Spin-Driven Jahn-Teller Distortion in a Pyrochlore System

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The ground-state properties of the spin-1 antiferromagnetic Heisenberg model on the corner-sharing tetrahedra, the pyrochlore lattice, are investigated. By breaking up each spin into a pair of 1/2-spins, the problem is reduced to the equivalent one of the spin-1/2 tetrahedral network in analogy with the valence bond solid state in one dimension. The twofold degeneracy of the spin singlets of a tetrahedron is lifted by a Jahn-Teller mechanism, leading to a cubic to tetragonal structural transition. It is proposed that the present mechanism is responsible for the phase transition observed in the spin-1 spinel compounds ZnV_2O_4 and MgV_2O_4.

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Geometrically frustrated spin systems have been a fascinating subject to study since Anderson's pioneering work on classical spins with a disordered ground state [1]. The pyrochlore and the spinel compounds, both including the three-dimensional (3D) tetrahedral network sharing the vertexes, are the typical examples of such systems in nature. As recent theoretical progress on pyrochlore spin systems, it may be mentioned that the spin-1/2 antiferromagnetic (AF) Heisenberg model is shown to have a spin liquid ground state [2] and that, even for the ferromagnetic Ising model, a nontrivial effect of frustration leads to a newly found spin ice ground state [3]. In this Letter, we investigate the ground-state properties of the spin-1 AF Heisenberg model on the pyrochlore lattice.

We follow a general strategy of constructing effective variational wave functions, which approximately describe the low energy states in the same spirit as the resonating valence bond (RVB) [4] or the 1D valence bond solid (VBS) approaches [5]. These simple pictures are of great use to understand essential physics of the systems in a more intuitive way. Our simple scenario, where the low energy effective Hilbert space is assumed to adiabatically continue to the manifold of the product wave functions of the twofold degenerate spin singlets at each tetrahedron, leads to a spontaneous breakdown of the lattice symmetry. This new effect of the magnetoelastic interaction in the pyrochlore spin system gives a consistent picture with the recent experimental results on the insulating spin-1 spinel compounds ZnV_2O_4 and MgV_2O_4 [6–11].

First, let us introduce the AF Heisenberg model on the pyrochlore lattice, Fig. 1, in two different but equivalent representations where the interactions are defined for the sets of bonds and tetrahedra, respectively,

$$H = J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j = J \sum_{k=1}^{N_4} \frac{(\vec{S}_k^{\mathrm{tot}})^2}{2} + \text{const}, \quad (J > 0), \tag{1}$$

where $\vec{S}$ is the spin-1 operator and $\langle i,j \rangle$ denotes a nearest neighbor pair. The index k, numbered from 1 to N_4, specifies a tetrahedron and $\vec{S}_k^{\mathrm{tot}}$ represents the sum of the four spins on the kth tetrahedron. For the present spinel compounds, we expect that the relatively small spin value makes the isotropic limit a good starting point. On the other hand, it is well known that there are strong anisotropies for some rare earth titanates [3].

To tackle this problem, we develop an analogous method with that of the VBS state, which captures essential physics of the Haldane phase in 1D spin-1 systems. By breaking up the original spin-1 into two spin-1/2 objects (denoted by $\vec{s}$), we rewrite the Hamiltonian neglecting a constant energy shift as follows:

$$H = \mathcal{P} \left\{ 4J \sum_{k=1}^{N_4} \frac{(\vec{s}_{k_1} + \vec{s}_{k_2} + \vec{s}_{k_3} + \vec{s}_{k_4})^2}{2} \right\} \mathcal{P}, \tag{2}$$

where $(\vec{s}_{k_1}, \vec{s}_{k_2}, \vec{s}_{k_3}, \vec{s}_{k_4})$ are the spin-1/2 operators forming a tetrahedron. $\mathcal{P}$ is the operator to symmetrize the states spanned for all pairs of the 1/2-spins on every vertex and thus restricts the expanded Hilbert space to that of the original spin-1 model. The 4 times larger coupling constants are required so as to describe the original exchange interactions by those within the 1/2-spins on each tetrahedron. The tetrahedron-unit representation of the spin-1 pyrochlore system has a significant difference from the 1D VBS state in the sense that our fundamental unit is not a bond with two 1/2-spins but a tetrahedron with four 1/2-spins [12]. In particular, there is twofold ground-state degeneracy which makes the situation more interesting as

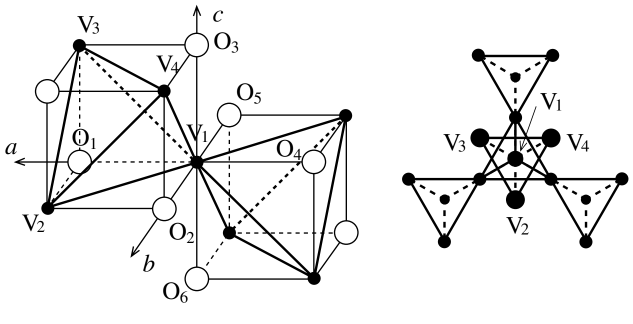

FIG. 1. The ideal locations of the vanadiums and oxygens in ZnV_2O_4 and the network of the vanadium ions viewed from the [111] axis.

discussed below. We believe that this simple transformation is useful to grasp the essence of the low energy physics of the original problem.

Following the general recipe for the 1D VBS state, we first discuss properties of the fundamental unit. Since the total spin of the tetrahedron is a good quantum number, the two spin singlets constitute the degenerate ground states. By using the linearly dependent three singlets whose total sum equals zero, $|2\rangle \equiv |\overrightarrow{12}\,\overrightarrow{34}\rangle$, $|3\rangle \equiv |\overrightarrow{13}\,\overrightarrow{42}\rangle$, and $|4\rangle \equiv |\overrightarrow{14}\,\overrightarrow{23}\rangle$, where $|\overrightarrow{ab}\,\overrightarrow{cd}\rangle$ is the product of the two valence bonds, $|\overrightarrow{ab}\rangle = (\uparrow_a \downarrow_b - \downarrow_a \uparrow_b)/\sqrt{2}$ and similarly defined $|\overrightarrow{cd}\rangle$, we express the tetrahedron singlets in orthonormal bases,

$$|R\rangle = \frac{\sqrt{2}}{3}(|2\rangle + \omega|3\rangle + \omega^*|4\rangle), \quad \text{and} \quad |L\rangle = |R\rangle^*, \tag{3}$$

where $\omega = \exp(2\pi i/3)$ and ω^* its complex conjugate. These are the bases of the E representation of the T_d group and are the eigenstates of the $\pm 2\pi/3$ rotation around the four different trigonal axes.

As a next step, we generate the direct products of the local singlets. By symmetrizing the two $1/2$-spins on every vertex, we obtain the states

$$|\psi_{\text{gs}}\rangle = \mathcal{P}\prod_{k=1}^{N_4}(r_k|R_k\rangle + l_k|L_k\rangle), \tag{4}$$

defined for arbitrary $\{r_k, l_k\}$ with $|r_k|^2 + |l_k|^2 = 1$. These states are the ground states of the Hamiltonian represented by a sum of the projection operators onto the total spin three subspace (represented by P^3) for the tetrahedron made of four 1-spins. Because the four $1/2$-spins, out of the broken-up eight $1/2$-spins, form a singlet state, then the maximum total spin of the original tetrahedron must be less than 3. To be explicit, the projection operator P^3 of the kth tetrahedron is given by

$$P_k^3 = \frac{1}{24}(S_k^{\text{tot}})^2 - \frac{43}{1440}(S_k^{\text{tot}})^4 + \frac{7}{1440}(S_k^{\text{tot}})^6 - \frac{1}{5760}(S_k^{\text{tot}})^8. \tag{5}$$

We assume that the Hamiltonian (1) and $\sum_k P_k^3$ belong to the same universality class and share the essential properties in the same way as the relation between the AF Heisenberg model and the VBS model in one dimension [13]. This assumption leads to a consistent picture for the properties of $\mathrm{ZnV_2O_4}$ as minutely discussed in the latter part of this Letter. In the above argument, we supposed that the symmetrized states do not vanish. As a matter of fact, one can show by using the Schwinger boson representation that the direct products of any linear combination of the form, Eq. (4), have the same nonzero norm even after the symmetrization. Accordingly, although the exact dimension of the symmetrized states is not known, a macroscopic ground-state degeneracy of the order of $\sim 2^{N_4}$ is expected for the model given by the projection operator. It is the key assumption of the present study that the low energy part of the Hilbert space of Eq. (1) adiabatically continues to these symmetrized states of the singlets' products.

In real materials, the ground-state entropy must be zero and it is quite natural to expect that the above-mentioned macroscopic degeneracy is lifted. In what follows, therefore, we concentrate on finding some reasonable mechanism which stabilizes the observed physical state among a number of nearly degenerate ground states. As long as the lattice symmetry remains cubic, it would be appropriate to treat the problem as a pure spin system and investigate the effects of the longer range interactions as well as the lattice topology as a source of lifting the degeneracy. One can argue that this type of lifting produces a kind of chiral ordering, which will be published elsewhere [14]. When the interaction between the lattice and spin degrees of freedom is more important, another way of lifting would take place with spontaneous breaking of the cubic lattice symmetry [15]. The energy loss from the lattice rigidity and gain from the magnetoelastic interaction determine the stable structure, a generalized Jahn-Teller effect of a novel type. Thus it has some similarity with the spin-Peierls transition usually discussed in 1D.

For this purpose we consider a single tetrahedron with four vanadium sites (V_1–V_4) as shown in Fig. 1. To describe lattice vibrations around the stationary points ($\vec{R}_i^0$), let us define small deviations by $\vec{R}_i = \vec{R}_i^0 + \Delta\vec{x}_i$. According to the symmetry of the tetrahedron (T_d point group), the normal modes are classified into the A_1 (Q_A: its normal coordinate), E (Q_u, Q_v), and T_2 (Q_ξ, Q_η, Q_ζ) representations after eliminating the uniform translation (T_2) and the uniform rotation (T_1). The normal coordinates of A_1 and E representations are written as

$$Q_A(A_1) = (X + Y + Z)/\sqrt{3}, \tag{6}$$

$$Q_u(E) = (X - Y)/\sqrt{2}, \tag{7}$$

$$Q_v(E) = (X + Y - 2Z)/\sqrt{6}, \tag{8}$$

where X, Y, and Z are the uniform elongation for x, y, and z directions, given by $(-\Delta x_1 + \Delta x_2 + \Delta x_3 - \Delta x_4)/2$, $(-\Delta y_1 + \Delta y_2 - \Delta y_3 + \Delta y_4)/2$, and $(-\Delta z_1 - \Delta z_2 + \Delta z_3 + \Delta z_4)/2$, respectively; see Fig. 2.

From simple group theoretical consideration, the local Hamiltonian, H_k, for a single tetrahedron is given, up to the first order of deviations, by

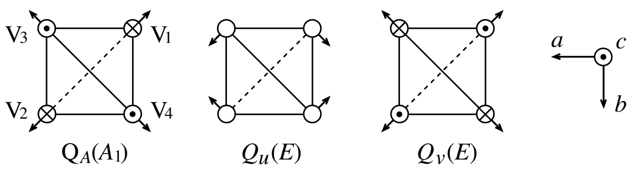

FIG. 2. The schematic representations of the normal modes viewed from the c axis.

$$\begin{aligned} H_k = \sqrt{6} J s_A &+ g_A \frac{\partial J}{\partial Q_A}\bigg|_0 Q_A s_A \\ &+ g_E \frac{\partial J}{\partial Q_E}\bigg|_0 (Q_u s_u + Q_v s_v) \\ &+ g_T \frac{\partial J}{\partial Q_{T_2}}\bigg|_0 (Q_\xi s_\xi + Q_\eta s_\eta + Q_\zeta s_\zeta), \end{aligned} \tag{9}$$

where s_Γ's are the bases of the irreducible representations made from the bilinear combinations of the spin operators,

$$\begin{pmatrix} s_A \\ s_u \\ s_v \\ s_\xi \\ s_\eta \\ s_\zeta \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} \\ 0 & \frac{1}{2} & \frac{-1}{2} & \frac{-1}{2} & \frac{1}{2} & 0 \\ \frac{2}{2\sqrt{3}} & \frac{-1}{2\sqrt{3}} & \frac{-1}{2\sqrt{3}} & \frac{-1}{2\sqrt{3}} & \frac{-1}{2\sqrt{3}} & \frac{2}{2\sqrt{3}} \\ 0 & 0 & \frac{1}{\sqrt{2}} & \frac{-1}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & 0 & 0 & \frac{-1}{\sqrt{2}} & 0 \\ \frac{1}{\sqrt{2}} & 0 & 0 & 0 & 0 & \frac{-1}{\sqrt{2}} \end{pmatrix} \times \begin{pmatrix} \vec{s}_1 \cdot \vec{s}_2 \\ \vec{s}_1 \cdot \vec{s}_3 \\ \vec{s}_1 \cdot \vec{s}_4 \\ \vec{s}_2 \cdot \vec{s}_3 \\ \vec{s}_2 \cdot \vec{s}_4 \\ \vec{s}_3 \cdot \vec{s}_4 \end{pmatrix}. \tag{10}$$

To illustrate the coupling constants, let us assume for simplicity that the exchange coupling depends only on the distance between the spins. Then $J = J(r)$ and the derivatives by each normal coordinate are given by $2\partial J/\partial r$ (A_1 mode), $\partial J/\partial r$ (E), and $\sqrt{2}\,\partial J/\partial r$ (T_2), respectively.

In the ground-state spin-singlet subspace, the matrix elements for the T_2 modes vanish and thus may be neglected. By including the lattice restoring energy, H_k is given by

$$\begin{aligned} H_k = -\frac{\sqrt{3} g_E}{2} \frac{\partial J}{\partial Q_E}\bigg|_0 &(Q_u \sigma_x + Q_v \sigma_z) \\ &+ \frac{k_E^2}{2}(Q_u^2 + Q_v^2). \end{aligned} \tag{11}$$

Here we have neglected the Q_A mode which simply renormalizes the Heisenberg coupling constant to $J + (\partial J/\partial Q_A) Q_A/\sqrt{6}$. We have used the real basis, $|u\rangle = (|L\rangle + |R\rangle)/\sqrt{2}$ and $|v\rangle = (|L\rangle - |R\rangle)/\sqrt{2}i$, and the Pauli matrices are defined by $\sigma_x = |u\rangle\langle v| + |v\rangle\langle u|$ and $\sigma_z = |u\rangle\langle u| - |v\rangle\langle v|$. Concerning the symmetrization $\mathcal{P}$, its effect may be taken as a renormalization factor of the order of unity [g_A, g_E, and g_T in Eq. (9)]. In other words, the form of the local Hamiltonian is determined by the symmetry and the important properties such as the equal coupling constants for the two components of the E mode and the vanishing of the matrix elements of the s_ξ, s_η, and s_ζ are generic independent of the symmetrization on *every* vertex.

Up to this order, there is no force to determine θ of $(Q_v, Q_u) = (\rho\cos\theta, \rho\sin\theta)$, with $\rho = \sqrt{3}\, g_E |\frac{\partial J}{\partial Q_E}| / 2k_E^2$. In order to fix this phase θ, it is necessary to take some anisotropies into consideration, such as the anharmonicity of the lattice restoration energy [16] or the higher order deviations of the magnetic exchange interaction [17]. After some calculations including up to the third (for the lattice part) and fourth orders (the spin part) of the lattice deviations, respectively, we find both terms to be proportional to $\cos 3\theta$, which means that the elongated or compressed lattice structure along one of the a, b, or c axes becomes the lowest state depending on the sign before the $\cos 3\theta$ term. We must distort each tetrahedron cooperatively all over the crystal without contradictions. For example, a uniform local tetrahedral distortion causes a uniform lattice metamorphosis and an alternating lattice distortion develops another type of lattice distortion. In any way, the many-fold degeneracy is lifted at this structural transition and a quenched local tetrahedral structure is realized.

Now let us discuss an application of the present scenario to the spin-1 normal fcc spinel compounds $\mathrm{ZnV_2O_4}$ [6–10] or isostructural $\mathrm{MgV_2O_4}$ [7–9,11], where the magnetic V^{3+} ion, with a $(3d)^2$ electronic state forming $S = 1$, resides on every lattice point of the pyrochlore lattice. These two compounds show similar properties and we will discuss $\mathrm{ZnV_2O_4}$ mainly. At $T_{\mathrm{st}} = 50$ K, a cubic to tetragonal structural phase transition is observed [6,9,10], where the crystal is uniformly compressed along the c axis with $c/a \sim 0.994$ without any magnetic ordering [6,9]. This lattice structure is just what we expect by taking $\theta = 0$, which leads to $Q_v > 0$ and $Q_u = 0$ in our theory. It is important to consider the effect of the difference of the u parameter ($u = 0.260$ [7,10,11]) from its ideal point (1/4), which exists even above T_{st}. The distance between vanadium and oxygen, l_{VO}, is given by $a(1 - 4\Delta u)/4$, and $\cos\angle\mathrm{VOV} = -8\Delta u$ in the lowest order of Δu, where $\Delta u = u - 1/4$. When the V-O-V angle is just the right angle, the superexchange path through the oxygen vanishes and the spin-spin interaction may be ferromagnetic (FM) due to the direct exchange. The experimental results imply that $\cos^{-1}(-8\Delta u)$ is sufficient for the AF superexchange interaction to overcome the direct FM one. By the distortion due to the Q_v mode, the cosines of the V-O-V in perpendicular and parallel to the c axis change to $-8\Delta u - 4\rho/\sqrt{6}\,a$ and $-8\Delta u + 2\rho/\sqrt{6}\,a$, respectively. The change of the angles means that the coupling constant $\frac{\partial J}{\partial Q_E}|_0$ is positive; see Eq. (10). Therefore for a positive Q_v, as the experiments indicate, there is an enhancement of the AF exchange in the perpendicular direction to the c axis and the $|u\rangle$ spin state is stabilized at each tetrahedron.

The experimental magnetic susceptibility, χ, shows a weak temperature dependence above 100 K with a large Weiss constant, $\theta_W = 420$ K [7]. Below $T_{\mathrm{clus}} = 95$ K, χ shows a splitting depending on the zero-field cooling and field cooling, which was interpreted as development of a short range or cluster ordering [6]. But its origin is not clear yet. Below T_{clus}, χ shows only a gradual increase with decreasing temperature [6,7] and at T_{st}, χ drops with a sharp cusp structure [8]. This structure may be consistent with the present scenario. Since the spin-singlet ground states themselves make no contribution to χ, the spin part concerned with thermally activated triplet states and the Van Vleck–type orbital part may be relevant to the total susceptibility. The separation of the doubly degenerate spin singlet at each tetrahedron [denoted by $\Delta_{S=0}(T)$] tends to suppress the spin part, and the orbital fluctuation in the vertical plane to the [111] axis is also suppressed. Both terms reduce χ with a sudden drop accompanied by the structural transition, which is qualitatively consistent with the experiments. With decreasing temperature, the increase of $\Delta_{S=0}(T)$ and the temperature dependent part of χ, still slightly increasing around T_{st}, may balance to result in the almost temperature independent χ below T_{st} [6,8].

At $T_N = 40$ K, a magnetic ordering sets in. The AF structure is observed by neutron diffraction experiment at 4.2 K [10], where 1D AF chains along [110] and [1$\bar{1}$0] directions stack one after the other along the c axis with the easy magnetization axis parallel to the c axis. This magnetic structure is consistent with the change of the AF coupling constants brought by the Jahn-Teller distortion of the Q_v mode. To understand the AF long range order from the 3D VBS-like $|u\rangle$ spin states symmetrized on every vertex realized at T_{st}, it is necessary to consider the effects of higher triplet states.

Finally, let us discuss the electronic entropy, S_{el}, of ZnV_2O_4. According to the trigonal distortion by the positive Δu, the threefold degenerate t_{2g} states are expected to split into the higher a_{1g} state and lower e_g states. This scheme of the splitting is expected since the wave functions of the a_{1g} and e_g states are parallel and perpendicular to the [111] direction, respectively. On the other hand, for LiV_2O_4, the LDA + U calculation [18] suggests that the a_{1g} state becomes lower than the e_g to gain the coulomb energy of the singly occupied electron level of the $(3d)^{1.5}$ configuration, but this may not be the case for the $(3d)^2$ state. Suppose that the orbital degree of freedom is almost quenched at higher temperatures, then the main contribution to the electronic entropy around the structural transition is the spin degrees of freedom in the spin-singlet sector, which is estimated to be $R \ln 2 = 5.76$ J/mol $\cdot$ K and the lattice part additionally. This is consistent with the experimental value of $S_{\text{el}} \sim 7$ J/mol $\cdot$ K just above the T_{st} [9].

Another possible scenario for the structural transition is, of course, the usual Jahn-Teller distortion at T_{st}. For this scenario, it is necessary to assume that the a_{1g} state is lower than the e_g states. However, the entropy associated with the orbital degrees of freedom is $2R \ln 2 = 11.52$ J/mol $\cdot$ K, which is much larger than the entropy observed experimentally. Note here that the spin degrees of freedom are not included yet. It is also worth mentioning that for the present scenario of the spin-driven lattice distortion, the energy scale should be a fraction of the exchange interaction $J \sim 10^2$ K. The smallness of the T_{st} and structural metamorphosis at T_{st} are compatible with this small energy scale. On the other hand, for the conventional Jahn-Teller effect concerned with the single electron states, the energy scale is typically a fraction of an electron volt ($\sim 10^4$ K).

In conclusion we have studied the frustrating quantum spin-1 system on the pyrochlore lattice as a theoretical model of the insulating spin-1 spinel compound. In this problem, it is essential to lift the many-fold degenerate spin-singlet manifold to discuss the low energy physics. As such a mechanism, a magnetoelastic interaction is considered in this Letter and we find the spontaneous breakdown of the lattice symmetry, which is consistent with the structural phase transition observed in ZnV_2O_4 and MgV_2O_4. Following this scenario, we can understand qualitatively the low temperature behaviors of the magnetic susceptibility and the electronic entropy, which seems to be difficult to explain by the usual Jahn-Teller effect. It is natural to expect that the spin-driven structural transition discussed in the present paper may be generalized to integer-spin pyrochlore systems with isotropic interactions.

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