Quantum Effects in a Half-Polarized Pyrochlore Antiferromagnet

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(Received 6 October 2005; published 9 March 2006)

We study quantum effects in a spin-3/2 antiferromagnet on the pyrochlore lattice in an external magnetic field, focusing on the vicinity of a plateau in the magnetization at half the saturation value, observed in $CdCr_2O_4$ and $HgCr_2O_4$. Our theory, based on quantum fluctuations, predicts the existence of a symmetry-broken state on the plateau, even with only nearest-neighbor microscopic exchange. This symmetry-broken state consists of a particular arrangement of spins polarized parallel and antiparallel to the field in a 3:1 ratio on each tetrahedron. It quadruples the lattice unit cell, and reduces the space group from $Fd\bar{3}m$ to $P4_332$. We also predict that for fields just above the plateau, the low-temperature phase has transverse spin order, describable as a Bose-Einstein condensate of magnons. Other comparisons to and suggestions for experiments are discussed.

DOI: 10.1103/PhysRevLett.96.097207 PACS numbers: 75.10.Jm, 75.25.+z

Frustrated quantum magnets, in which many symmetry-unrelated states are classically degenerate, are a fascinating venue in which to observe emergent phenomena. In most frustrated materials, the degeneracy is lifted classically, by lattice distortions (Jahn-Teller, spin-Peierls [1]), or longer-range (e.g., dipolar) interactions [2,3]. More intriguing is the possibility that the degeneracy can be removed by quantum fluctuations. In such a "quantum order by disorder" scenario, the system would pick a ground state by maximally delocalizing among many degenerate classical states, thereby minimizing its quantum zero point energy. In toy models, this can lead to exotic ordered states (such as valence bond solids), or even "quantum spin liquid" [4] states, where the classical degeneracy is split *without any symmetry breaking*. Experimentally, clean signatures of the lifting of degeneracy by quantum fluctuations have, however, remained elusive, presumably because of the dominance of the classical mechanisms discussed above.

In this Letter we describe a theoretical study of quantum effects in the insulating chromium oxides, $CdCr_2O_4$ and $HgCr_2O_4$, in which magnetic spin-3/2 Cr^{3+} ions form a pyrochlore lattice (a network of corner-sharing tetrahedra). Because of the half-filled t_{2g} magnetic levels, these materials lack orbital degeneracy, and are also very isotropic magnetically. An appropriate minimal theoretical model is thus the nearest-neighbor pyrochlore lattice Heisenberg antiferromagnet, with Hamiltonian

$$\mathcal{H} = J\sum_{\langle ij\rangle} \mathbf{S}_i \cdot \mathbf{S}_j - H\sum_j S_j^z, \qquad (1)$$

where $\mathbf{S}_i$ is a spin-3/2 operator on site i of the pyrochlore lattice, $\langle ij\rangle$ indicates the sum is over nearest-neighbor bonds, and we have taken the field H to point along the z axis. Most intriguingly, these materials display a robust low-temperature magnetization plateau in an applied magnetic field, with magnetization well quantized at half its saturation value [5]. While there has been a great deal of prior theoretical work on quantum effects in zero magnetic field [6,7], the connection to experiment seems unclear. Here we will instead focus on the physics on and near the plateau. First, we predict a magnetic structure on the plateau shown in Fig. 1, with space group $P4_332$, which we call the "R" state. Second, we predict the existence of XY order (i.e., transverse to the field) at low temperature for fields just above the plateau. If quantum fluctuations dominate over second neighbor exchange, the transverse order is *ferromagnetic*.

These conclusions obtain both for Eq. (1) *and* a modified model including spin-lattice coupling to local Einstein bond phonons, which Penc *et al.* [8] have suggested play an important role. While we agree such coupling likely supports the large *width* of the plateau, our conclusions with respect to the *ordering symmetry* are essentially in-

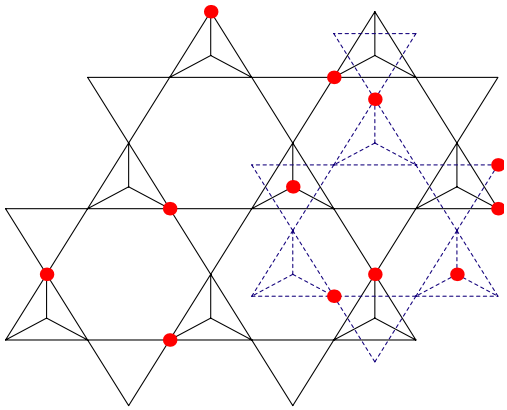

FIG. 1 (color online). Planar projection of the R state, stabilized by quantum fluctuations. Dots indicate minority spins. Empty triangles represent the projection of down pointing tetrahedra, while triangles with links from their center represent up pointing tetrahedra, and the upper corner above the plane of sites of the triangle corners. The dashed lines are parts of the next layer of tetrahedra.

dependent of it. For clarity of presentation, we therefore suppress spin-lattice coupling in the following.

Our approach relies on the substantial polarization in the vicinity of the plateau, which indicates that, on average, the transverse components of the spins are reduced. Moreover, the existence of a plateau with zero differential susceptibility $\chi = \partial m^z/\partial h = 0$ at $T = 0$ implies the absence of transverse ordering, $\langle S_i^{\pm}\rangle = 0$. We therefore split the Hamiltonian into terms involving longitudinal and transverse spin components, and *treat the latter perturbatively* (though we will work to rather high orders). Specifically, $\mathcal{H}' = \mathcal{H}_0 + \mathcal{H}_1$, with

$$\mathcal{H}_0 = \frac{J_z}{2}\sum_t [(S_t^z - h)^2 - h^2] - J_z \sum_i (S_i^z)^2, \qquad (2)$$

$$\mathcal{H}_1 = \frac{J_\perp}{2}\sum_{\langle ij\rangle} (S_i^+ S_j^- + \text{H.c.}), \qquad (3)$$

where $S_i^{\pm} = S_i^x \pm iS_i^y$ are the usual ladder operators, $S_t^z = \sum_{j\in t} S_j^z$ is the sum of longitudinal spin components on a tetrahedron labeled by t, and we have introduced the dimensionless magnetic field $h = H/2J$ (we take $h > 0$ without loss of generality). For bookkeeping purposes, we have written distinct longitudinal and transverse exchange couplings $J_z, J_\perp$, though we are ultimately interested in $J_z = J_\perp = J$. We note that "easy-axis" perturbation theory in $\alpha \equiv J_\perp/J_z$ becomes increasingly accurate at larger h, and that the symmetry of $\mathcal{H}'$ is preserved for any $\alpha > 0$. This gives us further confidence in the *qualitative* predictions of easy-axis perturbation theory.

We now sketch our derivation of an *effective model* describing the quantum mechanical lifting of the classical degeneracy. Consider first the zeroth order Hamiltonian, Eq. (2). It is straightforward to see that $\mathcal{H}_0$ has three types of ground states, depending upon h: for $h < 1.5$, each tetrahedron has two spins with $S_i^z = +\frac{3}{2}$ and two spins with $S_i^z = -\frac{3}{2}$; for $1.5 < h < 4.5$, the half-magnetized region, each tetrahedron has 3 "majority" spins with $S_i^z = +\frac{3}{2}$ and one "minority" spin $S_i^z = -\frac{3}{2}$; and all spins are fully polarized for $h > 4.5$. Therefore, this simplistic view predicts 3 magnetization plateaus exist—zero, half, and full magnetization.

Focusing first on the plateau of interest, the zeroth order "3:1" ground states are extensively degenerate, due to the freedom to locate the minority spin of each tetrahedron. We may view the transverse terms in Eq. (3) as inducing "quantum fluctuations" into these states; in particular, the action of $\mathcal{H}_1$ transfers a total spin $\Delta S^z = \pm 1$ between nearest-neighbor sites. Technically, this must be analyzed by degenerate perturbation theory (DPT).

We define the projection operator, $\mathcal{P}$, onto the ground state plateau subspace. Consider any exact eigenstate $|\Psi\rangle$. Its projection $|\Psi_0\rangle = \mathcal{P}|\Psi\rangle$ satisfies the "effective Schrödinger equation"

$$\left[E_0 + \mathcal{P}\mathcal{H}_1 \sum_{n=0}^{\infty} \mathcal{G}^n \mathcal{P}\right]|\Psi_0\rangle = E|\Psi_0\rangle, \qquad (4)$$

where the resolvent operator $\mathcal{G} = \frac{1}{E-\mathcal{H}_0}(1-\mathcal{P})\mathcal{H}_1$ is linear in $J_\perp$. Because the resolvent contains the exact energy E, Eq. (4) is actually a nonlinear eigenvalue problem. However, to any given order of DPT, E may be expanded in a series in $J_\perp$ to obtain an equation with a true Hamiltonian form within the degenerate manifold. Once $|\Psi_0\rangle$ and E are known, the full wave function can be reconstructed as $|\Psi\rangle = (1-\mathcal{G})^{-1}|\Psi_0\rangle = \sum_{n=0}^{\infty}\mathcal{G}^n|\Psi_0\rangle$.

To understand the ultimate nature of the ordered state on the plateau, we must carry out DPT at least to the lowest order at which the degeneracy is lifted. Our approach will be to derive the lowest-order *diagonal* (in the S_i^z basis) and *off-diagonal* terms in $J_\perp$ which remove the degeneracy. First, note that any *off-diagonal* term must flip spins in such a way as to preserve the 3:1 constraint on each tetrahedron. This can only be accomplished by flipping spins around a nontrivial closed loop on the pyrochlore lattice. The smallest such loop involves flipping spins on 3 different bonds, and flipping a spin from $\pm\frac{3}{2}$ to $\mp\frac{3}{2}$ requires $\mathcal{H}_1$ to act 3 times, so off-diagonal processes occur first at ninth order [for general S, they occur at $O(J_\perp^{6S})$]. Diagonal processes can occur sooner. The first-order splitting vanishes, since the action of $\mathcal{H}_1$ creates two tetrahedra with spin $S_t^z \neq 3$. The energy of the plateau state does shift relative to other levels at second order. Although it is more nontrivial to see, in fact, splitting *within* the classical manifold does not occur until *sixth* order (this is true for any S). The reason for this is somewhat involved [9], but follows from the *locality* of $\mathcal{H}_1$ and the strong 3:1 constraint.

By straightforward but somewhat involved calculations, including a similarity transformation to change the sign of the ring exchange term (same as in Ref. [4]), one can compute the lowest-order diagonal and off-diagonal contributions to the effective Hamiltonian, $\mathcal{H}_{\text{eff}}$, explicitly. We find

$$\mathcal{H}_{\text{eff}} = \alpha^6 J_z \sum_P \hat{\mathcal{E}}_P - c\alpha^9 J_z \sum_P (|\hexagon_A\rangle\langle\hexagon_B| + \text{H.c.}), \qquad (5)$$

where the sums are over all hexagonal plaquettes P, and the states $|\hexagon_A\rangle$, $|\hexagon_B\rangle$ represent the two "flippable" configurations (A/B) with alternating majority and minority spins around the plaquette. The operator $\hat{\mathcal{E}}_P$ is a diagonal operator representing the sixth order energy splitting of plaquette P. It takes the values $\hat{\mathcal{E}}_P = (0, -\frac{144}{25}, -\frac{27}{100}, -\frac{801}{500}, -\frac{9801}{6250}) \approx (0, -5.76, -0.27, -1.60, -1.57)$, respectively, for the configurations (↑↑↑↑↑↑, ↓↑↓↑↓↑, ↓↑↑↑↑↑, ↓↑↓↑↑↑, ↓↑↑↓↑↑) (and cyclic permutations), where $\uparrow/\downarrow$ denote majority/minority spin states, respectively. This diagonal interaction is equivalent to a combination of further neighbor Ising exchange couplings, plus an additional 3-spin interaction

term; the plaquette representation is, however, more convenient and simpler. The constant $c = \frac{53178588}{12371645} \approx 4.3$.

The Hamiltonian in Eq. (5) (acting within the 3:1 Hilbert space) is the basis for our discussion of the ordered state on the plateau. Inspection of $\hat{\mathcal{E}}_P$ shows that the A/B configurations are significantly more favorable than all others. A natural approximation is then to ignore the energy differences between other configurations, which gives

$$\mathcal{H}_{\mathrm{QDM}} = V\sum_P (|\hexagon_A\rangle\langle\hexagon_A| + |\hexagon_B\rangle\langle\hexagon_B|) - K\sum_P (|\hexagon_A\rangle\langle\hexagon_B| + \mathrm{H.c.}), \quad (6)$$

where, extrapolating to the physical limit $\alpha \to 1$, we have $V \approx -5.76$ J, $K = cJ \approx 4.3$ J, while in the strict small α limit, $V/K \to -\infty$. Equation (6) is useful because it maps directly to a type of ''quantum dimer model'' (QDM) [10]. In particular, the pyrochlore sites can be mapped onto the links of a diamond lattice, whose sites lie in the centers of pyrochlore tetrahedra. A minority spin can be represented as a ''dimer'' occupying the corresponding link, and the 3:1 states become nonoverlapping dimer coverings of the diamond lattice. The V and K terms map directly to standard ''potential'' and ''kinetic'' terms for these dimer configurations [10].

QDMs of this form have been considered on a number of two and three-dimensional lattices [10,11]. Fixing $K > 0$, the ground state depends upon the dimensionless parameter $v = V/K$, and a few general conclusions can be drawn. The Rokhsar-Kivelson point, $v = 1$, is exactly soluble, and demarks a boundary between ordering into configurations with no A/B plaquettes (for $v > 1$) and, for three-dimensional bipartite lattices like the diamond, a *spin liquid* phase with no broken symmetry (for $v_{c1} < v \lesssim 1$ [4], with some critical coupling v_{c1}, which is usually positive). For $v < v_{c2} < v_{c1}$, the ground state is again ordered, and adiabatically connected to the diagonal ground state selected by the diagonal $V < 0$ term alone. For the examples (square, honeycomb, and triangular lattices) in which the phase diagram has been studied by quantum Monte Carlo methods [12], the critical coupling v_{c2} is either slightly negative or even positive, $v_{c2} > -0.2$. The persistence of the ''diagonal'' state to small v can be readily understood. For $v \to -\infty$, the energy is minimized by the diagonal state which contains the maximum density of flippable A/B hexagons. Such a configuration is *also* the one most connected by the K term to other 3:1 states. Hence, by order by disorder reasoning, an appropriate superposition ''centered'' (in Hilbert space) around the diagonal ground state above is energetically favored by *both* terms. Explicit variational wave functions for $\mathcal{H}_{\mathrm{eff}}$ in this spirit will be described in a future long publication. What or how many intervening state(s?) might occur for $v_{c2} < v < v_{c1}$ is not known, and it is even possible that there might be no intermediate state, and instead a direct transition from the diagonal ordered state to a spin liquid at $v = v_{c2} = v_{c1}$.

From this reasoning, in the extrapolation to $\alpha = 1$, which gives $v \approx -1.3$, we expect the ground state selected by quantum fluctuations to have the same symmetry as that of the easy-axis limit $v \to -\infty$. In particular, for the QDM in this limit, we require the 3:1 configuration with the highest density of A/B hexagons. Because these hexagons overlap, and the 3:1 configuration space is highly constrained, this is not a trivial problem. It is instructive to examine a single primitive unit cell of the pyrochlore lattice, which is a region of space enclosed by 4 hexagonal plaquettes. By careful inspection, and making use of the 3:1 constraint, one finds that at most one of these hexagons can be of A/B type. Therefore the maximum fraction of A/B hexagons is $\frac{1}{4}$.

By extensive analysis [9], we have found one single candidate, shown in Fig. 1, which saturates this upper bound on the density of A/B hexagons, and moreover, gives the lowest energy that we have been able to find for the *full* diagonal term ($\sum_P \hat{\mathcal{E}}_P$) with *all* plaquette energies included. Having the maximal density of potential resonating plaquettes, we call it the R state. It has a magnetic unit cell consisting of 4 structural pyrochlore unit cells, and has the symmetries of the $P4_332$ space group—particularly significant is that this state preserves all rotation symmetries of the pyrochlore lattice (up to translations). This implies that, contrary to the suggestion in Ref. [5], only *isotropic* magnetostriction is expected for the R state, and not a rhombohedral distortion along a $\langle 111\rangle$ axis. We note that a Landau theory analysis predicts the symmetry-breaking transition from the $P4_332$ space group (R state) to $Fd\bar{3}m$ (pyrochlore symmetry) is first order [9], in agreement with the experimental conclusions [13].

We now turn to other effects of quantum fluctuations. Quantum effects lead to a *spin gap*, Δ, on the plateau, and consequently an activated temperature dependence, $M^z(T) - M^z(0) \propto \exp(-\Delta(h)/k_B T)$. Another quantum effect is a suppression of the local ''staggered'' moment, even at $T = 0$. To leading order in DPT, the difference of the moment on majority and minority sites is suppressed to $\langle S^z_{\mathrm{max}}\rangle - \langle S^z_{\mathrm{min}}\rangle < 2.2$, below the classical value $\langle S^z_{\mathrm{max}}\rangle - \langle S^z_{\mathrm{min}}\rangle = 3$.

Experiments have studied the low-temperature behavior on *exiting* the plateau at lower and higher fields, h_{c1}, h_{c2}, respectively. The lower edge of the plateau for both $CdCr_2O_4$ [5] and $HgCr_2O_4$ [13] shows a jump in magnetization, which then decreases linearly down to zero magnetic field, suggesting the low-field state is adiabatically connected with the zero field state. The higher field edge, observed only in $HgCr_2O_4$, shows a continuous transition out of the plateau, and a continuous evolution with no further jumps up to the highest fields measured. There is, however, some indication of a ''kink,'' possibly related to the expected lattice symmetry restoration, for fields above the plateau but below full saturation.

The first-order/continuous nature of the transitions at the upper or lower edges can be explained classically [8], and occurs already in the trivial problem of a *single* classical tetrahedron. Classically, however, above the plateau, though the spins become noncollinear, the *ordering* of the transverse moments, if present at all, is critically dependent upon the nature of further neighbor interactions.

By contrast, it is determined in the quantum theory even for the nearest-neighbor model. In general, a continuous quantum transition off the plateau should be described by the ''Bose-Einstein condensation'' (BEC) of a single magnon excitation with $\Delta S^z = +1$, above the R state, whose gap vanishes at the plateau edge. The resulting state above the plateau has therefore transverse spin order, $\langle S_i^+ \rangle \neq 0$, in agreement with classical expectations. The precise spatial arrangement of the transverse ordering is determined by the symmetry of the lowest energy magnon, which must form an irreducible representation (irrep) of $P4_332$. In the easy-axis DPT, the magnon is formed from a superposition of states with a single minority spin changed from $S_i^z = -\frac{3}{2}$ to $S_i^z = -\frac{1}{2}$. At $O(\alpha^2)$, the magnon can hop between minority sites, and crucially, the effective hopping amplitude is *negative*, despite $J > 0$, because it occurs by virtual hopping through a majority site. The minimum energy magnon state then is a *uniform* plane wave (trivial irrep), which implies the transverse spin order is *ferromagnetic*. That is, for $h \gtrsim h_{c2}$ the system has *the same space group symmetry as the R state*. While there is no guarantee the trivial irrep remains lowest in energy for $\alpha = 1$, it is our best guess for the nearest-neighbor model. If second neighbor exchange J_2 is significant, this conclusion may change. In particular, if J_2 is larger than the effective hopping amplitude and antiferromagnetic, the lowest energy magnon has a different symmetry. The resulting transverse order is more complex, with a magnetic unit at least 3 times larger than that of the R state [9]. In any case, the BEC picture implies quite generally that the symmetry for $h \gtrsim h_{c2}$ is as low or lower than that of the R state. Therefore, since the fully polarized state has the full pyrochlore symmetry, with increasing field there *must* be a transition from $P4_332$ to $Fd\bar{3}m$ before the saturation field. This may be associated with the kink observed experimentally.

The classical model of Penc *et al.* [8] successfully explains many experimental features of $CdCr_2O_4$ and $HgCr_2O_4$. However, classically, additional second and third neighbor microscopic Heisenberg interactions are required to stabilize the R state, as suggested by Ueda *et al.* [5]. Our results show that quantum fluctuations generate *effective* interactions that stabilize the R state even when the microscopic exchange is purely nearest neighbor. Furthermore, quantum fluctuations may determine the symmetry of the transverse spin order expected just above the plateau, which, if measured by neutrons, would be very telling. Experimentally, the second and third neighbor exchanges could be determined by inelastic neutron *measurements* of the magnon spectra in the fully polarized state, as has been done in Cs_2CuCl_4 [14]. A more direct test of the relevance of quantum fluctuations would be to look for signatures of BEC criticality (as in Refs. [15,16]) at the upper edge of the plateau in $HgCr_2O_4$. We note that Ueda *et al.* [13] observed an *increase* of h_{c2} with increasing temperature, concluding that ''thermal fluctuations stabilize collinear spin configurations.'' The BEC picture gives an alternative explanation: the BEC temperature grows as the magnon density increases.

Theoretically, it is intriguing to contemplate the possibility that the plateau phase might be close to a quantum phase transition to a spin liquid state. A field-theoretic analysis, based on the mapping of the 3:1 Hilbert space to a gauge theory with projective symmetry, indeed predicts the R state as the simplest phase proximate to the spin liquid [9]. Other calculations, predictions, and comparison to different theoretical approaches will be made in a future publication [9].

We are very pleased to acknowledge H. Ueda, Y. Motome, M. Matsuda, H. Takagi, and Y. Ueda. We are particularly grateful to the authors of Ref. [13] for supplying us their experimental data prior to publication. This work was supported by NSF Grant No. DMR04-57440, PHY99-07949, and the Packard Foundation.

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