
obtained by SBMFT, the conventional mean field solution is also plotted for comparison.
It shows that the mean-field $T_c$ decreases with the increase of hole doping concentration.
The highest SC transition temperature $T_c \approx 4 \text{ K}$ occurs at optimized doping concentration $\delta = 0.03$,
and the SC phase disappears at $\delta = 0.06 \ (\ll 1)$ in the mean-field approximation, as shown
in Fig.1. In the SBMFT solutions, we obtain the RVB state transition temperature $T_{RVB}$ which
indicates the formation of the singlet spin pairing, as shown the red line in Fig.1. It also decreases
Figure 2. (Color online) Dependence of the RVB order parameters $\Delta_{1-4}$ on interlayer NN spin coupling $J_c$ at optimized doping $\delta = 0.03$ in 3D $\text{In}_3\text{Cu}_2\text{VO}_9$.

with the increase of $\delta$. Then $T_{RVB}$ can also explain the SC pseudogap and the SC phase $T_c$ should have been below them.

We plot the $J_c$ dependence of the RVB order parameters $\Delta$ at optimized doping $\delta = 0.03$ in Fig.2. From Fig.2, we find that the moduli of the intralayer NN RVB order parameters $\Delta_1$ are much larger than the intralayer NNN and interlayer NN ones, $\Delta_2$ and $\Delta_3$ or $\Delta_4$ because $J_1 \gg J_2, J_c$. Therefore, the SC pairing symmetry mainly depends on the intralayer NN gap functions $\Delta_{\alpha\beta}(k)$. With the increase of $J_c$, all the RVB order parameters $\Delta_{1-4}$ increase monotonically, as shown in Fig.2, suggesting that the stronger the interlayer spin fluctuations are, the larger the SC pairing forces are.

Figure 3. (Color online) Hole doping concentration dependence of the moduli of the RVB order parameters $\Delta$ for $J_c = 4.2 \text{ meV}$ in 3D $\text{In}_3\text{Cu}_2\text{VO}_9$.

To get insight into the evolution of the SC pairing on the doping concentration, we plot the dependence of the RVB order parameters on the doping concentration of the holes in Fig.3. From Fig.3, we find that with the increase of doping hole $\delta$, all the moduli of the RVB order parameters $\Delta_1, \Delta_2, \Delta_3, \Delta_4$ decrease with the increase of $\delta$, until $\delta = 0.06$. After $\delta > 0.06$, the situation is rather abnormal. Since these order parameters $\Delta_{1-4}$ slightly increase with the
increase of doping concentration. This seems to show that there exists a second SC phase, which
deserves further study in the near future.

The SC paring symmetry is an important property for the present unconventional SC in doped
In$_3$Cu$_2$VO$_9$. Our analysis shows that the intralayer NN SC gap functions $\Delta_{\alpha\beta}(k)$ support the
$d_{x^2-y^2} + id_{xy}$ symmetry, since the mean-field solution $\Delta_{\alpha\beta}(k) = \Delta_1 e^{i2\pi(n_r-1)/3}$, here $n_r$ is the
serial number of $r$. This confirms the $C_3$ symmetry of the SC pairing order parameters [6]. The
intralayer NNN SC order parameters $\Delta_{\alpha\alpha}(k) = \Delta_2 e^{i2\pi(n_r-1)/3}$, which is also consistent with the
$C_3$ symmetry. Thus the intralayer NNN gap function $\Delta_{\alpha\alpha}(k)$ also satisfies the $d_{x^2-y^2} + id_{xy}$
symmetry. Meanwhile, the interlayer NN SC order parameters are real. Therefore, totally
speaking, doped In$_3$Cu$_2$VO$_9$ supports a SC ground state with a $d_{x^2-y^2} + id_{xy}$ pairing symmetry.

4. Conclusion

In summary, we have shown that in the presence of interlayer spin frustrations and quantum
fluctuations in doped 3D In$_3$Cu$_2$VO$_9$, the possible highest SC transition temperature $T_c \approx 4$ K
at optimum doping hole concentration $\delta = 0.03$ and the SC phase disappears at $\delta = 0.06$. The
interlayer NN exchange coupling is beneficial to the formation of SC pairing, since the SC order
parameters obtained by the mean field method increase with lifting $J_c$, though its enhancement
to $T_c$ is not significant. In contrast, our Slave boson solution shows that the intralayer NN
RVB order parameters $\Delta_1$ increase almost linearly with the lifting of $J_c$, and the holon hopping
parameters $P_{\alpha\beta}$ decrease almost linearly. Therefore, the interlayer spin frustrations and quantum
fluctuations favor to the possible superconductivity in doped In$_3$Cu$_2$VO$_9$. We expect more
experiments to verify our prediction.

Acknowledgments

This work was supported by the National Science Foundation of China under Grant no. 11474287
and 11274310. Numerical calculations were performed at the Center for Computational Science
of CASHIPS.

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