PHYSICAL REVIEW B VOLUME 54, NUMBER 13 1 OCTOBER 1996-I

# Valence-bond crystal phase of a frustrated spin-$\frac{1}{2}$ square-lattice antiferromagnet

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(Received 18 June 1996)

We propose a magnetically disordered ground state for a frustrated quantum antiferromagnet. This disordered state is an array of spin singlets spontaneously formed on four spin plaquettes. Both perturbation results and bond-operator calculations show that this phase has lower energy than the columnar dimer state. Analysis of available numerical data on finite clusters also supports the conclusion that this state is realized at intermediate frustrations. [S0163-1829(96)06837-3]

Frustrated two-dimensional quantum magnets have been a fascinating topic of numerous studies over the past decade. The interest has primarily focused on melting of long-range magnetic order and the appearance of disordered phases at $T=0$ as a result of enhanced quantum fluctuations. The simplest spin system having such a type of behavior is a frustrated square-lattice Heisenberg model with the nearest-neighbor antiferromagnetic exchange $J_1$ and the second-neighbor coupling $J_2$

$$\mathcal{H}=J_1\sum_{\mathrm{NN}} \mathbf{S}_i\cdot\mathbf{S}_j+J_2\sum_{\mathrm{2NN}} \mathbf{S}_i\cdot\mathbf{S}_j\,. \tag{1}$$

Analysis within the linear spin-wave theory reveals that for weak frustration the model has a Néel ground state, while for strong frustration spins are ordered at wave vector $(\pi,0)$ or $(0,\pi)$ (stripe or collinear state). For any finite $S$ there is a region around the classical critical point $J_2/J_1=0.5$ where sublattice magnetization vanishes.[1] This result raises a question about the ground state for intermediate frustrations which may be nonmagnetic and represent a kind of two-dimensional spin liquid.

Subsequent theoretical works have considered the problem of the intermediate phase of the frustrated antiferromagnet Eq. (1) mainly from three different points of view. The first group includes exact diagonalization studies on finite clusters, which clearly show existence of a disordered spin state in the region $0.4<J_2/J_1<0.65$, though a final conclusion about its nature has not been reached.[2,3] The second group of works address the problem by calculating higher-order $1/S$ corrections either in the framework of the modified spin-wave theory or using the Schwinger boson mean-field calculations.[4,5] Both approaches predict enhanced stabilities for the Néel and the collinear states resulting in a finite overlap of the magnetically ordered phases. Second-order corrections to the mean-field solution, on the other hand, suggest a small window $0.52<J_2/J_1<0.57$ between the two ordered states for $S=\frac{1}{2}$.[6]

The third group of works explore one particular possibility for the disordered ground state—a valence-bond crystal with broken translational symmetry and a finite gap in the excitation spectrum. Investigation of a nearest-neighbor SU $(N)$ antiferromagnet in the $N\gg 1$ limit has led to the conclusion about spontaneous columnar dimerization in the ground state.[7] Subsequent calculations for the spin-$\frac{1}{2}$ Hamiltonian Eq. (1) using series expansion[8] and boson techniques[9] supported stability of this phase around $J_2=0.5J_1$. Cluster results for dimerized susceptibility also yield its noticeable increase in the intermediate region.[2,3]

In this paper we propose a valence-bond crystal ground state of a frustrated spin-$\frac{1}{2}$ antiferromagnet Eq. (1). This is the plaquette state shown in Fig. 1(a). We calculate its energy by two methods and find that it is lower than for the columnar dimerization [Fig. 1(b)] in the same approximation. Then, by considering relevant order parameters, we show that the existing numerical data on the $6\times 6$ cluster[3] are, as a matter of fact, in favor of this state.

Two types of magnetically disordered singlet ground states have been widely discussed for a quantum square-lattice antiferromagnet. The first one is a featureless resonating-valence-bond (RVB) spin-liquid with long- or short-range correlations.[10] The second proposal is a spin-Pierls order of valence bonds which are frozen and break lattice symmetries.[7] There is also an intermediate situation: valence bonds resonate in finite spin blocks, which in the simplest case contain four lattice sites. This type of a disordered spin phase has earlier appeared as an unstable solution

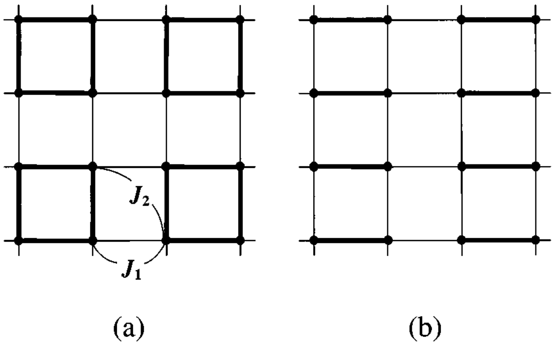

FIG. 1. (a) plaquette-RVB and (b) columnar dimer ground states; bold lines denote stronger spin bonds.

for the nearest-neighbor SU($N$) antiferromagnet which becomes degenerate with the columnar dimer state in the $N\rightarrow\infty$ limit only.[11] Considering the physical SU(2)-spin model with frustration Eq. (1) we come to the opposite conclusion about the energies of the two valence-bond crystals.

Similarly to discussion of dimerized phases, the first step is to investigate a restricted Hamiltonian of four spins on a square plaquette:

$$\mathcal{H}_{\rm plq}=J_1(\mathbf{S}_1+\mathbf{S}_3)\cdot(\mathbf{S}_2+\mathbf{S}_4)+J_2(\mathbf{S}_1\cdot\mathbf{S}_3+\mathbf{S}_2\cdot\mathbf{S}_4). \tag{2}$$

This Hamiltonian is easily diagonalized. The ground level for $J_2<J_1$ is a singlet characterized by the quantum numbers $S_{13}=S_{24}=1$ with the energy $E_s=-2J_1+\frac{1}{2}J_2$. Its wave function is $|s\rangle=(1/\sqrt{3})$ ([1,2][4,3]+[1,4][2,3]), where square brackets denote the singlet bond of a spin pair. This state can be considered as a RVB-like state in a four-spin subsystem with energy lower than for a frozen dimer configuration, e.g., [1,2][4,3]. Excited levels are three triplets $|t_\alpha\rangle$, $|p_\alpha\rangle$, $|q_\alpha\rangle$ $(\alpha=x,y,z)$, $E_t=-J_1+\frac{1}{2}J_2$, $E_p=E_q=-\frac{1}{2}J_2$, a quintet $|d_\nu\rangle$ $(\nu=1,\ldots,5)$, $E_d=J_1+\frac{1}{2}J_2$, and another singlet $|s'\rangle=[1,2][4,3]-[1,4][2,3]$, $E_{s'}=-\frac{3}{2}J_2$, which crosses with $|s\rangle$ and becomes the ground state for $J_2>J_1$.

Four spin singlets form a plaquette covering of a two-dimensional lattice. Previously, the plaquette-RVB state has been predicted for the disordered two-dimensional magnet CaV$_4$O$_9$, which is described by a spin-$\frac{1}{2}$ Heisenberg model on a 1/5-depleted square lattice.[12] In that case singlets correspond to spin blocks chosen by the lattice geometry. For the translationally invariant Hamiltonian Eq. (1) periodic array of plaquette singlets appears spontaneously. The ground state has in this case fourfold degeneracy determined by broken translations along two sides and diagonal of an elementary square. Using simple rules for products of dimer coverings[10] one can show that the overlap between the two states in Fig. 1 formed by pure singlets decreases to zero as $(\sqrt{3}/2)^{N/4}$ with increasing number of spins $N$. Consequently, the plaquette state cannot be represented as a superposition of two column states rotated by 90° with respect to each other. Later, we consider spin order parameters, which have different values for the two disordered phases.

Since the Hamiltonian Eq. (1) includes interaction of spins from different blocks, the ground state does not coincide with a simple product of block singlets and nonzero expectation values $\langle\mathbf{S}_i\cdot\mathbf{S}_j\rangle$ appear between all nearest-neighbor pairs. To compare energies of the columnar dimer and the plaquette-RVB phases we use a boson technique suited for perturbative analytical expansion around the local spin singlets. It was used previously to study dimerized phases.[9] We first generalize this method by deriving simultaneously boson representations for dimer and plaquette spins and then calculate energies of the two states in the mean-field approximation.

Let us consider an arbitrary spin block with singlet ground state and excited levels denoted by $|\mu\rangle$. A spin $\mathbf{S}_n$ in a block is expressed in terms of the basis states by

$$\mathbf{S}_n=\langle\mu|\mathbf{S}_n|\nu\rangle Z^{\mu\nu},$$

where $Z^{\mu\nu}$ is the projection operator $|\mu\rangle\langle\nu|$, $n$ is a local spin index inside the block, and the global block index in the lattice $i$ is omitted for brevity. We derive first the matrix elements in a subspace of the ground-state singlet and the lowest triplet states. These states form a complete set for dimers, whereas for plaquettes this is only a part of the local basis. Later, we partially take into account higher-energy states of plaquettes. Rotational invariance in spin space and time-reversal symmetry give

$$\langle s|\mathbf{S}^\alpha_n|s\rangle=0,\quad \langle s|\mathbf{S}^\alpha_n|t_\beta\rangle=\delta_{\alpha\beta}A^n_{st},$$

$$\langle t_\alpha|\mathbf{S}^\beta_n|t_\gamma\rangle=ie^{\alpha\beta\gamma}A^n_{tt},$$

where $e^{\alpha\beta\gamma}$ is the totally antisymmetric tensor and $A^n_{st}$ $A^n_{tt}$ are real constants. Using the explicit forms of singlet and triplet wave functions one straightforwardly gets $A^n_{st}=(-1)^n/2$, $A^n_{tt}=1/2$ for dimers, and $A^n_{st}=(-1)^n/\sqrt{6}$, $A^n_{tt}=1/4$ for plaquettes. Let us now define the vacuum $|0\rangle$ and four boson operators which yield the four physical states by $|s\rangle=s^+|0\rangle$, $|t_\alpha\rangle=t^+_\alpha|0\rangle$. The projection operators are expressed as $Z^{st_\alpha}=s^+t_\alpha$, $Z^{t_\alpha t_\beta}=t^+_\alpha t_\beta$, and so on. Block spins represented via these boson operators are

$$S^\alpha_n=\frac{(-1)^n}{2}(s^+t_\alpha+t^+_\alpha s)-\frac{i}{2}e^{\alpha\beta\gamma}t^+_\beta t_\gamma,\quad\text{for dimers,}$$

$$S^\alpha_n=\frac{(-1)^n}{\sqrt{6}}(s^+t_\alpha+t^+_\alpha s)-\frac{i}{4}e^{\alpha\beta\gamma}t^+_\beta t_\gamma,\quad\text{for plaquettes.} \tag{3}$$

Spin commutation relations are satisfied in the chosen subspace as long as the boson representation preserves the algebra of the projection operators: $Z^{\mu\nu}Z^{\mu'\nu'}=\delta_{\mu'\nu}Z^{\mu\nu'}$. This requirement restricts the boson occupation numbers:

$$s^+s+\sum_\alpha t^+_\alpha t_\alpha=1. \tag{4}$$

With this constraint the Hamiltonian of a single block, a dimer or a plaquette, takes a form, $\mathcal{H}_B=E_s s^+s+E_t t^+_\alpha t_\alpha$. The simplest way to deal with Eq. (4) is to impose it as ‘‘a constraint in average’’ enforced by a chemical potential.

Further calculations follow closely the work by Sachdev and Bhatt.[9] Using Eq. (3) we rewrite the Hamiltonian Eq. (1) in terms of bond operators for each of the two phases and assume a site-independent chemical potential $\mu$ and condensate of singlets $\langle s_i\rangle=\overline{s}$. Interaction terms in the boson Hamiltonian are classified by the number of triplet operators $t_{\alpha\mathbf{k}}$. It can be shown that the terms with three and four triplet operators affect the results only slightly.[9] Therefore, we omit them and after diagonalization of the quadratic form determine the parameters $\mu$ and $\overline{s}$ through the saddle-point equations

$$\partial E_{\rm gs}/\partial\mu=0,\quad \partial E_{\rm gs}/\partial\overline{s}=0. \tag{5}$$

The system is in a magnetically disordered phase if the gap in the excitation spectrum is positive. Vanishing of the gap leads to a condensation of triplet excitations: $\langle t_{i\alpha}\rangle\neq 0$. Note, that this does not mean transition, e.g., to the usual Néel state, since spontaneous dimerization of bonds will be preserved in such an ordered phase.

For the columnar dimer state we recover the results of Ref. 9. This state is stable in the region $0.19<J_2/J_1<0.66$.

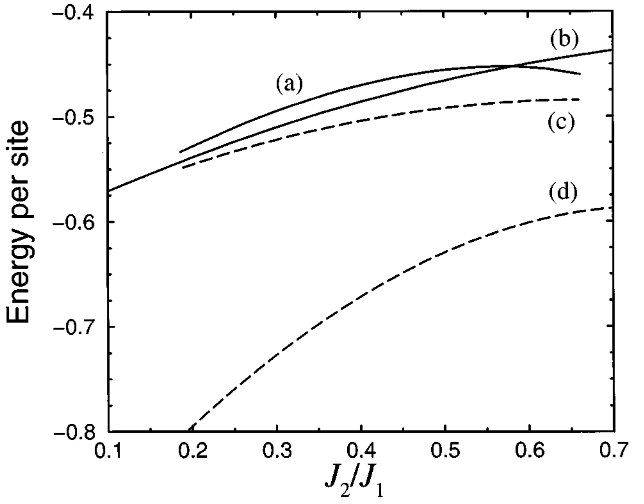

FIG. 2. Energies (in units of $J_1$) of (a) columnar dimerized and (b) plaquette-RVB phases calculated by bond-operator technique; (c) and (d) for the same phases by the second-order perturbation theory.

For the plaquette phase analogous treatment would underestimate the energy because of the neglection of the higher-lying states of the plaquette. Among the other excited levels the most significant energy corrections are given by higher triplets which have nonzero matrix elements with the ground state for spin operators. Extending calculations preceding Eq. (3) to these excited triplets we find the following representation of spins in each plaquette:

$$\begin{aligned} S^{\alpha}_{1,3}&=\frac{1}{\sqrt{6}}(s^{+}t_{\alpha}+t^{+}_{\alpha}s)\pm\frac{1}{2\sqrt{3}}(s^{+}p_{\alpha}+p^{+}_{\alpha}s),\\ S^{\alpha}_{2,4}&=-\frac{1}{\sqrt{6}}(s^{+}t_{\alpha}+t^{+}_{\alpha}s)\pm\frac{1}{2\sqrt{3}}(s^{+}q_{\alpha}+q^{+}_{\alpha}s), \end{aligned} \tag{6}$$

with the constraint Eq. (4) being changed to $s^{+}s+\Sigma_{\alpha}(t^{+}_{\alpha}t_{\alpha}+p^{+}_{\alpha}p_{\alpha}+q^{+}_{\alpha}q_{\alpha})=1$. According to the quadratic approximation we have omitted in Eq. (6) products of two triplet operators. The boson Hamiltonian obtained with this substitution can be further simplified by keeping interaction terms with only one of the higher triplets $p_{\alpha}$ and $q_{\alpha}$. Physically, this means that we take account of higher-lying triplets only via scattering of lowest excitations on them. As a result, one mode in the upper band remains constant, while the other acquires a finite dispersion.

Solution of the saddle-point equations (5) gives us parameters $\mu$ and $\bar{s}$, from which we calculate energy and spin gap of the plaquette-RVB phase. This disordered state is locally stable for $J_2>0.08J_1$. For large frustrations the stability boundary of this phase lies at $J_2>0.8J_1$, well inside the region where the collinear state is expected to appear. This boundary cannot be determined correctly in our approximation as it depends crucially on the behavior of the neglected higher singlet. Therefore, we restrict ourselves to the region $J_2\leqslant 0.7J_1$. At $J_2=0.5J_1$, the gap of the plaquette state is $\Delta_{\mathrm{plq}}=0.85J_1$, while for the column state $\Delta_{\mathrm{dmr}}=0.74J_1$. The results for the energies of these two phases in units of $J_1$ are presented in Fig. 2 by solid lines. In addition to significantly wider region of stability, the plaquette phase has lower energy than the dimerized state for $J_2<0.58J_1$. At $J_2=0.5J_1$ the difference between the two energies, $E_{\mathrm{plq}}=-0.466$ and $E_{\mathrm{dmr}}=-0.456$, is about 2%. (Without higher triplets $E_{\mathrm{plq}}=-0.458$.) Thus, the bond-operator formalism predicts the plaquette-RVB state instead of the columnar dimer state as the intermediate phase of the frustrated antiferromagnet Eq. (1).

Another way to estimate analytically the energies of the two valence-bond states is the second-order perturbation expansion starting from the singlets either on dimers or on plaquettes. This approximation corresponds to the first two nonzero terms in the series expansion method.[8] The results are shown in Fig. 2 by dashed lines. At $J_2=0.5J_1$ the difference between $E_{\mathrm{plq}}=-0.63$ and $E_{\mathrm{dmr}}=-0.492$ is much bigger than in the bond-operator scheme. Though significant corrections are expected in higher orders of series expansions, these calculations agree with our proposal of the plaquette state for the ground state of the Hamiltonian Eq. (1).

Both results for the energies of the two disordered phases have been obtained by approximate analytical methods and, hence, may be questioned. We, therefore, now discuss how to distinguish the column and the plaquette phases in exact numerical diagonalization studies. The key step is to construct appropriate order parameters, which measure nonequivalence of spin bonds in a disordered state. A set of such spin operators have been proposed by Sachdev.[13] The appearance of the column phase has been tested[2,3] by using the parameter

$$\Psi_{\mathbf{i}}=\mathbf{S}_{\mathbf{i}}\cdot[(-1)^{i_x}(\mathbf{S}_{\mathbf{i}-\hat{\mathbf{x}}}-\mathbf{S}_{\mathbf{i}+\hat{\mathbf{x}}})+i(-1)^{i_y}(\mathbf{S}_{\mathbf{i}-\hat{\mathbf{y}}}-\mathbf{S}_{\mathbf{i}+\hat{\mathbf{y}}})]. \tag{7}$$

This operator is proportional to $1$, $i$, $-1$, and $-i$ for the four degenerate column states. On the other hand, for the four plaquette states $\Psi_{\mathbf{i}}$ equals $e^{i\pi/4}$, $e^{i3\pi/4}$, $-e^{i\pi/4}$, and $-e^{i3\pi/4}$ up to a constant factor. Since in numerical studies on finite systems one measures only the correlation function $\chi_{\psi}=1/N^{2}\langle|\Sigma_{\mathbf{i}}\Psi_{\mathbf{i}}|^{2}\rangle$, it is impossible to distinguish the two states by observing an anomaly in $\chi_{\psi}(J_2)$. To overcome this problem another order parameter should be considered

$$\Phi_{\mathbf{i}}=\mathbf{S}_{\mathbf{i}}\cdot(\mathbf{S}_{\mathbf{i}+\hat{\mathbf{y}}}+\mathbf{S}_{\mathbf{i}-\hat{\mathbf{y}}}-\mathbf{S}_{\mathbf{i}+\hat{\mathbf{x}}}-\mathbf{S}_{\mathbf{i}-\hat{\mathbf{x}}}). \tag{8}$$

For the four column states $\Phi_{\mathbf{i}}$ has values $1,-1,1$, and $-1$, whereas it becomes zero for each of the plaquette states. Consequently, the two crystalline valence-bond states can be distinguished by measuring two quantaties $\chi_{\psi}$ and $\chi_{\phi}$ simultaneously. The parameter $\Phi_{\mathbf{i}}$ coincides with the magnetic structure factor at the wave vector ($\pi$,0) and has been studied to check the difference between the two ordered magnetic phases: $\Phi_{\mathbf{i}}\equiv\mathbf{0}$ in the Néel state, $\Phi_{\mathbf{i}}\neq 0$ in the collinear state. Thus, numerical results for both $\chi_{\psi}$ and $\chi_{\phi}$ are currently available. We refer to the most reliable data obtained on the $6\times 6$ cluster. Figure 3 of Ref. 3 plots two correlation functions $\chi_{\psi}(J_2)$ and $\chi_{\phi}(J_2)$. It is clearly seen that at the peak point of $\chi_{\psi}(J_2)$ the other function differs only slightly from its value at $J_2=0$, whereas $\chi_{\phi}(J_2)$ starts to increase simultaneously with the decreasing of $\chi_{\psi}$. This observation is direct evidence of the plaquette-RVB ground state for the model (1) at intermediate frustrations.

We now turn to physical consequences of the translational symmetry breaking in a magnetically disordered ground state. The first property we address is a nature of the phase transitions at $T=0$. If transformation from such a disordered state to a spin ordered state, e.g., to the Néel state, is continuous, the usual group-subgroup relations should be satisfied for symmetry groups of the two phases. However, this is not the case for the Néel and the plaquette (or columnar dimer) states, since neither the former has a higher symmetry than the latter (because of the absence of rotational invariance in spin space), nor is the latter more symmetric than the former (due to translational symmetry breaking). Analogous arguments are applied to the transition into the collinear state. Thus, the magnetically disordered ground-state region of the model (1) is bounded by two points of first-order transitions. This conclusion explains diverse estimates of its width[4–6,8,9] found by studying *stabilities* of the different phases.

Finally, we comment on the finite temperature behavior of valence bond crystals. As they break only the discrete lattice symmetries, there should be transition from the symmetric paramagnetic phase with decreasing temperature. An analogous conclusion for the collinear state has been reached in Ref. 14. The difference between these two cases lies in the symmetry properties of the corresponding order parameters. At $T\neq 0$, when sublattice magnetization of the collinear phase vanishes, the order parameter is a soft Ising-type quantity $\Phi_{\mathbf{i}}$ having values $+1$ and $-1$ on each lattice site. In this case only the rotational lattice symmetry is broken in the low-temperature phase. Singlet formation in the bond crystalline phases is accompanied by translational symmetry breaking and corresponds to $\mathbf{k}\neq 0$. Bond strength modulations appear at wave vectors $(\pi,0)$ or $(0,\pi)$ for the columnar dimerization and the spin bond order parameter has two components: $\mathbf{S}_{\mathbf{i}}\cdot(\mathbf{S}_{\mathbf{i}-\hat{\mathbf{x}}}-\mathbf{S}_{\mathbf{i}+\hat{\mathbf{x}}})$ and $\mathbf{S}_{\mathbf{i}}\cdot(\mathbf{S}_{\mathbf{i}-\hat{\mathbf{y}}}-\mathbf{S}_{\mathbf{i}+\hat{\mathbf{y}}})$. For each of the four column phases only one component is nonzero. The plaquette state also corresponds to these wave vectors having both components nonzero at the same time. One can straightforwardly construct a two-component Landau free-energy functional for this irreducible representation and show that the choice between (1,0) and (1,1) symmetries is determined by minimization of the ''anisotropic'' fourth-order term. Our calculations for the energies of these two states at $T=0$ suggest that the minimum occurs for $(\pm 1,\pm 1)$ states.

We thank O. A. Starykh and M. Troyer for helpful discussions and S. Sachdev for bringing Ref. 11 to our attention. This work has been financially supported by a Grant-in-Aid from the Ministry of Education, Science and Culture of Japan.

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