Spin-Peierls States of Quantum Antiferromagnets on the CaV_4O_9 Lattice

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(Received 17 April 1996)

We discuss the quantum paramagnetic phases of Heisenberg antiferromagnets on the 1/5-depleted square lattice found in CaV_4O_9. The possible phases of the quantum dimer model on this lattice are obtained by a mapping to a quantum-mechanical height model. In addition to the "decoupled" phases found earlier, we find a possible intermediate spin-Peierls phase with spontaneously broken lattice symmetry. Experimental signatures of the different quantum paramagnetic phases are discussed. [S0031-9007(96)01749-8]

PACS numbers: 75.10.Jm

The recent observation of a two-dimensional gapped quantum paramagnet in CaV_4O_9 [1,2] has stimulated a number of theoretical studies [3–5] of the spin $S = 1/2$ antiferromagnetic Heisenberg model with Hamiltonian $H = \sum_{\langle ij \rangle} J_{ij} \hat{S}_i \cdot \hat{S}_j$, with $\hat{S}_i$ a spin S operator on each site i of the 1/5-diluted square lattice (Fig. 1) of V ions. The largest J_{ij} are the nearest neighbor J_A, J_{BC} (see Fig. 1), but we also allow additional, moderately frustrating, short-range exchanges. Theoretically, one possibility for the ground state is an ordinary Néel state in which the spins are ordered in opposite directions on the two sublattices. Alternatively, for $J_A \gg J_{BC}$ or $J_{BC} \gg J_A$, the ground state is paramagnetic and its excitations are well understood; the lattice can be divided into essentially decoupled pairs ($J_{BC} \gg J_A$) or quadruplets ($J_A \gg J_{BC}$) of spins. However, the real material is near neither limit [5], and if the ground state is not Néel ordered, then there are a number of experimentally important questions about the resulting quantum paramagnet state. Among them are: Does the ground state always have the full symmetry of the underlying lattice, as do the two states mentioned above, or can this symmetry be spontaneously broken? If the latter is the case, what is the nature of the excitations above the gap—does the system have unbound spin-1/2 spinons, or are they permanently bound into excitations with integer spin? Here, we will address these questions using the framework of earlier work on quantum paramagnet states of two-dimensional antiferromagnets [6–8]. We will find that while some of the physics is similar to that studied earlier on other bipartite lattices (the square and the honeycomb), the 1/5-diluted square lattice also displays some interesting new phenomena.

Earlier work considered both unfrustrated [6,7] and frustrated [8] Heisenberg antiferromagnetic Hamiltonians on the square and honeycomb lattices. Based on various methods, a general theory of the quantum paramagnet phases of such systems was obtained, and also applied to the triangular and kagomé lattices [9]. The results are: (i) on bipartite lattices, with an unfrustrated or weakly frustrated Hamiltonian, the spinons are confined to form integer-spin excitations, and the ground state must exhibit some form of spin-Peierls ordering that breaks the symmetry of the lattice, except possibly in the case when $2S$ is a multiple of the coordination number z of the lattice, when a nondegenerate state with the full lattice symmetry that has only integer-spin excitations is possible [10]; (ii) for strongly frustrated systems, such as those with third-neighbor couplings on bipartite lattices [8], or on nonbipartite lattices [9], a ground state without spin-Peierls order can occur regardless of the value of $2S$ (mod z), with unconfined spinon excitations, which behave as bosons [11]. All these states have an energy gap for local excitations, except at the second-order zero-temperature transitions that occur between some of them.

The earlier results for bipartite lattices use the equivalence under lattice symmetries of all the links (and, thus, nearest-neighbor interactions). This property does

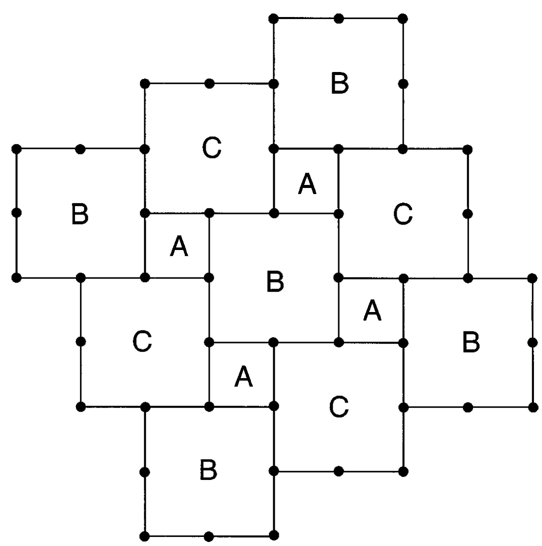

FIG. 1. The 1/5-depleted square lattice, and the three sublattices (A, B, C) of its dual lattice. The exchange J_A acts between spins on a link in an A plaquette, while J_{BC} acts on links shared by the B and C plaquettes. For $J_{BC} \gg J_A$, the ground state is in the "flat" phase of Fig. 2, and for $J_A \gg J_{BC}$ it is in the "disordered flat" phase.

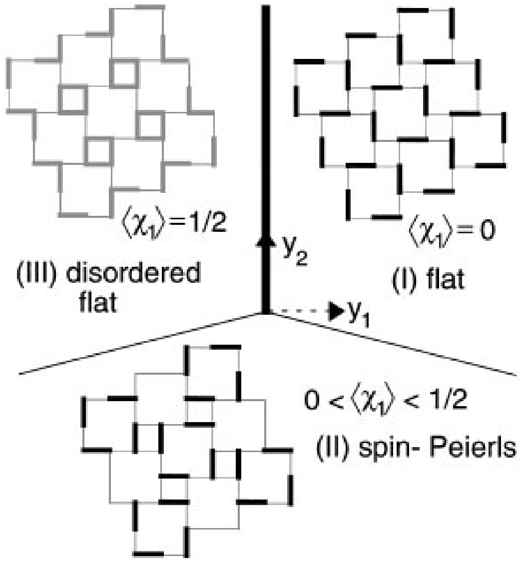

FIG. 2. Mean-field phase diagram of the model defined by S_1 [Eq. (4)] with the potential truncated to two cosines. The thick line is a first-order transition, while the thin lines are second order. Effects of fluctuations are discussed in the text.

not hold for the $1/5$-diluted square lattice, and for the spin-$1/2$ antiferromagnet there are limiting cases $J_A \gg J_{BC}$, and $J_{BC} \gg J_A$, in which it is evident that the ground state is invariant under all the symmetries of the lattice. However, these states fit into the general picture if we remark that, for non-Bravais lattices, it is clearly natural to consider the spin per unit cell as the analog of the spin per site on a Bravais lattice. For the present case, the spin Hamiltonian has a unit cell of 4 sites [12], and we have possible total spin values of 0, 1, or 2 on a lattice with square symmetry, so a nondegenerate ground state along the lines of Ref. [10] is possible for the spin-2 case; if the sites of the square lattice are taken to be the A plaquettes, this can be interpreted as the ground state of the decoupled pair limit ($J_{BC} \gg J_A$). The decoupled quadruplet limit ($J_A \gg J_{BC}$) is obviously the case of spin 0 on each A plaquette. On the other hand, when the interactions are more nearly equal, a full analysis that treats each site as distinct may be more appropriate. We will show here that the limiting results, and a spin-Peierls phase, emerge in a unified way by a careful use of our earlier methods.

Among the various approaches [6,7,13–15] to the unfrustrated case that lead to the same effective action (all of which can be applied here), one of the most appealing is the quantum dimer (QD) model [6,16]. This model represents the low-energy spin-singlet states by forming singlet "valence bonds" out of two spins of $1/2$ on nearest-neighbor sites. Spin S at a site can be represented by the symmetrized product of $2S$ spins of $1/2$, and hence there must be $2S$ bonds ending at each site. Here, however, we will consider $S = 1/2$ (the properties for other S are quite similar) and in this case each basis state of the QD model is associated with a close-packed dimer covering of the lattice under consideration, each dimer representing a valence bond. The effective Hamiltonian in this space consists of local diagonal potential energy terms, and off-diagonal terms which produce local rearrangements of the dimer packing.

It has been shown [7,14,17] that the imaginary time path integral of the QD model can be recast as a "height" or "roughening" model in space and imaginary time. The mapping relies on a one-to-one mapping between every state of the QD model and the equivalence classes of a configuration of heights, h_a [on the sites, a, of the dual lattice (Fig. 1)], under $h_a \rightarrow h_a + 1$. For the $1/5$-depleted square lattice we have

$$h_a = n_a + \zeta_a \,, \qquad (1)$$

where n_a is an integer which fluctuates from site to site, while ζ_a is a fixed fractional offset: $\zeta_a = 0, \alpha, -\alpha$ for $a \in A, B, C$, respectively, with $1/4 < \alpha < 1/2$ a fixed real constant. All configurations of h_a which satisfy the constraint $|h_a - h_b| < 1$, for every nearest-neighbor pair a, b are permitted (two sites are nearest neighbors if their plaquettes on the direct lattice share a link). To map the h_a configurations onto states of the QD model, examine the value of $h_a - h_b$ for every pair of nearest neighbors, and if $|h_a - h_b| > 1/2$, only then place a dimer on the link of the direct lattice shared by the plaquettes around a and b. It can be shown that our choices for the offsets ζ_a ensure that there is exactly one dimer terminating at each site of the direct lattice.

It is helpful to examine the heights associated with some regular dimer coverings of the $1/5$-depleted square lattice. The covering (I) ("flat") in Fig. 2 corresponds to $h_A = 0$, $h_B = \alpha$, and $h_C = -\alpha$; notice that this is the unique covering which is invariant under all the symmetries of the underlying lattice. The covering (II) ("spin-Peierls") corresponds to $h_A = 0$, $h_B = \alpha$, and $h_C = 1 - \alpha$; this covering has a partner, under the symmetry operations of the lattice that interchange B and C, which has $h_A = 1$, $h_B = \alpha$, $h_C = 1 - \alpha$.

The path integral of the quantum-mechanical height model involves summing over spacetime-dependent configurations of the heights, subject to the constraints, with an action related to the effective Hamiltonian. We will next write down a phenomenological effective action, S, that correctly describes the height model at long length and time scales; the same method can also be used for the classical dimer packing problem simply by making all the fields time independent. We begin by using Poisson summation to promote the field h_a, which can only take the discrete set of values (1), to a field χ_a which can take all real values [the ζ_a offsets in (1) require only a slight modification of the usual method [7,14]]. The constraints on h_a are "softened" by adding appropriate potential energy terms in the action; we will argue later that this softening cannot modify the main qualitative features of the results.

We have

$$S = \int d\tau \left\{ \sum_{\langle ab \rangle} K_{ab}(\chi_a - \chi_b)^2 + \sum_a [K_{\tau a}(\partial_\tau \chi_a)^2 - y_a \cos(2\pi(\chi_a - \zeta_a))] + \cdots \right\}. \quad (2)$$

The terms shown are only representative; any term obeying the"translational" symmetry of the height model, $\chi_a \rightarrow \chi_a + 1$, is permitted. The coupling constants, K_{ab}, $K_{\tau a}$, and y_a, depend only on the sublattice label of the sites, a, b, and the symmetry of the lattice requires that $K_{AB} = K_{AC}$, $y_C = y_B$, etc.

We now change variables from the three sublattice fields χ_A, χ_B, χ_C to the fields χ_1, χ_2, χ_3 which are related by $\chi_A = \chi_1 + \chi_2$, $\chi_B = \chi_1 - \chi_2 + \chi_3$, $\chi_C = \chi_1 - \chi_2 - \chi_3$. Now the translational symmetry of the height model affects only χ_1, $\chi_1 \rightarrow \chi_1 + 1$, and this will lead to important simplifications. It is useful to note here the values of χ_1, χ_2, χ_3 for the regular dimer coverings considered earlier. The state (I) ("flat") in Fig. 2 now corresponds to $\chi_1 = 0$, $\chi_2 = 0$, $\chi_3 = \alpha$. The two spin-Peierls states [(II)] have $\chi_1 = 1/4$, $\chi_2 = -1/4$, $\chi_3 = \alpha - 1/2$, and $\chi_1 = 3/4$, $\chi_2 = 1/4$, $\chi_3 = \alpha - 1/2$. These values suggest that χ_2 plays the role of the spin-Peierls order parameter, and that a nonzero mean value of χ_2 implies a spontaneous breaking of the $B \rightarrow C$ interchange symmetry.

The invariance of χ_2 and χ_3 under translations in height space implies that "mass" terms like $m_2^2\chi_2^2 + m_3^2\chi_3^2$ can, and do, appear in the action S. It is therefore safe to integrate out χ_2 and χ_3, which obey

$$\chi_2 \sim -\sin(2\pi\chi_1), \qquad \chi_3 \sim \cos(2\pi\chi_1), \quad (3)$$

at their saddle points, and obtain an effective action for the single scalar field χ_1. We take the spatial continuum limit for χ_1 and obtain

$$S_1 = \int d\tau\, d^2x [K(\nabla\chi_1)^2 + K_\tau(\partial_\tau\chi_1)^2 - y_1\cos(2\pi\chi_1) - y_2\cos(4\pi\chi_1) - \cdots]. \quad (4)$$

Additional terms with more gradients of χ_1, or cosines of higher integral multiples of $2\pi\chi_1$ are also present. Note that, while, for the square (honeycomb) lattices considered earlier [7], lattice symmetries require that the effective potential for χ_1 contain only cosines of integral multiples of $8\pi\chi_1$ ($6\pi\chi_1$) (a fact intimately linked to the ubiquity of spin-Peierls order), here, lattice symmetries only impose the requirement that the effective potential be even in χ_1, and we will see that phases without spin-Peierls order are also possible.

As S_1 describes a three-dimensional interface, the interface must always be flat, and the symmetry $\chi_1 \rightarrow \chi_1 + 1$ is spontaneously broken, even if all y_1, y_2, $\ldots$, are zero. The value of $\langle\chi_1\rangle$, along with (3), identifies the state of the interface, and also of the QD model. A simple picture of the phases and phase transitions is obtained by truncating the on-site periodic potential to the two cosine terms explicitly displayed in (4), and minimizing the energy; more general potentials have the same qualitative features. The results are shown in Fig. 2. There are three possible phases (modulo global translations of χ_1 by integers).

(I) $\langle\chi_1\rangle = 0$: This is the "flat" phase. There is no broken lattice symmetry, which is consistent with $\langle\chi_2\rangle = 0$.

(II) $0 < \langle\chi_1\rangle < 1/2$: This state has spin-Peierls order and has spontaneously broken the $B \rightarrow C$ interchange symmetry because $\langle\chi_2\rangle \neq 0$. The partner state is obtained by $\chi_1 \rightarrow 1 - \chi_1$, $\chi_2 \rightarrow -\chi_2$, $\chi_3 \rightarrow \chi_3$.

(III) $\langle\chi_1\rangle = 1/2$: This phase is similar to the "disordered flat" phase found in earlier work on two-dimensional interfaces [18], so we will use that terminology [19]. The interface is flat on large scales, but each h_A fluctuates between two neighboring values with equal probability for each, and correlations between h_A's at different sites decay exponentially with separation. In the QD language, each A plaquette has two dimers which resonate between the two possible orientations, with correlations between the orientation of two plaquettes decaying exponentially. There is again no broken symmetry as $\langle\chi_2\rangle = 0$. Both the phases (I) and (III) are invariant under all lattice symmetries. They are nevertheless distinct states [4] which cannot be continuously connected. There is a nontrivial "topological order," measured by the mean height, which distinguishes them.

It is clear that phases (I) and (III) correspond to the $J_{BC} \gg J_A$ and $J_A \gg J_{BC}$ limits [4] of the underlying antiferromagnet, respectively. Upon interpolating between these limits, we move along a section through the phase diagram, and there are two basic possibilities: (a) There is a direct first-order transition between phases (I) and (III) as occurs in Fig. 2 for $y_2 > 0$. (b) The spin Peierls phase [(II)] appears in between (I) and (III), as is the case in Fig. 2 for $y_2 < 0$. A third possibility is, (c), an intermediate phase with Néel long-range order. This phase clearly lies beyond the scope of the QD model, and we expect that it can undergo direct second-order transitions to any of the three quantum paramagnetic phases, though if Néel and spin-Peierls phases are both present, we expect them to be adjacent. Finally, we also remark that the paramagnetic and Néel phases are stable under the addition of not too large, non-nearest-neighbor, frustrating exchange interactions, although the Néel region is expected to shrink in size as frustration increases, as in Ref. [8].

Beyond mean-field theory, fluctuations are expected to be relatively innocuous. First, as the interface is flat in each phase, the softening of the constraints is not expected to have serious consequences; indeed, imposing the constraints rigidly can only make the interface flatter. A direct transition between (I) and (III) (or other flat phases with different mean heights) must always be first order when the dimension of spacetime is greater than 2, because of the spontaneous breakdown of translational symmetry in χ_1 even when the cosines are absent. In the spin-Peierls phase, the mean height varies continuously, and we expect a $d = 3$ Ising transition to both (I) and (III), though first-order behavior is not ruled out. The Ising-like behavior can best be understood by expanding the action in powers of χ_1 about zero (or 1/2) to obtain a Landau-Ginzburg-Wilson ϕ^4 action, with χ_1 (or $\chi_1 - 1/2$) playing the role of ϕ; the periodicity can be neglected here, since there is a much larger energy barrier for fluctuations changing χ by ± 1.

To describe excitations of the antiferromagnet with nonzero spin, we use earlier results [7], which go beyond the QD model, and show that a flat interface implies that spinons are confined. For the present model, this means that all three paramagnetic phases have only integer-spin excitations.

We have also studied the finite temperature (T) properties of S but will not discuss them here. The results are similar to those in a paper by Weichman and Prasad [20] (which appeared while we were completing this paper), who analyzed S_1 for τ-independent χ_1, for application to roughening of atomic layers.

An experimental signature of the spin-Peierls phase (II) would be an accompanying lattice distortion, in which the links on which the spin-spin correlation is strongest, as shown in Fig. 2, would be shortened relative to the others, reducing the symmetry of the *three* dimensional lattice structure [1]. This would set in below a transition temperature T_c set by the antiferromagnetic interactions. It is not yet clear to us how the other phases (I) and (III) can be experimentally distinguished from one another, although in principle a jump in the lattice constants should be observable when the first-order transition, also present at low T, is crossed. In all three phases, the elementary spin-carrying excitations have integer spin, and spin-1 is most likely. This should have a clear signature in polarized neutron scattering: the dynamic structure factor $S(k, \omega)$ (k and ω are the transferred momentum and frequency) should have a quasiparticle delta function $\sim\delta(\omega - \epsilon(k))$ at $T = 0$, where $\epsilon(k)$ is the dispersion relation of the spin-1 quasiparticle. This signature is analogous to those of $S = 1$ Haldane gap antiferromagnets in $d = 1$, and is common to all phases in which spinons are confined, of which a survey was given at the beginning of this paper.

To conclude, our main prediction is the appearance of the spin-Peierls phase, as shown in the phase diagram in Fig. 2.

We thank R. R. P. Singh and C. L. Henley for stimulating our interest on this problem, and especially the latter for pointing out that height formulations of the QD model could be extended to the 1/5-depleted square lattice. This research was supported by NSF Grants No. DMR-96-23181 and No. DMR-91-57484.

[1] J.-C. Bouloux and J. Galy, Acta Crystallogr. Sec. B **29**, 1335 (1973).
[2] S. Taniguchi *et al.*, J. Phys. Soc. Jpn. **64**, 2758 (1995).
[3] N. Katoh and M. Imada, J. Phys. Soc. Jpn. **64**, 4105 (1995); K. Sano and A. Takano, Report No. cond-mat/9510160; M. Albrecht and F. Mila, Report No. cond-mat/9510160; M. Troyer, H. Kontani, and K. Ueda, Phys. Rev. Lett. **76**, 3822 (1996); O.A. Starykh, M.E. Zhitomirsky, D.I. Khomskii, R.R.P. Singh, and K. Ueda, Report No. cond-mat/9601145; T. Miyazaki and D. Yoshioka, Report No. cond-mat/9602133.
[4] K. Ueda, H. Kontani, M. Sigrist, and P.A. Lee, Phys. Rev. Lett. **76**, 1932 (1996); **76**, 4650(E) (1996).
[5] M.P. Gelfand, Z. Weihong, R.R.P. Singh, J. Oitmaa, and C.J. Hamer, Report No. cond-mat/9603025.
[6] N. Read and S. Sachdev, Nucl. Phys. **B316**, 609 (1989).
[7] N. Read and S. Sachdev, Phys. Rev. Lett. **62**, 1694 (1989); Phys. Rev. B **42**, 4568 (1990).
[8] N. Read and S. Sachdev, Phys. Rev. Lett. **66**, 1773 (1991); S. Sachdev and N. Read, Int. J. Mod. Phys. B **5**, 219 (1991).
[9] S. Sachdev, Phys. Rev. B **45**, 12 377 (1992).
[10] I. Affleck, T. Kennedy, E. H. Lieb, and H. Tasaki, Phys. Rev. Lett. **59**, 799 (1987); Commun. Math. Phys. **115**, 477 (1988); D. Arovas, A. Auerbach, and F.D.M. Haldane, Phys. Rev. Lett. **60**, 531 (1988).
[11] N. Read and B. Chakraborty, Phys. Rev. B **40**, 7133 (1989); H. Levine and F.D.M. Haldane, Phys. Rev. B **40**, 7340 (1989).
[12] The three-dimensional lattice has 8 V sites in its unit cell [1], but a glide-plane symmetry implies that the unit cell of the two-dimensional spin model has 4 sites. Also note that the environment of an *individual* V ion does not have a symmetry of 90° rotations in the plane, and so the d orbital degeneracy is completely lifted in the structure of Ref. [1].
[13] W. Zheng and S. Sachdev, Phys. Rev. B **40**, 2704 (1989).
[14] E. Fradkin and S. Kivelson, Mod. Phys. Lett. B **4**, 225 (1990).
[15] R. Jalabert and S. Sachdev, Mod. Phys. Lett. B **4**, 1043 (1990).
[16] D. Rokhsar and S. Kivelson, Phys. Rev. Lett. **61**, 2376 (1988).
[17] L. Levitov, Phys. Rev. Lett. **64**, 92 (1990).
[18] K. Rommelse and M. den Nijs, Phys. Rev. Lett. **59**, 2578 (1987); M. den Nijs and K. Rommelse, Phys. Rev. B **40**, 4709 (1989).
[19] In Ref. [7], the square lattice antiferromagnet had an effective potential $\sim\cos(8\pi\chi_1)$, with the minima at $\chi_1 = 1/8, 3/8, 5/8, 7/8$ corresponding to a columnar spin-Peierls phase. More generally, however, the sign in front of the $\cos(8\pi\chi_1)$ potential could change, in which case the minima would be at $\chi_1 = 0, 1/4, 1/2, 3/4$; this is another "disordered flat" phase, and corresponds to the fourfold degenerate "decoupled plaquette" phase considered in T. Dombre and G. Kotliar, Phys. Rev. B **39**, 855 (1989), and in Ref. [6]. In a study which appeared while this paper was being written, M.E. Zhitomirsky and K. Ueda, Report No. cond-mat/9603152, proposed that this is the ground state for certain frustrated square lattice antiferromagnets.
[20] P.B. Weichman and A. Prasad, Phys. Rev. Lett. **76**, 2322 (1996).