Lattice-coupled antiferromagnet on frustrated lattices

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The lattice-coupled antiferromagnetic spin model is analyzed for a number of frustrated lattices: triangular, Kagomé, and pyrochlore. We show, within the mean-field theory, that the classical ground state is free of lattice deformation in the triangular, Kagomé, and the tetrahedron-based, $\mathbf{q}=0$, E_g phonon mode of the pyrochlore lattice. The $\mathbf{q}=0$, E_u phonon mode of pyrochlore is shown to have an energy gain of $-2\alpha^2$ per spin over the undistorted ground state, where α is the spin-lattice interaction strength. Motivated by the picture of the hexagon spin cluster proposed in the recent experiment on $ZnCr_2O_4$ [S. H. Lee *et al.*, Nature (London) **418**, 856 (2002)], we also analyze the hexagon-based distortion within our model. Hexagon distortions give rise to mutually orthogonal arrangement of spins for nearby hexagons, and has an energy gain of $-\alpha^2/2$ per spin. A general criterion for the lattice instability in the spin-lattice model is discussed.

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Understanding the nature of the ground states, and the phase transitions between various possible phases, of an insulating antiferromagnet is an interesting and a lively subject. The fundamental starting point is the Heisenberg Hamiltonian

$$H=\sum_{\langle ij\rangle} J_{ij}S_i\cdot S_j \quad (J_{ij}>0) \tag{1}$$

defined for an appropriate set of bonds $\langle ij\rangle$. Recently, the importance of a lattice distortion in relieving frustrations which are inherent in certain lattices has attracted a lot of attention.[1,2] Noting that the exchange energy J_{ij} should depend generically on the separation of orbitals, one can generalize the exchange constant J_{ij} as

$$J_{ij}=J(|i+u_i-j-u_j|)\approx J_0-J_1\hat{e}_{ji}\cdot(u_j-u_i), \tag{2}$$

where $\hat{e}_{ji}=(j-i)/|j-i|$ is the unit vector connecting the equilibrium ionic sites, i and j, and J_0 and J_1 are positive constants. Displacements of each site are denoted u_i and u_j, respectively. Existing experimental data suggests that J_{ij} falls off as 6th–14th power of the separation.[3]

For an Einstein, or optical, phonon mode, and ignoring the kinetic energy of the displacement, we arrive at the lattice-coupled spin model[4]

$$H=\sum_{\langle ij\rangle}[J_0-J_1\hat{e}_{ji}\cdot(u_j-u_i)]S_i\cdot S_j+\frac{K}{2}\sum_i u_i^2. \tag{3}$$

The purpose of this paper is to analyze the ground state of the model Hamiltonian, Eq. (3), in the classical limit $S\to\infty$, for a number of frustrated lattices: triangular, Kagomé, and pyrochlore.[5] Although a similar spin-lattice coupled model has been analyzed by a number of authors for the pyrochlore structure, much less attention has been devoted to the study of the two-dimensional frustrated lattices. We show, by a general argument, that local spin order (to be defined more precisely later) inherent in the two-dimensional cases makes the spin-lattice coupling ineffective in producing any structural changes. Then, we turn our attention to the much-studied pyrochlore case. We emphasize that the difference for the pyrochlore structure is the absence of local spin order. Previous works have assumed that all the nonoverlapping tetrahedra in the pyrochlore lattice undergo the same structural change ($\mathbf{q}=0$ mode). Motivated by the remarkable experiment in Ref. 6, we consider a different type of structural deformation based on hexagon units. Ground state energies for both types of distortions are calculated based on our microscopic Hamiltonian. Below, we present the details of our work.

By rescaling the displacements, $u_i\to u_i/\sqrt{K}$, in Eq. (3), J_1 is rescaled to $J_1/\sqrt{K}\equiv\alpha$, while the overall energy scale is fixed by J_0, which is set to one. The reduced Hamiltonian has the form

$$H=\sum_{\langle ij\rangle} S_i\cdot S_j-\alpha\sum_i u_i\cdot f_i+\frac{1}{2}\sum_i u_i^2, \tag{4}$$

with $f_i=\Sigma_{j\in i}\hat{e}_{ij}S_i\cdot S_j$. We indicate all the sites j exchange coupled to i by the symbol $j\in i$. The nearest-neighbor exchange interaction is assumed throughout the paper. We also scale the spin magnitude S to be one. Minimizing the energy with respect to u_i gives the condition relating the lattice position with the spin averages

$$u_i/\alpha=\langle f_i\rangle=\sum_{j\in i}\hat{e}_{ij}\langle S_i\cdot S_j\rangle. \tag{5}$$

The meaning of this equation is intuitively clear. Lattice positions move in such a way that bonds with a large exchange coupling $|\langle S_i\cdot S_j\rangle|$ shrink while the less tightly coupled bonds have a longer bond length. The right-hand side (rhs) of Eq. (5) is the sum over all nearest-neighbor magnetoelastic forces acting on site i, with the force given in proportion to the local spin-spin correlation $\langle S_i\cdot S_j\rangle$.

The average $\langle S_i\cdot S_j\rangle$ breaks up into a product of averages $\langle S_i\rangle\cdot\langle S_j\rangle$ within the mean-field theory. We have carried out a mean-field analysis of the classical energy functional, Eq.

(4), and found that, despite the presence of spin-lattice coupling, mean-field solution is characterized by a zero displacement, $u_i=0$, for both triangular and Kagomé lattices.

Classical antiferromagnet on triangular as well as Kagomé lattices are characterized by a 120° angle between a pair of adjacent spins at the mean-field level. The difference in the ground-state degeneracy for the two lattices does not play a role here, because Eq. (5) depends solely on the spin-spin correlation $\langle S_i \cdot S_j \rangle$ for the nearest-neighbor pairs, which in both lattices are $-\frac{1}{2}$. Therefore, $u_i \propto \Sigma_{j \in i} \hat{e}_{ij}=0$. Employing the acoustic phonon model, $(K/2)\Sigma_{\langle ij \rangle}(u_i-u_j)^2$, does not alter the conclusion. The local rotational symmetry of the $\langle S_i \cdot S_j \rangle$ in these lattices removes the possible linear gain in the exchange energy from the distortion. As we shall see now, this symmetry condition is violated for the pyrochlore lattice and there is a spontaneous displacement from spin-lattice coupling.

The product $\langle S_i \cdot S_j \rangle = \langle S_i \rangle \cdot \langle S_j \rangle$ can no longer be decomposed into a product of averages if, for example, there is a valence bond across the $\langle ij \rangle$ bond. There we have $\langle S_i \cdot S_j \rangle \neq 0$ without having any magnetic order. Valence bond solid order may condense for certain values of spin S.[7] The symmetry argument used to detect the local deformation of lattice holds for the valence bond-ordered case, because the rhs of Eq. (5) can be a measure of either the magnetic order, or the valence-bond order without the concomitant magnetic order.

Ground state manifold of classical spins on the pyrochlore lattice is defined by the condition

$$\sum_{i \in \tau} S_i = 0, \tag{6}$$

where the basic building block τ is a tetrahedron, for all the tetrahedra forming the lattice. The requirement is not sufficient to determine $\langle S_i \cdot S_j \rangle$ uniquely for nearest-neighbor sites. The local spin symmetry we discussed in the context of two-dimensional lattices is generally lacking for the ground states of pyrochlore spins. Within the manifold of spin states satisfying Eq. (6), the classical energy is given by

$$E = E_0 - \alpha \sum_i u_i \cdot \langle f_i \rangle + \frac{1}{2}\sum_i u_i^2 = E_0 - \frac{1}{2}\sum_i u_i^2, \tag{7}$$

where E_0 is the energy without the spin-lattice coupling. Mean-field condition $u_i=\alpha\langle f_i \rangle$ is used to arrive at the final expression.

For an isolated tetrahedron, interaction energy $-(\alpha^2/2)\Sigma_i f_i^2$ is minimized for a collinear arrangement of spins, with two pairs of $(\uparrow\downarrow)$ spins on opposite edges of the tetrahedron. There is a threefold degeneracy, not counting the spin reversal, corresponding to different ways to arrange the two pairs over the tetrahedron. Accompanying structural distortion is tetragonal.

Generalization to the network of tetrahedra which forms the pyrochlore lattice was carried out by Tschernyshyov, Moessner, and Sondhi (TMS),[2] assuming all the nonoverlapping tetrahedra undergo the same distortion ($\mathbf{q}=0$ phonons). Even within the $\mathbf{q}=0$ mode, spins can be arranged in several different ways. Spin arrangements that are repeated over all the nonoverlapping tetrahedra (E_g phonon in Ref. 2) give $u_i=0$ according to Eq. (5). Energy per site for the undistorted pyrochlore lattice is $E_0=-1$. For the E_u phonon mode, Eq. (5) gives $|u_i|=2\alpha$, and the energy per site $-1-2\alpha^2$ according to Eq. (7). The difference between the two modes is that for the E_g phonon, spins on opposite nearest neighbors of site i are always the same, leading to the cancellation of magnetoelastic forces. In the E_u case, two ferromagnetic bonds are joined by two antiferromagnetic bonds on the other side of i for a net displacement, while the remaining two antiferromagnetic bonds cancel out.

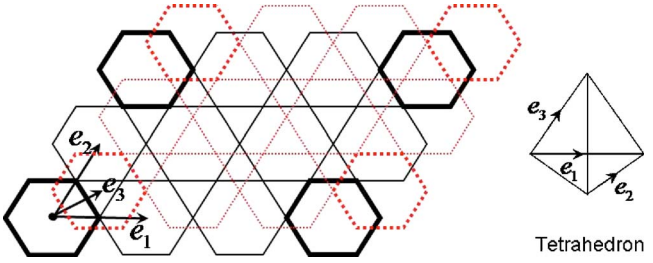

FIG. 1. (Color online) Nonoverlapping hexagons that span the pyrochlore lattice, shown in bold black and red for two adjacent Kagomé planes. Pyrochlore lattice has four types of Kagomé plane stacks intersecting one another at the angle of the four faces of a tetrahedron.

It is not *a priori* clear what kind of spin configurations within the manifold defined by Eq. (6) will condense once we relax the $\mathbf{q}=0$ condition. While an unrestricted mean-field calculation would be desirable, in practice convergence to a unique ground state appears impossible starting from a random initial set of spins. Difficulty to find a true ground state is presumably a consequence of the very complicated energy landscape, with many competing metastable states, that is characteristic of highly frustrated lattices.

In this regard, an inspiring observation has been made in a recent neutron scattering experiment of the pyrochlore compound $ZnCr_2O_2$. Although the low-temperature phase, below $T_c=12.5$ K, has the tetragonal structure with coplanar spins,[8] the paramagnetic, cubic phase appears to be characterized by hexagonal clusters of antiferromagnetically correlated spins. The resulting block spins are christened "spin-loop directors," or directors for short, in Ref. 6. While this picture is extraordinary no quantitative justification for the formation, and the stability, of such a hexagonal spin cluster appears to exist to date. We speculate that it is the spin-lattice coupling that aids the formation of hexagon clusters. To give support of such a claim, we ask whether the hexagon-based distortion is a viable, metastable solution of Eq. (5), and if so, to compare the energy to that of the tetrahedron-based $\mathbf{q}=0$ mode.

Pyrochlore lattice is built up of four different types of nonoverlapping hexagons, depending on the orientation of the face of each hexagon.[6] Each hexagon type lies in one of the four Kagomé planes that are buried inside the pyrochlore. For a given Kagomé plane, the nonoverlapping hexagons are located as in Fig. 1. Each site in the pyrochlore lattice belongs to one, and only one such hexagon. The deformation

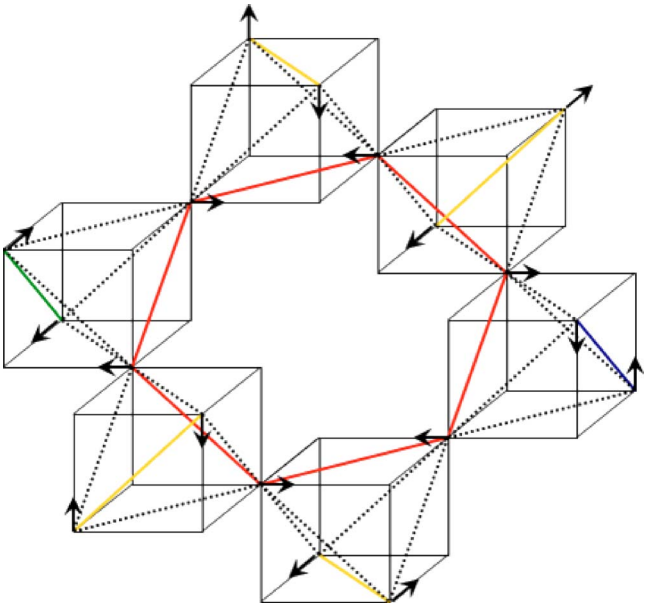

FIG. 2. (Color online) Local spin configuration of the hexagon-distorted pyrochlore lattice. Short (long) bonds are denoted by colored (dashed) lines after the lattice distortion. Each short bond belongs to one and only one hexagon cluster. Spins are collinear within a hexagon and orthogonal for nearby hexagons. Different colors represent orientation of the hexagon.

mode we consider assumes that each nonoverlapping hexagon uniformly shrinks in size while the hexagon-hexagon distances remain unchanged.

First, a single hexagonal antiferromagnetic chain coupled to the lattice as in Eq. (3) has a mean-field ground state given by staggered spins, $S_i^0 = \pm\hat{z}$, and the corresponding u_i all pointing inward to the center of the hexagon (uniform contraction) with $|u_i| = \alpha$. The energy of the hexagon per site is $-1-\alpha^2/2$. The orientation of the antiferromagnetic spins defines the spin-loop director of Ref. 6.

Each adjacent pair of spins in the hexagon forms one edge of a tetrahedron, with the other edge associated with a neighboring hexagon (Fig. 2). Each hexagon is a neighbor to six other hexagons. We are assuming that each hexagon contracts towards its center of mass. This fixes the direction of all u_i's in the lattice, and the only solution of Eq. (5) consistent with this requirement on u_i is when spins of the nearby hexagons are mutually orthogonal as shown in Fig. 2. This means that in the sum, $\Sigma_{j\in i}\hat{e}_{ij}\langle S_i \cdot S_j\rangle$, four pairs give zero because of orthogonality, and the remaining two which are antiferromagnetically coupled give $-\Sigma'_{j\in i}\hat{e}_{ij}$ which points to the center of a given hexagon. So, our hexagon-based distortion will be a consistent solution of Eq. (5) provided that we can assign one of the three mutually orthogonal director

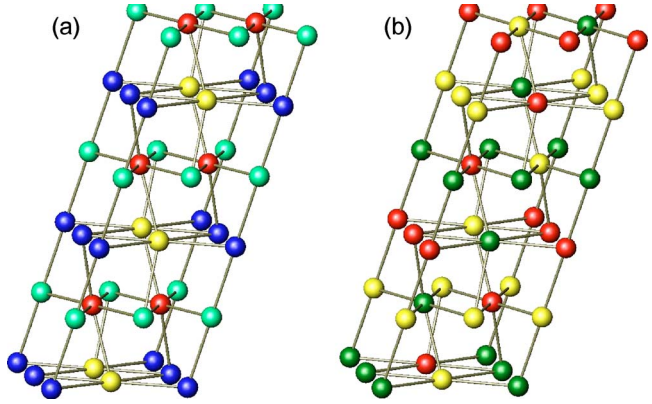

FIG. 3. (Color online); (a) Each colored dot represents the center-of-mass of a hexagon of given type embedded inside the pyrochlore. Four types of hexagons cover the entire lattice. Rods connect the nearest-neighbor hexagons. (b) Each hexagon represented as a dot is colored according to the director orientation, which is chosen from one of three orthogonal directions indicated by green, yellow, and red.

orientations—X, Y, and Z—for all the hexagons, with the nearby hexagons always having orthogonal directors.

To demonstrate that this is indeed possible, we first build a "superlattice" of hexagons, treating the center of each hexagon as a lattice site of this superstructure. Figure 3(a) shows hexagons of a given orientational type as a colored dot, with the rods connecting the adjacent hexagons in the real-space pyrochlore lattice. The unit cell in Fig. 3(a) consists of $2\times2\times2$ hexagons, with two of each type in a unit cell. Each hexagon is surrounded by six nearest-neighbor hexagons as expected.

Next, we demonstrate that the hexagon-based lattice of Fig. 3(a) can be colored using only three colors, X, Y, Z, in such a way that no two points connected by the rod carry the same color. In Fig. 3(b) we show how this can be achieved, using the unit cell consisting of $2\times2\times6=24$ points. The energy per site for this arrangement of spins is $-1-\alpha^2/2$, same as that of a single contracted hexagon, because the interhexagon exchange energy is zero from orthogonality of spins. Each site of the pyrochlore lattice has two antiferromagnetically coupled neighbors, and the other four with orthogonal spins. The energy is lower than that of the undistorted lattice, but higher than the E_u phonon mode which has an energy $-1-2\alpha^2$. The factor of four difference stems from the amount of displacement in the hexagon-contraction scenario which is $|u_i| = \alpha$, half that of the E_u phonon. It is possible, however, that addition of higher-order spin interactions or application of external perturbation such as magnetic field can change the relative energetics of the distortion modes. At any rate, we have proved the existence of a metastable con-

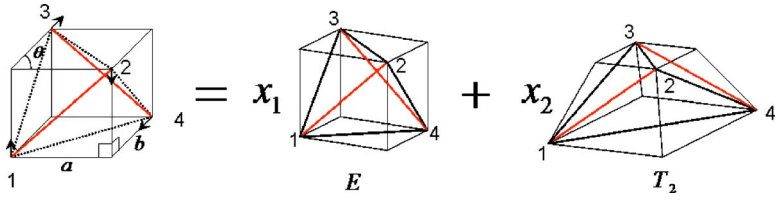

FIG. 4. (Color online) Distortion of an isolated tetrahedron consistent with hexagon contraction.

figuration in the pyrochlore lattice with a very different spin-lattice structure than previously proposed, which appears to account for the experimental indication of Ref. 6.

For a single tetrahedron, there are six vibrational modes: singlet A_1, a doublet E, and a triplet ${T_2}^2$. When the pyrochlore lattice assumes the hexagonal distortion we discuss, the resulting distortion for an isolated tetrhedron is not tetragonal (E) as discussed in TMS, but is a linear combination of a doublet E and a triplet T_2 (Fig. 4).

A few words can be said about the effects of valence-bond order on the lattice distortion. For example, $S=1/2$ spins can form at most only one singlet bond for each site. In this case, a nonzero displacement is guaranteed by Eq. (5). A similar situation occurs for half-odd integer spins, for which odd number of bonds emanate from a given site. The interplay between valence bond order formation and spin-lattice coupling is an exciting issue, to which we shall return in the future. The lowering of symmetry in the bond ordered, but magnetically disordered phase and the concomitant lattice distortion was also pointed out by TMS.

In conclusion, we analyzed a model of the lattice-coupled antiferromagnetic spins on a variety of frustrated lattices. We derived Eq. (5) relating the local lattice displacement with the local spin-spin correlation $\langle S_i S_j \rangle$. Within the mean-field theory of the magnetic order, a number of situations including triangular, Kagomé, and $\mathbf{q}=0$, E_g phonon mode in the pyrochlore lattice were shown to be free of lattice deformation, due to the symmetric cancellation of magnetoelastic forces. The $\mathbf{q}=0$, E_u phonon mode has an energy of $-1-2\alpha^2$ per spin. Inspired by the picture of hexagonal spin cluster proposed for the paramagnetic $ZnCrO_4$, we considered the hexagon contraction of the pyrochlore lattice. The hexagon clustering is shown to have an energy $-1-\alpha^2/2$ per site.

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