

## Coexisting Order and Disorder Hidden in a Quasi-Two-Dimensional Frustrated Magnet

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Frustrated magnetic interactions in a quasi-two-dimensional  $\langle 111 \rangle$  slab of pyrochlore lattice were studied. For uniform nearest neighbor (NN) interactions, we show that the complex magnetic problem can be mapped onto a model with two independent degrees of freedom, tricolor and binary sign. This provides a systematic way to construct the complex classical spin ground states with collinear and coplanar bipyramidal spins. We also identify “partial but extended” zero-energy excitations amongst the ground states. For nonuniform NN interactions, the coplanar ground state can be obtained from the collinear bipyramidal spin state by collectively rotating two spins of each tetrahedron with an angle  $\alpha$  in an opposite direction. The latter model with  $\alpha \sim 30^\circ$  fits the experimental neutron data from  $\text{SrCr}_9\text{pGa}_{12-9\text{p}}\text{O}_{19}$  well.

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In ordinary magnets, when the temperature is lowered, the spins freeze into a long-range ordered state or a spin solid. Some magnets, however, do not order even at low temperatures [1–8]. The simplest examples are a triangle of three antiferromagnetic (AFM) spins and a tetrahedron of four AFM spins. For both systems, any spin configuration with total zero spin can be a ground state. When such triangles (tetrahedra) are arranged in a two-dimensional (three-dimensional) corner-sharing network or kagome (pyrochlore) lattice, there is an infinite way of covering the entire lattice with the total-zero-spin building blocks. As a result, instead of ordering at low temperatures, the kagome and pyrochlore antiferromagnets remain in a spin liquid state [9–11]. A hallmark of the frustration-driven spin liquid is the existence of local zero-energy excitation modes that continuously connect their degenerate ground states in the phase space of spin configuration and energy: the so-called weather-vane mode for the kagome [12,13] and the hexagonal mode for the pyrochlore [14,15] antiferromagnets.

Some frustrated magnets, however, exhibit nonconventional spin-glass behaviors: field-cooled and zero-field-cooled hysteresis in the bulk susceptibility [5] and static short-range spin correlations but with a strongly momentum-dependent structure factor in neutron scattering [16]. Among them,  $\text{SrCr}_9\text{pGa}_{12-9\text{p}}\text{O}_{19}$  [SCGO(*p*)] [16–24] and  $\text{Ba}_2\text{Sn}_2\text{ZnGa}_3\text{Cr}_7\text{O}_{22}$  [24–27] are particularly interesting because in both systems the magnetic  $\text{Cr}^{3+}$  ( $3d^3$ ;  $s = 3/2$ ) ions form a kagome-triangular-kagome trilayer [28]. Due to the ligand environment and the electronic orbitals of the  $\text{Cr}^{3+}$  ions [19], the spin Hamiltonian can be described by  $\mathcal{H} = J \sum_k \mathbf{S}_i \cdot \mathbf{S}_j + J' \sum_{k-l} \mathbf{S}_i \cdot \mathbf{S}_j$ , where the first sum is over the nearest neighbor (NN) bonds between the kagome spins, and the second sum is over the bonds between the kagome and triangular spins [Fig. 1(a)]. The different values of  $J$  and  $J'$  are due to their different bond lengths. Since the discovery of SCGO more than two

decades ago [17], understanding the origin of the nonconventional spin glass behavior has been a challenging issue.

In this Letter, by mapping the magnetic interaction problem onto a model with two independent degrees of freedom, tricolor and binary sign, we present a methodical way to construct the complex classical spin ground states with collinear and coplanar bipyramidal spins for uniform and nonuniform NN interactions. We also identify “partial but extended” zero-energy excitations amongst the ground states that are qualitatively different from the “local” zero-energy excitations found in spin liquid states of other frustrating magnets. By comparing the resulting theoretical

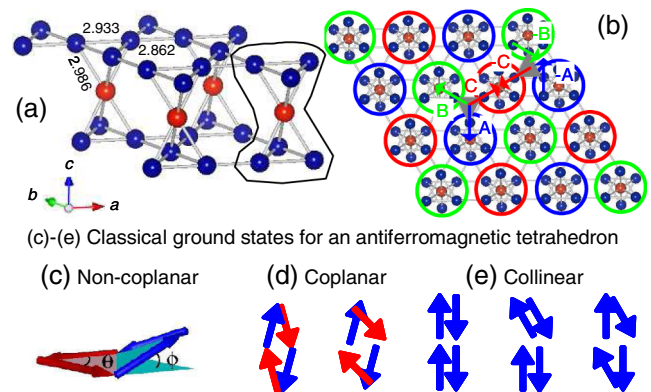


FIG. 1 (color online). (a) The  $\langle 111 \rangle$  slab of pyrochlore lattice made up by a kagome-triangular-kagome trilayer realized by the magnetic  $\text{Cr}^{3+}$  ions in SCGO. The numbers are the bond lengths in Å. The blue (darker gray) and red (lighter gray) spheres represent kagome and triangular sites, respectively. (b) The lattice is projected on the *ab* plane. The red ( $\pm C$ ), blue ( $\pm A$ ), and green ( $\pm B$ ) arrows represent the three spin directions of a  $120^\circ$  configuration. (c) Noncoplanar, (d) coplanar, and (e) collinear classical ground states for an AFM tetrahedron. In (e), the first figure represents a collinear state and the other two represent the possible zero-energy modes.

magnetic scattering to the experimental neutron intensities obtained from single crystals of SCGO ( $p = 0.67$ ), the ratio of  $J'/J \sim 0.70(15)$  was obtained, which is reasonable for SCGO. We argue that a topological spin glass might be the ground state of the magnetic lattice.

Elastic neutron scattering measurements on single crystals of SCGO ( $p = 0.67$ ) with total mass of  $\sim 300$  mg were performed on the cold neutron triple-axis spectrometer SPINS at the NIST Center for Neutron Research. Energy of neutrons was fixed to  $E_i = 5$  meV with an energy resolution of 0.25 meV. A horizontally focusing analyzer with seven PG(002) blades was utilized to enhance the intensity of scattered neutrons. The background and nuclear contributions to the detector count rate have been measured at  $T = 20$  K, that is above its spin glass transition,  $T_g = 4.5$  K, and subtracted from the 1.6 K data.

Let us first consider the perfect quasi-two-dimensional lattice with  $J' = J$ . We consider two corner-sharing tetrahedra or a bipyramid with a triangular base circled by a solid line in Fig. 1(a) as a “molecular” unit. As shown in Fig. 1(b), the bipyramids form a triangular superlattice. This is crucial because triangles and tetrahedra behave quite differently; the triangle favors a  $120^\circ$  spin configuration [Fig. 1(b)], while the tetrahedron favors any configuration with total zero spin [Figs. 1(c)–1(e)]. The challenge is then to find spin configurations where every tetrahedron within the bipyramids and the triangles that link neighboring bipyramids [highlighted by gray triangles in Fig. 1(b)] satisfies its different AFM constraints. One can easily see that there will be an infinite number of such configurations. One class of spin configurations that we will focus on first is those where spins within the bipyramids are collinear. This approach can be justified by the following argument. Let us consider the zero-energy excitations possible for noncoplanar, coplanar, and collinear spin configurations for an AFM tetrahedron. For the noncoplanar state, if one spin rotates, then the other three spins must rotate to keep the total spin at zero [Fig. 1(c)]. For the coplanar state with two pairs of antiparallel spins, on the other hand, if one spin rotates, only its counterpart forming one pair can rotate by the same angle to keep the total spin zero without moving the other pair [Fig. 1(d)]. Such zero-energy excitations involving only a fraction (half) of spins would favor a coplanar ground state over a noncoplanar state. For the collinear case, the two pairs are along the same direction, and thus there are two choices forming a pair [Fig. 1(e)]. Thus, for a single bipyramid, the collinear structure is favored by entropy. Of course, the coplanar state also has extensive entropy and cannot be ignored. After finding the possible collinear bipyramid spin states for the hybrid lattice, we will show that the coplanar bipyramid spin states can be generated from the collinear states.

To find possible collinear bipyramid spin states, let us start by assigning, for a linking triangle, a  $120^\circ$  spin configuration with three spins ( $A, B, C$ ) colored in blue,

green, and red, respectively [Fig. 1(b)]. Since the three spins belong to three different bipyramids, the three different colors can be assigned to the bipyramids to show that all seven spins within each bipyramid point either parallel or antiparallel to the assigned spin direction. Since the bipyramids are connected in a triangular superlattice, the interbipyramid interactions for the collinear bipyramids can only be minimized when the colors form a long-range  $\sqrt{3} \times \sqrt{3}$  color structure [see the colored circles in Fig. 1(b)]. The remaining task is to find the internal spin state of the collinear bipyramid. This can be done simply by assigning plus or minus signs to the seven spins forming a bipyramid with the constraint that each tetrahedron must have two plus and two minus signs. When such bipyramids are arranged in the triangular superlattice, only one constraint has to be satisfied: the linking triangle must have a  $120^\circ$  spin configuration, i.e., either  $(A, B, C)$  or  $(-A, -B, -C)$ , leading to a strict constraint of ferro-sign bonds for the triangles [Fig. 1(b)]. The spin degrees of freedom are thus mapped onto two different degrees of freedom, the long-range ordered tricolor and the disordered binary sign.

Each collinear bipyramid has 18 possible sign states, nine of which are shown in Fig. 2(a), and the other nine can be generated by a sign flip. Thus, for a noninteracting  $N$  number of bipyramids, there are  $18^N$  possible sign states. The ferro-sign bond constraint, however, severely limits the options. To see this, let us assign a sign state (say state 1) to a central bipyramid and determine all possible sign states for the 6 nearest neighboring bipyramids of a hexagonal ring. It is tedious but straightforward to see that there are only 111 sign states allowed by the ferro-sign bonds. When the 12 bipyramids on the next large hexagonal ring are included, there are 13 238 possible sign states for the 18 neighboring bipyramids. There is, however, only one sign state that has a long-range order and is formed by the three sign states, 1, 6, and 8, as shown in Fig. 3(a). It is easy to find that there are three similar long-range ordered sign states formed by the sign states 1 to 9: 1-6-8 [Fig. 3(a)], 2-4-9, and 3-5-7. There is another set of such three states that can be obtained by the sign flip symmetry.

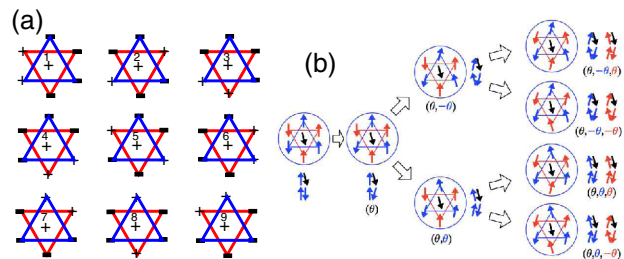


FIG. 2 (color online). (a) Nine possible sign states for a bipyramid, where each tetrahedron has total zero spin. (b) Collective zero-energy excitations for a bipyramid, involving all seven spins and satisfying the total zero-spin constraint.

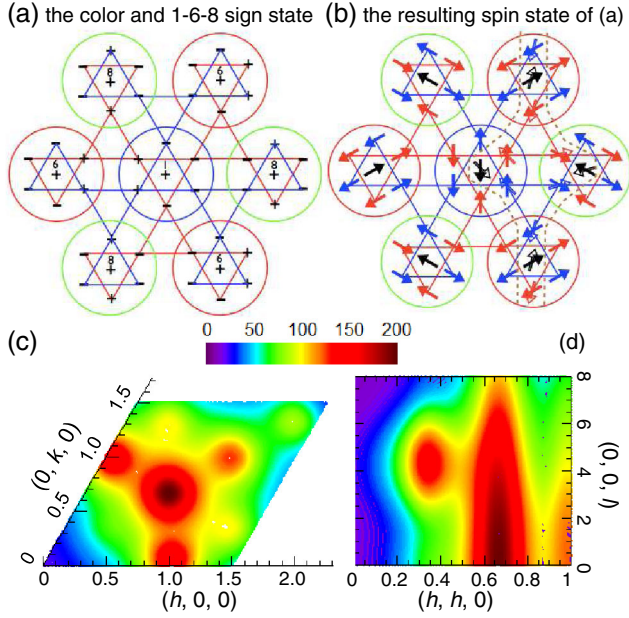


FIG. 3 (color online). (a) A sign state for the triangular lattice of bipyramids that has a long-range  $\sqrt{3} \times \sqrt{3}$  structure. (b) Filled arrows represent spins in a collinear bipyramid spin state constructed by the color and the 1-6-8 sign state shown in (a). Open arrows are explained in the text. (c),(d) The calculated neutron scattering intensities for  $J' = J$  in the  $(hk0)$  and  $(hhl)$  planes.

Once the sign state is determined for the lattice, the actual spin state can be easily constructed by imposing the color state on the sign state, as shown in Figs. 3(a) and 3(b).

Let us now turn to the coplanar bipyramid spin states. A coplanar state can be generated from a collinear state by rotating the 7 spins in several collective ways [see Fig. 2(b)]. For the entire lattice, because of the color and ferro-sign bond constraints, three angles with the same magnitude ( $\theta, \pm\theta, \pm\theta$ ) are sufficient to generate a long-range ordered coplanar state. An arbitrary value of  $\theta$  corresponds to a coplanar state, which leads to macroscopically degenerate coplanar states. The collinear spin state and its resulting coplanar states are continuously connected with each other in the spin-energy phase space, and the excitations among them realize the zero-energy excitations involving all spins—“global” spin zero-energy excitations. Different types of zero-energy excitations are also possible for the long-range ordered collinear and coplanar bipyramid spin states. As illustrated in Figs. 1(d) and 1(e), only one pair of the antiparallel spins of a coplanar or collinear tetrahedron can rotate without moving the other pair. This kind of excitation leads to “partial but extended” spin zero-energy excitations. An example is the excitations of an uneven spaghetti shape that propagates along only one direction in the  $ab$  plane, as illustrated by the open arrows and the dashed line in Fig. 3(b).

If a real material realizes the model of  $\mathcal{H}$  with  $J' = J$ , upon cooling the spins would freeze into numerous finite-size domains with every collinear and coplanar bipyramid

spin state. We generated all possible long-range coplanar states by the angle  $\theta$ , with a step of  $5^\circ$  for the “global” spin zero-energy motion starting from the aforementioned three long-range collinear states, and calculated the square of the magnetic structure factor  $|F_M(\mathbf{Q})|^2$  for each state. For long-range order,  $I(\mathbf{Q}) \propto \sum_{\mathbf{Q}_M} |F_M(\mathbf{Q})|^2 \delta^2(\mathbf{Q} - \mathbf{Q}_M)$ , with two-dimensional reciprocal lattice vectors  $\mathbf{Q}_M = (n/3, m/3, 0)$ , where  $n$  and  $m$  are integers. For short-range order, however, the two-dimensional delta function  $\delta^2(\mathbf{Q} - \mathbf{Q}_M)$  is replaced by the two-dimensional Lorentzian  $1/[\kappa^2 + (\mathbf{Q}_{ab} - \mathbf{Q}_M)^2]$ , where  $\mathbf{Q}_{ab}$  is the  $ab$  component of  $\mathbf{Q}$ , and  $\kappa$  is the inverse of the in-plane correlation length,  $\xi$ ,  $\kappa = 2\pi/\xi$ . Figures 3(c) and 3(d) show the calculated  $I_{\text{ave}}(\mathbf{Q})$  with  $\xi \sim 20 \text{ \AA}$ . The  $I_{\text{ave}}(\mathbf{Q})$  produces strong broad scattering at around  $(2/3, 2/3, l)$  and  $(1/3, 1/3, l)$  in the  $(hhl)$  plane and  $(2/3, 2/3, 0)$  in the  $(hk0)$  plane. It also produces additional peaks at  $(1, 0, 0)$  and  $(1, 1, 0)$  in the  $(hk0)$  plane and along  $(1, 1, l)$  in the  $(hhl)$  plane.

Figures 4(a) and 4(b) show contour maps of magnetic neutron scattering intensities obtained from single crystals of SCGO ( $p = 0.67$ ). The experimental data have similarities and differences with the calculated intensities for  $J' = J$ : their similarity is the strong broad peaks at  $(2/3, 2/3, 0)$  in the  $(hk0)$  plane and along the  $(1/3, 1/3, l)$  and  $(2/3, 2/3, l)$  directions, while their difference is the

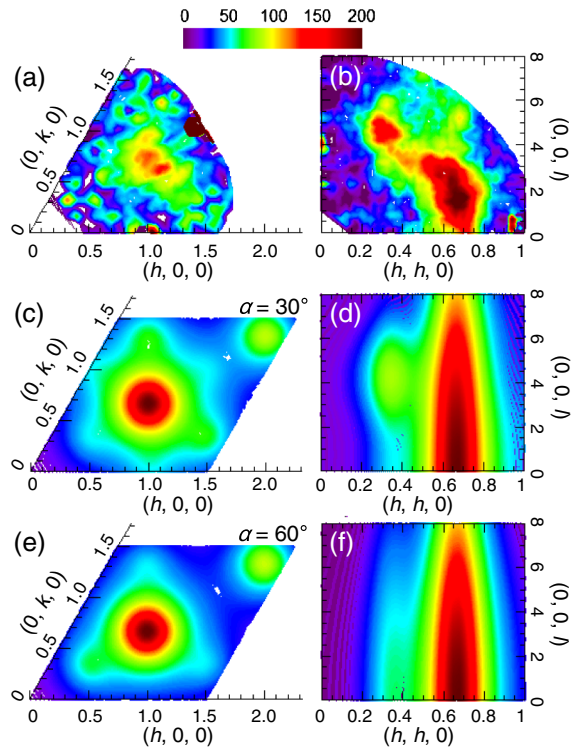


FIG. 4 (color online). (a),(b) The experimental magnetic neutron scattering intensities in the  $(hk0)$  and  $(hhl)$  planes. (c)–(f) The calculated elastic magnetic scattering intensities (c),(d) with  $\alpha = 30^\circ$  and (e),(f) with  $\alpha = 60^\circ$ .

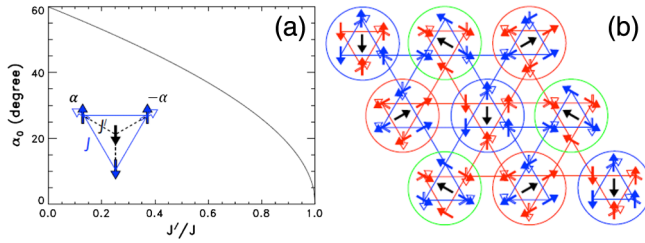


FIG. 5 (color online). (a) The optimal  $\alpha_0$  is plotted as a function of  $J'/J$  for the tetrahedron. (b) The long-range ordered conventional  $\sqrt{3} \times \sqrt{3}$  structure constructed for  $J' = 0$ , explained in the text. A similar rotation with  $(-60^\circ, 60^\circ)$  will lead to the  $q = 0$  structure.

lack of scattering at the integer  $Q$  points in the  $(hk0)$  plane and along the  $(1, 1, l)$  direction in the  $(hhl)$  plane. The discrepancy comes from the fact that SCGO does not realize the perfect hybrid lattice with  $J' = J$ . Instead, the lattice is distorted to yield different coupling constants for the in-plane and out-of-plane interactions, as shown in Fig. 1(a).

While the tricolor sign state, i.e., the collinear bipyramid spin state, can no longer be the ground state for the nonuniform exchange interactions, here we show that the collinear state can be a good reference point to construct the ground state for the nonuniform case. Consider a collinear state for a single tetrahedron, shown as the filled arrows in the inset of Fig. 5(a). The ground state for  $J' < J$  can be obtained by rotating two kagome spins (unfilled arrows) that are antiparallel to the triangular spin in opposite direction,  $(\alpha, -\alpha)$ . The magnetic energy of the resulting spin configuration becomes  $E_\alpha = J[(-2 \cos \alpha + \cos 2\alpha) + J'/J(1 - 2 \cos \alpha)]$  that is lower than the energy of the collinear state  $E_{\alpha=0} = -J - J'$ . The optimal angle,  $\alpha_0$ , for a given value of  $J'/J$  can be obtained by differentiating  $E_\alpha$  with respect to  $\alpha$ , which yields  $J'/J = 2 \cos \alpha_0 - 1$ . Figure 5(a) shows the  $\alpha_0$  as a function of  $0 \leq J'/J \leq 1$ . For  $J' = J$ ,  $\alpha_0 = 0$  represents the collinear state, while for  $J' = 0$ ,  $\alpha_0 = 60^\circ$  represents the conventional  $120^\circ$  non-collinear spin configuration. There are only two ways to rotate the two kagome spins:  $(\alpha, -\alpha)$  or  $(-\alpha, \alpha)$ . When such bipyramids are arranged to form the triangular lattice of bipyramids as realized in SCGO, due to the strict antiferromagnetic constraint for the linking triangles, each rotation leads to a single long-range state. A resulting long-range ordered noncollinear coplanar bipyramid state with  $(\alpha, -\alpha)$  is shown in Fig. 5(b) for the special angle of  $\alpha_0 = 60^\circ$  for  $J' = 0$ , which is the conventional  $\sqrt{3} \times \sqrt{3}$  structure for kagome planes.

We considered the three long-range ordered collinear bipyramid states described above and performed the collective  $\alpha$  rotation towards the conventional  $\sqrt{3} \times \sqrt{3}$  structure. In each case, the square of the magnetic structure factor,  $|F(\mathbf{Q})|^2$ , was averaged over three crystallographic domains, and in the end, all three cases were added. The

same two-dimensional Lorentzians used in the uniform  $J$  case to account for the short-range order were multiplied to  $|F(\mathbf{Q})|^2$  to obtain the magnetic neutron scattering intensities  $I(\mathbf{Q})$  for various values of  $\alpha$ , as shown in Figs. 4(c)–4(f) for  $\alpha = 30^\circ$  and  $60^\circ$ . When  $\alpha$  increases, the intensities at the  $q = 0$  points such as  $(1, 0, 0)$ ,  $(0, 1, 0)$ , and  $(1, 1, 0)$  in the  $(hk0)$  plane decrease, as well as those at  $(1/3, 1/3, l \sim 4.2)$  and along the  $(1, 1, l)$  direction in the  $(hhl)$  plane. For  $\alpha = 60^\circ$ , the  $(1/3, 1/3, l \sim 4.2)$  peak almost disappears, which is inconsistent with the data. This means that  $\alpha < 60^\circ$  for SCGO. Because of the  $\sim 30\%$  nonmagnetic defects in the single crystals of SCGO ( $p = 0.67$ ), it is not possible to quantitatively compare the data to the theoretical model. However, qualitative comparison with the calculated  $I(\mathbf{Q})$  with  $\alpha \sim 30(10)^\circ$  reproduces the salient features of the data, as shown in Fig. 4. The  $\alpha \sim 30(10)^\circ$  corresponds to  $J'/J \sim 0.70(15)$ , which is a reasonable value for SCGO considering their bond lengths.

In summary, we have presented a systematic approach, involving a mapping into two degrees of freedom, to dealing with the complex magnetic interactions in the quasi-two-dimensional  $\langle 111 \rangle$  slab of pyrochlore lattice. This method can be used to obtain the ground states not only for the uniform NN  $J$  case but also for the nonuniform  $J$  case. Both uniform and nonuniform  $J$  cases have degenerate ground states that provide a topological argument for the nonconventional spin glass state of this system. We expect such spin glassy behaviors to be enhanced in the uniform  $J$  case because of the existence of the unique “partial” spin zero-energy excitation modes.

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- [28] These systems have vacancies in the magnetic lattice. Several studies using different experimental techniques, such as NMR [23], specific heat [20], and neutron scattering [16,18], however, have shown that the observed spin freezing is not due to the defects but is intrinsic to the trilayer antiferromagnet.