Order by Distortion and String Modes in Pyrochlore Antiferromagnets

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We study the effects of magnetoelastic couplings on pyrochlore antiferromagnets. We employ Landau theory, extending an investigation begun by Yamashita and Ueda for the case of $S = 1$, and classical analyses to argue that such couplings generate bond order via a spin-Peierls transition. This is followed by, or concurrent with, a transition into one of several possible low-temperature Néel phases, with most simply collinear, but also coplanar or mixed spin patterns. In a collinear Néel phase, a dispersionless string-like magnon mode dominates the resulting excitation spectrum, providing a distinctive signature of the parent geometrically frustrated state. We comment on the experimental situation.

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Geometrically frustrated magnets [1–3] are examples of strongly interacting systems: the vast degeneracy of their classical ground states makes them highly susceptible even to small perturbations. By analogy with quantum Hall systems, where the Landau levels are also macroscopically degenerate, one expects a variety of phases in perturbed frustrated magnets, from Néel states to spin glasses or liquids, with valence-bond solids along the way.

Probably the world's most frustrated spin system is the classical Heisenberg antiferromagnet on the pyrochlore lattice (Fig. 1) where spins reside at vertices of tetrahedra. The number of its classical ground states, which are attained when total spin on each tetrahedron $\mathbf{S}_{\text{tot}} = \sum_{i=1}^{4} \mathbf{S}_i = 0$, is so large that, exceptionally, it does not order at any finite temperature [4]. In real compounds, *deviations* from the classical Heisenberg model (e.g., dipolar interactions, single-ion anisotropy, or quantum fluctuations) determine which ground state is selected at the lowest temperatures.

In this note, we discuss an elegant mechanism for lifting the frustration through a coupling between spin and lattice degrees of freedom. The high symmetry of the pyrochlore lattice and the spin degeneracy drive a distortion of tetrahedra via a magnetic Jahn-Teller ("spin-Teller") effect. The resulting state exhibits a reduction from cubic to tetragonal symmetry and the development of bond order in the spin system with unequal spin correlations $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ on different bonds of a tetrahedron. In the ordered phase, there are 4 strong and 2 weak bonds per tetrahedron — or vice versa. This phenomenon was uncovered by Yamashita and Ueda [5] for pyrochlore antiferromagnets with spins $S = 1$, for which they described an AKLT-style wave function [6] with the requisite bond order. In the following we study this phenomenon in the classical limit with added insight from Landau theory, and discuss its consequences for the excitation spectrum. As many of the candidate systems have moderately large spins and order at finite temperatures, our methods should work well — in particular, they allow us to treat the Néel order that can (and experimentally does) appear in addition to the bond order.

We begin by identifying a two-component bond order parameter at the level of a single tetrahedron and proceed to construct its Landau free energy for states of the infinite lattice. In one family of cases the spin-Peierls transition can be first order, as indeed observed in many pyrochlore antiferromagnets [7–12].

Once the system is in a bond-ordered phase, the lowered symmetry of valence bonds reduces frustration of spins and sets the stage for Néel (spin) ordering. In general, we expect a separate phase transition into an antiferromagnetic state. However, the first-order spin-Peierls transition may turn the system directly into an antiferromagnet, bypassing a metastable spin-Peierls phase. Both possibilities seem to be realized in different materials [11,12]. The particular type of the Néel order depends on the underlying bond ordered state. While collinear order is most easily generated, we show that unusual coplanar states are also possible.

Finally, we obtain a striking signature of the Jahn-Teller distortion in collinear Néel states. The spectrum of spin excitations in the distorted antiferromagnet contains a large number of modes clustered near a finite frequency. These magnons, a remnant of pyrochlore zero modes, are confined to strings of parallel spins. We therefore call them *string* modes. A resonance highly reminiscent of

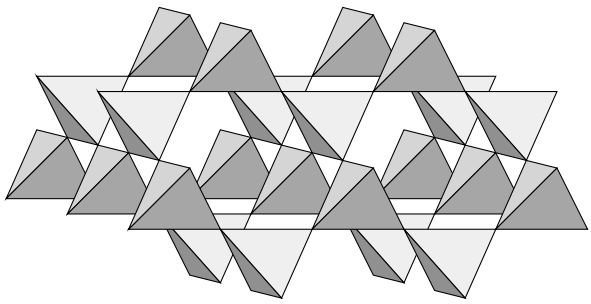

FIG. 1. The pyrochlore lattice.

such modes has been observed by S.-H. Lee *et al.* [12] in $ZnCr_2O_4$. The strings should also be observable in ZnV_2O_4 where a structural distortion and a collinear Néel order at low temperatures have been firmly established [8,10]. A weaker feature might exist in the itinerant magnet YMn_2. We turn now to the details of our results.

Single tetrahedron.—Yamashita and Ueda [5] have discussed the Jahn-Teller distortion on a single tetrahedron for the case of spins $S = 1/2$. Their analysis can be applied to general spin virtually unchanged. On an undistorted tetrahedron, all exchange constants are equal and any state with total spin $\mathbf{S}_{\text{tot}} = 0$ minimizes the classical Heisenberg energy $J\sum_{i>j}\mathbf{S}_i \cdot \mathbf{S}_j$. To see which of these is selected in the presence of a small spontaneous distortion, we minimize the sum of spin and elastic energies. The energy of a bond $J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$ depends on ionic displacements through variation of Heisenberg exchange J_{ij} with the length of interatomic bonds and bond angles. Expanding magnetic and elastic energies to lowest order in the displacements x_α ($\alpha = 1, \ldots, 12$) we obtain

$$E = \sum_{i,j,\alpha} (\partial J_{ij}/\partial x_\alpha)\,(\mathbf{S}_i \cdot \mathbf{S}_j)x_\alpha + \sum_{\alpha,\beta} k_{\alpha\beta}x_\alpha x_\beta/2\,. \quad (1)$$

As the reduction of magnetic energy is linear in x_α, it will beat the quadratic cost in elastic energy. Hence a Jahn-Teller distortion will result from the spin degeneracy.

For tetrahedral (T_d) symmetry, displacements x_α that contribute to the magnetoelastic energy (1) must belong to the same irreducible representation as the six bond variables $\mathbf{S}_i \cdot \mathbf{S}_j$. These bond variables can be thought of as classical quantities or, for quantum systems, as expectation values of the corresponding operators; our symmetry analysis applies to both cases.

In the experimentally relevant regime well below the Weiss temperature, $\mathbf{S}_{\text{tot}} \approx 0$, and we are left with only three independent quantities. One of them, the ground-state energy $\sum_{i>j}\mathbf{S}_i \cdot \mathbf{S}_j$, invariant under all symmetry operations, induces a uniform rescaling of the tetrahedron (which is not a distortion). The other two, $(f_1, f_2) \equiv \mathbf{f}$, measure the disparity of the bond variables:

$$f_1 = [(\mathbf{S}_1 + \mathbf{S}_2) \cdot (\mathbf{S}_3 + \mathbf{S}_4) - 2\mathbf{S}_1 \cdot \mathbf{S}_2 - 2\mathbf{S}_3 \cdot \mathbf{S}_4]/\sqrt{12}\,,$$
$$f_2 = (\mathbf{S}_1 \cdot \mathbf{S}_3 + \mathbf{S}_2 \cdot \mathbf{S}_4 - \mathbf{S}_2 \cdot \mathbf{S}_3 - \mathbf{S}_1 \cdot \mathbf{S}_4)/2\,. \quad (2)$$

They transform as the E representation of the group T_d and couple to phonons of the same symmetry. For a given configuration of spins, the minimum magnetoelastic energy (1) can be written in two ways ($C_i = \text{const}$):

$$E = -(\partial J/\partial x_E)^2 f^2/(2k_E) = C_0 - C_4 \sum_{i>j} (\mathbf{S}_i \cdot \mathbf{S}_j)^2; \quad (3)$$

here $\partial J/\partial x_E$ and k_E are the appropriate magnetic and elastic constants. Minimization of total energy is achieved when the vector $\mathbf{f}$ has maximum length. From a classical analysis, we find that $\mathbf{f}$ is restricted to lie in an equilateral triangle, at the corners of which its length is maximized (filled circles in Fig. 2). This corresponds to two weakened and four strengthened bonds, a result which is easily rationalized in terms of classical ground states of the tetrahedron: only one of them (modulo symmetries) fully satisfies four bonds and completely frustrates the remaining two, which are then, respectively, strengthened and weakened by the distortion. This state is the collinear state, which is of course favored by the effective "biquadratic exchange" (3).

Infinite pyrochlore lattice.—The Jahn-Teller distortion of individual tetrahedra will analogously drive a spin-Peierls phase transition on the infinite pyrochlore lattice. There now exist an infinite number of phonons that could become soft. We here discuss the simplest but already very rich case of a phonon condensate with lattice momentum $\mathbf{q} = 0$, for which all tetrahedra of a given type distort in the same way. The two inequivalent tetrahedra (types A and B) which make up the pyrochlore lattice reside on a bipartite (diamond) lattice (Fig. 1).

The symmetry group of the pyrochlore lattice, O_h, is enlarged from T_d by the operation of inversion through a site, which exchanges A and B tetrahedra: $T_d \otimes C_i = O_h$. Irreducible representations of the cubic group O_h are those of T_d with an additional quantum number, parity under the inversion. Thus, there are two doubly degenerate displacement modes that couple to bonds in a nontrivial way. The even phonon doublet E_g creates a uniform distortion

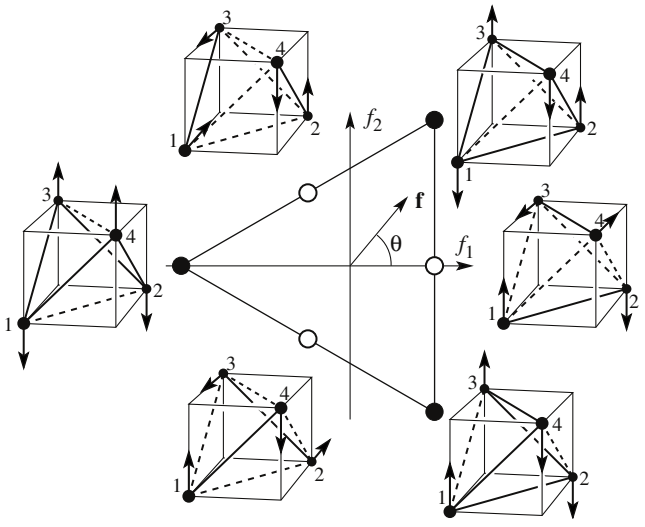

FIG. 2. Possible values of the two components of the bond vector $\mathbf{f} = (f_1, f_2) = (f\cos\theta, f\sin\theta)$ are bounded by an equilateral triangle in the (f_1, f_2) plane. Also shown are six extremal spin configurations (filled and open circles). Strong (weak) bonds are denoted by solid (dashed) lines.

of the entire lattice; the odd doublet E_u causes a staggered distortion ($\mathbf{f}_A = -\mathbf{f}_B$).

Generalizing Eq. (3) for the energy, using small subscripts for parity and capitals for tetrahedron type, gives

$$E = -\left(\frac{\partial J}{\partial x_E}\right)^2\left[\frac{(\mathbf{f}_A + \mathbf{f}_B)^2}{2k_g} + \frac{(\mathbf{f}_A - \mathbf{f}_B)^2}{2k_u}\right]. \quad (4)$$

For $k_g = k_u$, f_A and f_B are separately maximized. For a stiffer odd phonon, $k_u > k_g$, $\mathbf{f_A}$ and $\mathbf{f_B}$ are in the same corner of the triangle in Fig. 2. When $k_g > k_u$, "antiferromagnetic" coupling puts $\mathbf{f}_A$ and $\mathbf{f}_B$ in two different corners. Figures 3(a) and 3(b) display spin arrangements corresponding to these two types of bond order. The latter has been observed in YMn_2 and MgV_2O_4 [7,9,10].

We next discuss the nature of spin-Peierls phases and transitions by considering the Landau free energy $\mathcal{A}(\mathbf{g}, \mathbf{u})$, where $\mathbf{g}, \mathbf{u}$ are the uniform and staggered bond *order parameters* [13], $\mathbf{g}, \mathbf{u} = (\mathbf{f}_A \pm \mathbf{f}_B)/2$. In a paramagnetic state, the bond order parameters $\mathbf{g}, \mathbf{u} = 0$; note that spin-Peierls order $\mathbf{g}, \mathbf{u} \neq 0$ does not necessarily imply a Néel order. The terms allowed by O_h symmetry are

$$\begin{aligned}\mathcal{A}(\mathbf{g}, \mathbf{u}) = {} & a_g g^2 + b_g g^3 \cos 3\theta_g + c_g g^4 + \ldots \\ & + a_u u^2 + c_u u^4 + d_u u^6 \cos 6\theta_u + \ldots \\ & + b_u u^2 g \cos(2\theta_u + \theta_g) + \ldots . \end{aligned} \quad (5)$$

Quite generally, one can read off that the phase transition will be discontinuous if it is driven by the even phonon E_g: the symmetric cube $[E_g^3]$ contains the trivial representation making it possible to write a cubic invariant $g_1(g_1^2 - 3g_2^3) = 4g^3 \cos 3\theta_g$ in polar coordinates of Fig. 2. On the other hand, the transition will be continuous if it is driven mainly by the odd phonon E_u. We also note that both $\mathbf{g}$ and $\mathbf{u}$ can be present owing to a nonlinear coupling. Then $0 \neq \mathbf{f}_A \neq \mathbf{f}_B \neq 0$, as in the case depicted in Fig. 3(b). Below the transition temperature, either a_g or a_u becomes negative. Omission of higher-order terms requires that $c_g, c_u > 0$. Signs of b_g, b_u, and d_u will determine the nature of spin-Peierls phases. In our classical model, $b_u > 0$, which we assume in what follows.

For the phase transition driven by the uniform distortion E_g, only the first line of Eq. (5) needs to be taken into account. Depending on the sign of b_g, the ordered phase features either two strong and four weak bonds per tetrahedron [Fig. 4(a)], or two weak and four strong ones [Fig. 4(b)]. In the ordered phase, a growing $\mathbf{g}$ softens the staggered mode $\mathbf{u}$ through mode coupling, the third line in Eq. (5). Once $g > a_u/b_u$, there is a second transition into a phase with both $\mathbf{g}, \mathbf{u} \neq 0$ ($\mathbf{f}_A \neq \mathbf{f}_B$). The two possible sequences of transitions are shown in Figs. 4(c) and 4(d).

Néel order.—Lowering the bond symmetry relieves frustration and thus encourages spin ordering [14]. However, as bond and spin ordering are not required to coincide even *classically,* the former will likely precede the latter. Indeed, frustrated systems are the ideal setting for this to happen: the classical ground state degeneracy supplies a plethora of local zero-energy modes [4], which can allow spins to fluctuate strongly even in the presence of bond order. This, essentially classical, mechanism is distinct from the more conventional avenue of obtaining valence-bond solids through enhanced quantum fluctuations for small spins. Nonetheless, if the spin-Peierls transition is discontinuous, it can take the paramagnet directly into the Néel phase, past the metastable spin-Peierls state. Both variants seem to occur in nature [11,12].

The phase transition from a bond-ordered state to a Néel phase can also be analyzed within the Landau framework by adding spin averages $\langle \mathbf{S}_i \rangle$. For the sake of simplicity, we make the assumption that the contribution of the spin condensate $\langle \mathbf{S}_i \rangle \cdot \langle \mathbf{S}_j \rangle$ will tend to reinforce, rather than weaken or alter, bond order $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$. Then one can use Fig. 2 as a guide to identify the appropriate low-temperature Néel phase for each of the spin-Peierls phases of Fig. 4. The spin-Peierls states shown in Figs. 4(a) and 4(d) exhibit the collinear Néel order shown in Figs. 3(a) and 3(b), respectively. The spin-Peierls phase of Fig. 4(e) orders into the exotic Néel phase of Fig. 3(c) where spins on tetrahedra A are collinear, while spins on tetrahedra B are coplanar. Note that, whereas the bond order we have

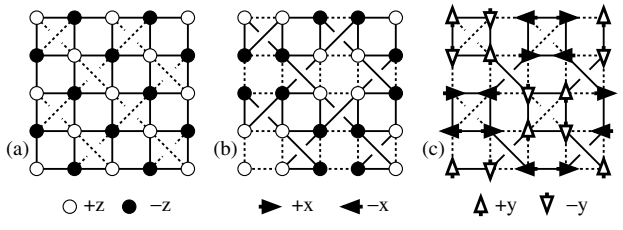

FIG. 3. (a),(b) Sample collinear states of classical spins on the pyrochlore lattice, projected along ⟨001⟩. Frustrated bonds are shown as broken lines. They form (a) infinite chains and (b) infinite spirals. (c) Néel order with collinear spins on tetrahedra A and coplanar spins on tetrahedra B.

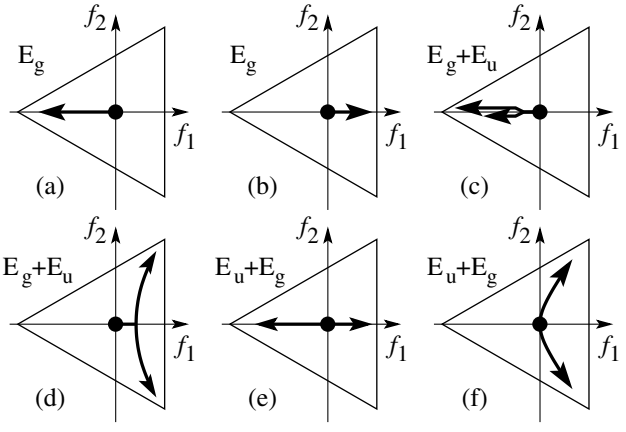

FIG. 4. Evolution of the spin-Peierls order parameters $\mathbf{f}_A = \mathbf{g} + \mathbf{u}$ and $\mathbf{f}_B = \mathbf{g} - \mathbf{u}$. (a),(b) $\mathbf{g}$ condenses, $\mathbf{u} = 0$. (c),(d) $\mathbf{g}$ condenses first, $\mathbf{u}$ appears later. (e),(f) $\mathbf{u}$ condenses, $\mathbf{g}$ is generated as a subdominant order parameter. In the paramagnetic phase (filled circle), $\mathbf{f}_A = \mathbf{f}_B = 0$.

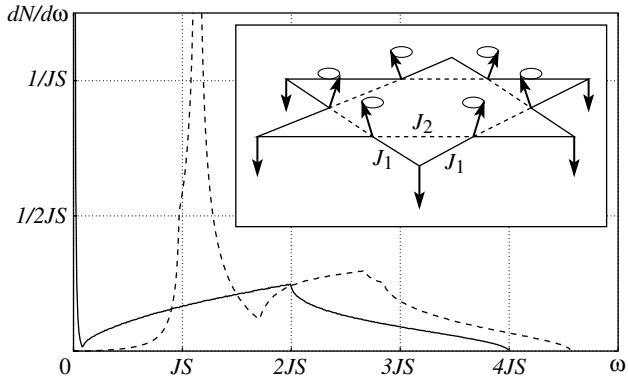

FIG. 5. Spectrum of spin waves of the elastic pyrochlore lattice for the collinear Néel state of Fig. 3(a) for $J_2{:}J_1 = 1{:}1$ (solid line) and 3:4 (dashed line). In the undistorted magnet $J_2 = J_1$, half of the modes are at $\omega = 0$. The dominant peak at $\omega_0 = 4S(J_1 - J_2)$ is due to a large number of string modes. Inset: Local mode on a hexagonal loop of parallel spins. For clarity, spins above and below the kagomé plane (a [111] pyrochlore plane) are not shown.

considered is at $\mathbf{q} = 0$, the concomitant spin order need not be.

String modes.—The extreme frustration of pyrochlore antiferromagnets is reflected in their spin-wave spectrum. A large degeneracy of the ground state leads to a macroscopic number of zero-frequency modes. Although a Jahn-Teller distortion lifts the frustration and moves the zero modes to finite frequencies, we find that the spin-wave spectrum contains a remnant of that degeneracy. Remarkably, a large fraction of spin waves can *remain degenerate* in the deformed magnet, appearing as a resonance at the frequency $\omega_0 = 4S\delta J$. The effective difference of exchange couplings δJ between satisfied and frustrated bonds $J_{ij} = J - 2C_4(\mathbf{S}_i \cdot \mathbf{S}_j)$ is due to the biquadratic exchange (3). The resonance is a local spin wave reminiscent of the weather-vane mode of the kagomé antiferromagnet [15]. In the present context, the mode is confined to *any* line of parallel spins. Such lines are abundant in collinearly ordered states: each spin has exactly two parallel neighbors. When successive spins on the string precess with a phase shift of π, spins adjacent to that line can remain unaffected because the exchange field at their locations does not precess. (It can be shown that, despite the magnetoelastic coupling, harmonic spin waves and phonons are decoupled in any collinearly ordered magnet.)

For various kinds of collinear ground states, the string mode can live on straight lines of parallel spins [Fig. 3(a)], spirals [Fig. 3(b)], irregular lines, or even closed loops. A mode living on a short loop is truly a local resonance: the local density of spin waves $dN/d\omega$ contains a δ function. Open strings are localized in only two directions and will therefore be seen in the local density of states as a strong van Hove singularity $dN/d\omega \propto |\omega - \omega_0|^{-1/2}$ (Fig. 5). The shape of the strings determines the form factor of the resonance observable, e.g., by inelastic neutron scattering. A recently found resonance [12] in $ZnCr_2O_4$ has the form factor of a hexagonal string mode [16] (the shortest possible loop, Fig. 5, inset).

Discussion.—We have demonstrated that a large spin degeneracy and high symmetry of the pyrochlore network provide a robust way to relieve spin frustration: by means of a Jahn-Teller distortion of tetrahedra. A transition to a spin-Peierls state with a two-component order parameter, which can be spatially nonuniform, may precede, or coincide with, a Néel transition. A unique feature of such a distorted antiferromagnet is a large number of degenerate spin waves confined to lines of parallel spins. Our theory has direct relevance to the observed magnetic and structural phase transitions and local modes in pyrochlore antiferromagnets YMn_2, ZnV_2O_4, MgV_2O_4, $ZnCr_2O_4$, and $MgCr_2O_4$. The extension of the above mechanism to other frustrated lattices such as the triangular and kagomé is immediate for the case of Ising magnets; for Heisenberg symmetry the $S = 1/2$ kagomé system with its high density of low energy states [2] appears to be a promising candidate for future work.

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