Supersolid phases of a doped valence-bond quantum antiferromagnet: Evidence for a coexisting superconducting order parameter

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Motivated by numerical evidence of the valence bond groundstate of the two-dimensional Heisenberg pyrochlore lattice, we argue using a $t$-$J$ model that it evolves under doping into novel phases characterized by superconductivity coexisting with the underlying valence-bond solid order. A fermionic mean-field theory supplemented by exact diagonalization results provide strong arguments in favor of the stability of such supersolid phases. The resemblance with modulated superconducting patterns in high-$T_c$ cuprates as well as possible relevance to frustrated noncuprate superconductors such as spinels and pyrochlores is discussed.

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The so-called supersolid (SS) $^1$, an exotic state of matter that breaks both the spatial lattice translation symmetry and the internal $U(1)$ symmetry, associated with particle number conservation, has attracted much attention following its possible discovery in the solid phase of $^4$He $^2$. On the one hand, studies of various models with hard-core bosons on a frustrated triangular lattice demonstrate that bosons may condense forming a superfluid on top of the crystalline background $^3$. Moreover, there has been a convergence of agreement concerning nonuniform condensation of magnons in spin models with external magnetic field $^4$, suggesting an exciting possibility of the formation of a spin SS in real quantum magnets. On the other hand, high-$T_c$ superconductivity potentially described by the resonating valence bond (RVB) state on the square lattice with a superconducting (SC) parameter of $d$-wave orbital symmetry turns out to be robust against spontaneous breaking of translation symmetry $^5, 6$. Hence, charge order coexisting with modulated SC order in Ca$_{2-x}$Na$_x$CuO$_2$Cl$_2$ revealed by recent scanning tunneling microscopy $^7$ may well have an extrinsic origin $^8$.

It is therefore legitimate to question the relevance of a fermionic analog of the bosonic SS and its possible stabilization by geometrical magnetic frustration. In this respect, among of two-dimensional structures, the quantum antiferromagnet on the checkerboard lattice (see Fig. 1) provides a priori conducive conditions to the appearance of a fermionic SS upon doping. Let us briefly summarize remarkable properties of the checkerboard lattice: (i) Made out of corner-sharing plaquettes with crossed bonds, it might be considered as a projection of a more realistic corner-sharing tetrahedra pyrochlore lattice known to host superconductivity, e.g., spinel LiTi$_2$O$_4$, as well as $\alpha$-Cd$_2$Re$_2$O$_7$ and $\beta$-pyrochlore KO$_{5.5}$O$_6$ $^4$. (ii) Exact diagonalization (ED) $^9$ and other intensive studies of the spin-$1/2$ Heisenberg model on the checkerboard lattice $^{10}$ suggest that its ground state is twofold degenerate being a product of plaquette singlets. It breaks translation symmetry while preserving the $C_{4v}$ rotation symmetry around the center of the void plaquette and as such it is a good example of a valence bond crystal (VBC) $^{12}$; (iii) Lastly, particularly important suggestion for supersolidity in this case comes from a recent discovery of hole pairing $^{13}$, since alone the existence of a spin gap at half-filling is not sufficient to guaranty SC behavior at finite doping $^{14}$.

In this Letter we show that a fermionic valence bond supersolid (VBSS), characterized by the coexistence of the SC order parameter and solid component of spin singlet order, can appear by doping the VBC characterizing the Mott phase of some frustrated lattices like the checkerboard lattice. Interestingly, such a scenario has close correspondence with the RVB theory in which the translationally invariant $d$-wave superconductor emerges out of the spin-liquid Mott phase. The alternative that the VBC is destroyed upon doping leading to an exotic $d+id$ and $d+is$ superconductor $^{15}$ with broken time-

![FIG. 1: (color online) Schematic pattern of $d_{(\pi,\pi)}$-VBSS (a) and $s_{(\pi,\pi)}$-VBSS (b) phases. In the checkerboard lattice, diagonal bonds are on every second plaquettes. Rotation symmetry of the pairing amplitude $\Delta_{ij}$ reduces the number of inequivalent bonds down to three. The line widths of these bonds labelled by $a$ (running from 1 to 3) are proportional to the magnitude of the corresponding spin-spin correlations (for $t'/t = -1$). Different types of those lines (solid and dashed) correspond to opposite signs of $\Delta_a$.](cond-mat.str-el)
reversal symmetry is being reconsidered \[16\]. In contrast, we find a very rich phase diagram with various VBSS phases as summarized in Fig. 2. These phases differ from their bosonic analog not only in the way lattice symmetry is broken, exhibiting bond modulation rather than charge order but, in addition, from the fact that off-diagonal and solid orders involve different (charge and spin) degrees of freedom.

To address this intriguing issue, we consider a $t$-$J$ model on the checkerboard lattice, at doping $x = 1 - n$, $n$ being the electron density (per site):

$$\mathcal{H} = - \sum_{(ij),\sigma} t_{ij} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + h.c.) + \sum_{(ij)} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1)$$

where the sums run over all bonds of the checkerboard lattice. For sake of generality, we allow for different hopping amplitudes and antiferromagnetic superexchange couplings on the diagonal bonds, $t_{ij} = t'$ and $J_{ij} = J'$, and on the vertical and horizontal bonds, $t_{ij} = t$ and $J_{ij} = J$. Note that under electron-hole transformation $t'$ changes into $-t'$ so that hole and electron doping correspond to opposite signs of $t'$ (while $t > 0$ can always be assumed). Hereafter, we assume a typical value $t/J = 3$ and set $J'/J = (t'/t)^2$ which follows from the superexchange relation $J = 4t^2/U$ valid in the large $U$ limit of the Hubbard model. Next, we replace local constraints that restrict electron creation operators $\hat{c}_{i\sigma}^\dagger$ to the subspace with no doubly occupied sites by statistical Gutzwiller weights, while decoupling in both particlehole and particle-particle channels yields a renormalized mean-field theory (RMFT) Hamiltonian \[17\],

$$H = - \sum_{(ij),\sigma} g_{ij}^t t_{ij} (c_{i\sigma}^\dagger c_{j\sigma} + h.c.) - \mu \sum_{i,\sigma} n_{i,\sigma}$$

$$- \frac{3}{4} \sum_{(ij),\sigma} g_{ij}^t J_{ij} (\chi_{ij} c_{i\sigma}^\dagger c_{j\sigma} + h.c. - \chi_{ij}^2)$$

$$- \frac{3}{4} \sum_{(ij),\sigma} g_{ij}^t J_{ij} (\Delta_{ij} c_{i\sigma}^\dagger c_{j\sigma} + h.c. - |\Delta_{ij}|^2), \quad (2)$$

with the Bogoliubov-de Gennes self-consistency conditions for the bond- $\chi_{ij} = (c_{j\sigma}^\dagger c_{i\sigma})$ (assumed here to be real) and pair-order $\Delta_{ij} = (c_{i-\sigma}^\dagger c_{j\sigma} - c_{i\sigma}^\dagger c_{j-\sigma})$ parameters in the unprojected state that we solve on a $48 \times 48$ cluster at low temperature $\beta J = 200$. Note that since we restrict our study to strong frustration ($|t'| \approx t$), we do not consider here long-range antiferromagnetic order, known to coexist with superconductivity at low doping on the square lattice \[18\]. Finally, to allow for small nonuniform charge modulations (if any), the Gutzwiller weights have been expressed in terms of local doped hole densities $x_i = 1 - \sum_{\sigma} (c_{i\sigma}^\dagger c_{i\sigma})$ as $g_{ij}^t = \sqrt{x_i x_j}$ and $g_{ij} = (2 - z_i)(2 - z_j)$ with $z_i = 2x_i/(1 + x_i)$.

We mostly concentrate here on the $t' < 0$ case with emergent supersolidity. Guided by the earlier studies at half-filling \[11\], in addition to usual $d$- and $s$-RVB superconductivity we also allow for coexisting VBC order in the mean-field equations. The $d$-wave symmetry \[17\] is a natural choice compatible with the required $C_4$ rotation symmetry of $|\Delta_{ij}|$ around the centers of void plaquettes (bonds labeled by 1 in Fig. 1). It yields at half-filling a strong insulating VBC with decoupled void plaquette singlets (i.e. $\chi_a = \Delta_a = 0$ on the $a = 2, 3$ bonds) which provides the lowest magnetic energy $E_J/J = -3/4$ in good agreement with numerics \[10\]. Upon finite doping $x$, an additional $\Delta_3$ component arises along the diagonals as depicted in Fig. 1(a). Unit cell doubling together with $d$-wave symmetry implies a $(\pi, \pi)$ phase modulation of $\Delta_3$ so that this phase is referred to as $d(\pi, \pi)$-VBSS. In fact, away from half-filling, another SS state, labeled by $s(\pi, \pi)$-VBSS and shown in Fig. 1(b), is competing with the $d(\pi, \pi)$-VBSS. In this phase, all neighboring void plaquettes have opposite signs of the pairing parameters and $s$-wave rotation symmetry on every void plaquette.

The spontaneous lattice symmetry breaking of the discovered VBSS phases is seen in Fig. 3(a-d) showing bond charge hopping $T_a = 2g_a^t \chi_a$ and spin-spin correlations $S_a = -4g_a^t (\chi_a^2 + |\Delta_a|^2)$ (corresponding to the two terms of Eq. 1, respectively) on the three inequivalent bonds defined in Fig. 1. The $s(\pi, \pi)$-VBSS is characterized by a weaker modulation of $S_a$ as compared to its $d$-wave counterpart. Even though the $d$-wave RVB order is known to yield a better kinetic energy than the $s$-wave RVB one \[17\], the $s(\pi, \pi)$-VBSS has better total kinetic energy $E_t$ \[10\] due to the absence of phase modulation in the pairing $\Delta_3$. Next, in Fig. 3(e,f), we present the SC order parameter components $\Delta_{ij}^{SC}$ which are related in RMFT to pairing amplitudes by $\Delta_{ij}^{SC} = g_{ij}^t \Delta_{ij}$ and hence vanish as expected at half-filling \[11\]. Remarkably, all of them show a non-monotonic dome shape as a function of...
doping. Although the Gutzwiller RMFT is a zero temperature scheme, we expect that SC properties will be boosted to higher temperatures compared to the $d$-RVB phase with $t' = 0$. Note that VBC and SC orders can give rise to separate critical $T_c$. Finally, the low-energy fermionic quasiparticle band structures of the SS phases are shown in Fig. 4. Interestingly, in the $d_{(\pi,\pi)}$-VBSS, the $\Delta_3 s$-wave component on the diagonal bonds suppresses the usual zero-energy Dirac cone of the $d$-wave superconductor along its $(0,0)-(\pi/2,\pi/2)$ nodal direction. Upon further doping, a gapless spectrum is recovered in the $d$-RVB phase with $\Delta_3 = 0$ due to melting of the valence bond order. In contrast, the energy gap of the $s_{(\pi,\pi)}$-VBSS is less modulated as expected for isotropic pairing.

It is known that doping a Mott insulator can lead to phase separation (PS), i.e., a macroscopic segregation into two phases, commonly the undoped phase and a phase with a finite doping [19]. Hence, we have performed the standard Maxwell construction and calculated the slope of the ground state energy density $S(x) = [E(x) – E(0)]/x$ as a function of doping $x$. Technically, PS is signaled by a negative curvature of $E(x)$ when $x \rightarrow 0$ (i.e., a negative compressibility) and a minimum of $S(x)$ at a given doping $x_c$ (cf. Fig. 5). We expect that below $x_c$ the system phase separates into a two-component mixture of the undoped ($x=0$) VBC and a doped phase (see the phase diagram) with $x = x_c$. Note that other phase separated mixtures which could in principle appear in the vicinity of some first-order transitions within the $0 < x < x_c$ region (seen e.g. as kinks in Fig. 5) are here prevented by the PS between the above-mentioned “extremal” phases.

We now briefly discuss the case $t' > 0$. First, under doping, the emergent $d_{(\pi,\pi)}$-VBSS is now much more fragile w.r.t. the melting of the VBC order. Secondly, a smaller range of stability is found for the $d$-RVB phase compared to the previous $t' < 0$ case consistently with the strong electron-hole asymmetry of pairing found in numerics [13 21]. On top, as deduced from the Maxwell construction shown in Fig. 5(b), these narrow VBSS and $d$-RVB regions appear to be unstable towards PS between a hole-free VBC and a homogeneous metallic Fermi liquid (FL) with $x = x_c \simeq 0.15$ at $t' = t$.

Our findings are summarized in a global RMFT phase diagram in the $(x, |t'/t|)$ plane reported in Fig. 2. It emphasizes the crucial role of the frustration in stabilizing the VBSS states for $t' < 0$. Indeed, increasing frustration strength $|t'/t|$ shifts the second-order phase transition to the nearby $d$-wave RVB phase towards higher...
doping level. A region of \(s_{(\pi, \pi)}\)-VBSS is squeezed into a narrow range 0.94 \(\lesssim |t'/t| \lesssim 1.07\) limited below (above) by a first-order phase transition line to the \(d_{(\pi, \pi)}\)-VBSS (s-RVB) phase. In fact, for maximum frustration, both \(d_{(\pi, \pi)}\)- and \(s_{(\pi, \pi)}\)-VBSS states extend up to quarter-filling \(x = 1/2\) where they merge to a VBC similar to the one at half-filling (albeit with no pairing, i.e., \(\Delta_0 = 0\)). Note that in the whole PS region, the role of the so far neglected long-range Coulomb repulsion will become important and lead to microscopic (possibly stripe-like) PS instead of true macroscopic PS. Also, although quantum fluctuations can play an important role, here we can nevertheless provide simple additional arguments supporting our mean-field phase diagram. First of all, the large spin fluctuations can play an important role, here we can nevertheless provide simple additional arguments supporting our mean-field phase diagram. First of all, the large spin fluctuations can play an important role, here we can nevertheless provide simple additional arguments supporting our mean-field phase diagram. First of all, the large spin fluctuations can play an important role. In agreement with Variational Monte Carlo simulations for \(t' = 0\) [21].

Experimentally, examples where spatial frustration and superconductivity coexist are KO\(_2\)O\(_6\) and Li\(_2\)Ti\(_2\)O\(_4\). Although electron correlations are usually associated to nodal pairing, recent experiments show the evidence for fully gapped superconductivity in both compounds [22], so conventional phonon-mediated pairing has been advocated. However, our results indicate that, on a strongly frustrated lattice, electron correlations can also lead to gapful pairing and a modulated structure. We also note that, despite interesting similarities, the \(C_{4v}\)-symmetric VBSS states differ from the unidirectional \(C_{2v}\) SS found on the square lattice of Ca\(_2\)CuO\(_2\)Cl\(_2\) [7] by the absence of spatial modulation in the local hole density.

In summary, we have shown that the interplay between electron correlations and geometrical frustration can stabilize novel states of matter exhibiting microscopic coexistence of superconductivity and spin dimer-crystalline order. In contrast to the inhomogeneous superconductor of the frustrated Shastry-Sutherland lattice which is disconnected from the half-filled dimer ground state [23], fermionic supersolids emerge naturally upon doping a parent Mott insulator with spontaneous spin dimer order. We have identified on the checkerboard lattice two different competing supersolids with either \(s\)-wave or \(d\)-wave pairing symmetry w.r.t. the centers of the void plaquettes. We believe that our findings open a new route to search for new exotic frustrated superconductors.

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In our Letter, we have provided strong arguments in favor of the formation of a fermionic valence bond supersolid (VBSS) on the checkerboard lattice. It is a new alternative scenario to the one in which the valence bond crystal (VBC) known to set in at half-filling \[10, 11\] is destroyed upon doping while frustration produces an exotic \(d+id\) and \(d+is\) superconductivity with broken time-reversal symmetry \[12\]. Hence, we have applied the renormalized mean-field theory (RMFT) to study the stability of various VBSS structures on equal footing with the \(d+id\) and \(d+is\) superconductors that preserve the translation symmetry of the lattice. The results for two representative cases: half-filling \(x = 0\) and \(x = 1/4\) doping (the latter chosen to be outside the expected phase separated region) are summarized in Table I. They clearly show that the half-filled Mott insulating ground state corresponds to the VBC with \(d\)-wave (spin) pairing amplitude and has substantially better energy as compared to the next low-energy \(d+id\) order. Under doping it evolves into \(d_{(\pi,\pi)}\)-VBSS (in fact, thermodynamically unstable towards phase separation below a small critical doping). Further doping results in a first-order phase transition towards a new \(s\)-wave superconducting ground state which is found to coexist with (spin dimer) crystalline order forming thus the \(s_{(\pi,\pi)}\)-VBSS. Note also that around \(x = 1/4\) a simple homogeneous \(s_{(\pi,\pi)}\)-RVB phase\(^1\) with the same pairing symmetry as the \(s_{(\pi,\pi)}\)-VBSS (but with \(|\Delta_1| = |\Delta_2|\) and \(\Delta_3 = 0\)) also becomes very competitive.

\(^1\) Similar “plaquette” SC state appears on the Shastry-Sutherland lattice, see B.-J. Yang, Y. B. Kim, J. Yu, and K. Park, Phys. Rev. B 77, 104507 (2008).

| phase              | \(x = 0\) | \(x = 1/4\) |
|--------------------|------------|-------------|
| \(s\)-RVB          | –          | –2.0848     | –1.7928   |
| \(d+is\)           | –          | –2.0868     | –1.7859   |
| \(s_{(\pi,\pi)}\)-RVB | –0.5944    | –2.1064     | –1.7954   |
| \(s_{(\pi,\pi)}\)-VBSS/VBC | –0.6134    | –2.1062     | –1.7945   |
| \(d\)-RVB          | –0.6884    | –2.0776     | –1.7752   |
| \(d+id\)           | –0.6886    | –          |          |
| \(d_{(\pi,\pi)}\)-VBSS/VBC | –0.7500    | –2.0980     | –1.7729   |

Table I: Site-normalized RMFT energy \(E\) and kinetic energy \(E_t\) of various wave functions considered in our Letter obtained for \(t'/t = -1\). Pure \(s\)-RVB and \(d+is\) phases converge at half-filling to a homogeneous Fermi liquid; \(d+id\) phase is unstable at \(x = 1/4\) towards \(d\)-RVB.