Origin of Spin Gap in CaV_4O_9: Effects of Frustration and Lattice Distortions

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Spin gap behavior of CaV_4O_9 is studied by including the effects of frustrating magnetic interactions and lattice distortions. The spectrum of triplet excitations is calculated for a Heisenberg model on the 1/5-depleted square lattice. In the spin gap phase, the location of the minima of the spectrum in the Brillouin zone is found to depend nontrivially on the exchange parameters. Experimental consequences of the temperature-dependent lattice distortion including its effect on the uniform susceptibility and the spin gap are explored. [S0031-9007(96)01173-8]

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Recent discovery [1] of a quantum disordered phase and spin gap in the layered magnet CaV_4O_9 has attracted considerable interest [2–6]. The magnetic system can be described by a Heisenberg model for spins of vanadium ions ($S = 1/2$) on a 1/5-depleted square lattice. At each site of this bipartite lattice three bonds meet: two of them belong to the 4-spin plaquettes covering the lattice (plaquette bonds), whereas the third one (dimer bond) connects a plaquette with its neighbor (Fig. 1). Since the coupling between spins is mediated by superexchange via intermediate oxygens, a strong next nearest neighbor interaction is also expected [2,4].

We are thus led to the following Hamiltonian [2]:

$$\hat{H} = \sum_{\mathrm{nn}} J_{\mathrm{nn}} \mathbf{S}_i \cdot \mathbf{S}_j + J_2 \sum_{\mathrm{nnn}} \mathbf{S}_i \cdot \mathbf{S}_j , \qquad (1)$$

where the nn interaction J_{nn} equals J_0 (J_1) for plaquette (dimer) bond. It is evident that this model has disordered singlet ground states in two limits: for $J_0 \gg J_1, J_2$ the ground state is a product of singlets on each plaquette, and for $J_1 \gg J_0, J_2$ it consists of singlets on the dimers. However, a physically relevant choice of exchange parameters is $J_0 \approx J_1$.

The model (1) has been studied by a number of analytical and numerical works [2–6]. Ueda *et al.* [2] combined linear spin wave, strong coupling perturbation, and cluster approaches to find the phase diagram of the model. The quantum Monte Carlo (QMC) study of Troyer *et al.* [6] determined the phase boundaries between ordered and disordered phases at $J_2 = 0$. We note that most of these studies are restricted to the unfrustrated case $J_2 = 0$, which does not account for the experiments.

Here we wish to argue that even including frustration the Hamiltonian (1) does not fully describe the spin gap phenomena in this material. What is missing is a coupling between the spins and the lattice. The very fact that each spin is connected to others by three nonequivalent lattice bonds makes lattice distortions, which uniformly shorten plaquette bonds and enlarge dimer ones, as shown on Fig. 1, energetically favorable. Magnetic energy gain is *linear* in lattice displacement u. As usual, elastic energy loss due to the distortion is quadratic in u, and, as a result of this competition, some nonzero equilibrium displacement u will always be present. Importantly, this distortion does not break lattice symmetry, and is not associated with a phase transition.

In this Letter we present a unified approach that incorporates both effects of frustration and spin-lattice coupling. Our main results are as follows: (i) Spin-lattice coupling cooperates with the magnetic mechanism in driving the system into a spin gap phase. Within an adiabatic approximation, the lattice distortion is determined by the short-range spin correlations, and evolves gradually from $u = 0$ at high temperatures to a nonzero value u_0 at $T = 0$. This leads to the effective T dependence of the exchange integrals and of the spin gap itself, and causes a modification of the high-T tail of the uniform susceptibility. (ii) The spectrum of triplet excitations in the disordered magnetic phases is calculated using a bosonization technique that accounts correctly for the short-range spin correlations inside

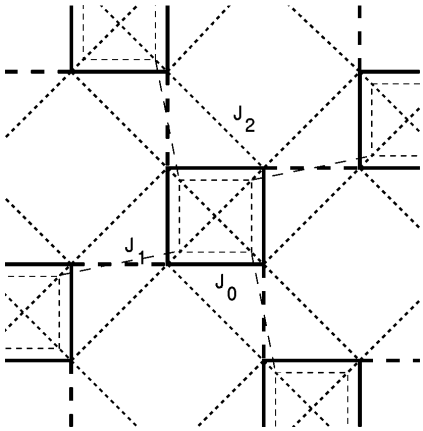

FIG. 1. Lattice structure of CaV_4O_9. Three types of exchange bonds are indicated by thick lines. The pattern of lattice distortion is shown schematically by thin dashed lines.

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the plaquette and dimer blocks. Position of the minima of the spectrum (i.e., the spin gap) in the Brillouin zone depends on parameters J_i. (iii) The available low-T experimental data can be explained both by moderate frustration $J_2 \sim 0.2J_0$, as well as by strong frustration $J_2 \sim 0.7J_0$. The two cases can be distinguished by the location of the gap minimum in the Brillouin zone, which can be obtained in neutron scattering.

The paper is organized as follows: we start by analyzing the magnetic Hamiltonian (1), and then include effects of the spin-lattice coupling. At various stages we make comparisons with the experimental situation.

Following Ueda *et al.* we consider two different types of disordered short-range resonating valence bond (RVB) states, with spin singlets formed on plaquettes and dimers [2,3]. For different values of model parameters we consider representations for spin operators in terms of both dimer and plaquette states. We generalize previous derivations of such representations [7–9] for the two cases.

The starting point of these representations is noninteracting spin blocks. Let states of a single block be given by $|\alpha\rangle$. In case of dimers, they are a singlet $|s\rangle$ ($E_s = -\frac{3}{4}J_1$) and a triplet $|t_\alpha\rangle$, $\alpha = x$, y, and z ($E_t = \frac{1}{4}J_1$). All 16 states of a four spin plaquette can be found in Refs. [2,8]. The lowest levels, once again, are a singlet with energy $E_s = -2J_0 + \frac{1}{2}J_2$, and a triplet with $E_t = -J_0 + \frac{1}{2}J_2$. Assuming that frustration is weak we omit all the higher energy states of the plaquette.

The site spins $\mathbf{S}_i$ are expressed in terms of the basis block states as $\mathbf{S}_i = \langle\alpha|\mathbf{S}_i|\beta\rangle Z^{\alpha\beta}$, where $Z^{\alpha\beta}$ is the projection operator $|\alpha\rangle\langle\beta|$ and summation over repeated indices is assumed. We define the vacuum $|0\rangle$ and four boson operators that yield the four physical states $|s\rangle = s^\dagger|0\rangle$, $|t_\alpha\rangle = t_\alpha^\dagger|0\rangle$. The projection operators are naturally expressed as $Z^{st_\alpha} = s^\dagger t_\alpha$, $Z^{t_\alpha t_\beta} = t_\alpha^\dagger t_\beta$, and so on. Calculating necessary matrix elements one finds that block spins represented via these boson operators as

$$S_i^\alpha = \frac{(-1)^i}{2}(s^\dagger t_\alpha + t_\alpha^\dagger s) - \frac{i}{2}e^{\alpha\beta\gamma}t_\beta^\dagger t_\gamma \quad \text{for dimers,}$$
$$S_i^\alpha = \frac{(-1)^i}{\sqrt{6}}(s^\dagger t_\alpha + t_\alpha^\dagger s) - \frac{i}{4}e^{\alpha\beta\gamma}t_\beta^\dagger t_\gamma \quad \text{for plaquettes.} \tag{2}$$

Commutation relations between the spins are satisfied as long as the bosonic representation preserves the algebra of the projection operators. This requirement restricts the number of bosons allowed on each block to one: $s^\dagger s + t_\alpha^\dagger t_\alpha = 1$. With the help of this constraint the Hamiltonian of a single block becomes $\hat{H}_B = E_s s^\dagger s + E_t t_\alpha^\dagger t_\alpha$. We choose to implement this constraint via a Holstein-Primakoff representation [9,10], $s^\dagger = s = \sqrt{1 - t_\alpha^\dagger t_\alpha}$.

As in the case of spin wave theory for ordered magnetic phases, one expects the linear approximation, which neglects interaction between excitations, to work well. It consists of replacing s and $s^\dagger$ by 1 when calculating $(\mathbf{S}_i \cdot \mathbf{S}_j)$ for pairs of spins from different blocks. Also, only terms of second order in triplet operators should be kept. Diagonalization of the resulting quadratic form is done by a standard Bogoliubov transformation, and one finds a threefold degenerate spectrum of triplet excitations. For small coupling between the blocks the spectrum is positive with a gap. Increasing the interaction between the blocks decreases the gap, which finally vanishes at the transition between disordered and ordered phases.

First, consider the plaquette singlet phase which exists for large J_0. The spectrum of spin-1 excitations is threefold degenerate and has the dispersion

$$\omega_p^2(\mathbf{k}) = J_0[J_0 + \tfrac{2}{3}(J_1 - 2J_2)(\cos k_x + \cos k_y)]. \tag{3}$$

The minimum of the spectrum is at(π, π) for $(J_1 - 2J_2) > 0$ and at $(0, 0)$ for $(J_1 - 2J_2) < 0$. From Eq. (3) one finds the region of stability of the plaquette phase, shown in Fig. 2. At $J_2 = 0$, singlets on 4-spin plaquettes become unstable at the critical ratio $J_0/J_1|_{\text{cr}} = \frac{4}{3}$, which is not far from the QMC estimate $J_0/J_1|_{\text{cr}} = 1.1$ [6]. The total energy of this phase, per spin, is

$$E_{\text{g.s.}}^p = -\tfrac{1}{2}J_0 + \tfrac{1}{8}J_2 + \tfrac{3}{8N}\sum_{\mathbf{k}}[\omega_p(\mathbf{k}) - J_0]. \tag{4}$$

In the dimer state each crystal unit cell has two dimers. Therefore, there are two different branches of $S = 1$ magnons in the Brillouin zone. However, calculations are greatly simplified if instead we consider only one type of dimers, which are defined in the new Brillouin zone corresponding to the lattice formed by the centers of dimer bonds. As a result, we obtain one triply degenerate excitation mode in the new Brillouin zone, which is twice the original one,

$$\omega_d^2(\mathbf{k}) = J_1[J_1 - (J_0 - J_2)(\cos k_x - \cos k_y) - J_2\cos(k_x + k_y)]. \tag{5}$$

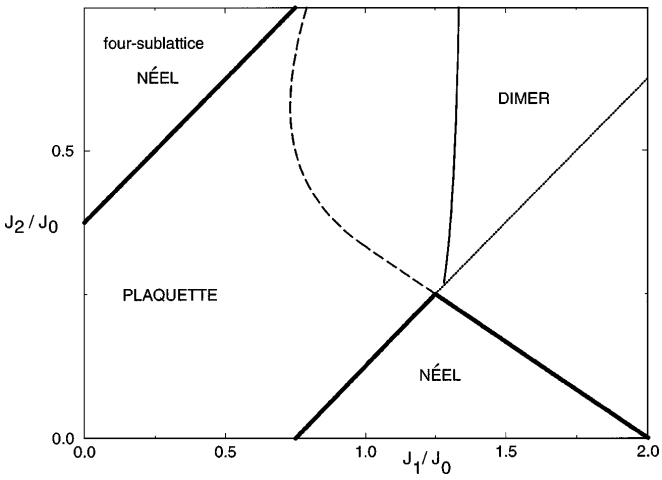

FIG. 2. Phase diagram of the model in linear approximation. Thick (thin) solid line denotes second (first) order phase transitions. Regions of stability of dimer (plaquette) phase are shown by long (short) dashed lines.

The minimum of the spectrum (5) is at $\mathbf{k} = (0, \pi)$ for $J_2 < \frac{1}{3}J_0$, and moves into the interior of the zone for larger J_2. At $J_2 = 0$, the dimer phase is unstable for $J_0/J_1 > \frac{1}{2}$; the corresponding critical ratio from QMC is $J_0/J_1|_{\rm cr} = 0.6 \pm 0.05$ [6]. The total energy per spin is

$$E^d_{\rm g.s.} = -\tfrac{3}{8}J_1 + \tfrac{3}{4N}\sum_{\mathbf{k}}[\omega_d(\mathbf{k}) - J_1]. \qquad (6)$$

Phase diagram of the model (1) follows from Eqs. (3)–(6). For $J_2^{\rm cr} > 0.25J_0$, the Néel phase ceases to exist. Within our approach, comparing the ground state energies of the two disordered phases leads to a line of first order phase transitions between them [2,11].

As J_2 grows, the energies of the omitted plaquette states decrease, making the linear approximation less satisfactory, and at $J_2 = J_0$ the second singlet which consists of two crossing dimers becomes the ground state of the 4-spin plaquette [2,8]. We have checked that this phase is not stable in the linear approximation for any value of the parameters. Another possible short-range RVB state is the plaquette RVB (PRVB) on larger squares, which are centered around the missing sites of the lattice and formed by J_2 bonds, but it was also found to be unstable. Therefore, for large values of J_2 magnetic order should be stabilized again. It is easy to see that for large J_2 the spins are arranged into two interpenetrating Néel ordered sublattices which are decoupled at the classical level. The degeneracy with respect to a relative orientation of antiferromagnetic vectors should be removed by quantum fluctuations, providing an example of "order-from-disorder" phenomenon [12]. We have presented in Fig. 2 a transition line between this ordered state and the disordered plaquette phase.

A first estimate for the experimental parameters at low T can be gained by looking at the plaquette RVB phase with $J_0 = J_1$. From Eq. (2), the uniform susceptibility is $\chi = \frac{1}{16NT}\sum_{\mathbf{k}} n(\omega_{\mathbf{k}})[1 + n(\omega_{\mathbf{k}})]$, where $n(\omega)$ is the Bose factor. We can compare the Curie-Weiss relation $\theta_0 = \frac{3}{4}(J_0 + J_2)$ and the gap Δ, in Eq. (3) appropriate for the PRVB phase, with the experimental Curie-Weiss constant and the gap determined from the exponential decay of the susceptibility at low T. We find that the experimental numbers $\Delta = 107$ K and $\theta = 220$ K [1] can arise from two sets of exchange constants (a) $J_0 = 245$ K, $J_2 = 48$ K [gap at $\vec{k} = (\pi, \pi)$, "weak frustration"] and (b) $J_0 = 170$ K, $J_2 = 123$ K [gap at $\vec{k} = (0, 0)$, "strong frustration"]. The spin gap is given by

$$\Delta_0 = \sqrt{J_0[J_0 \mp \tfrac{4}{3}(J_1 - 2J_2)]}, \qquad (7)$$

where $-$ $(+)$ sign corresponds to weak (strong) frustration. Thus, measurement of the triplet excitation spectrum by neutron scattering should provide important additional information that will enable one to decide between the two cases as relevant for CaV_4O_9. Note that the degeneracy of the spectrum (3) at $J_1 = 2J_2$ is a consequence of the linear approximation. However, we expect the dispersion to be weak in this parameter region, which is also confirmed in Ref. [13].

Let us now consider the spin-lattice coupling. As discussed earlier, this coupling arises from distance dependence of exchange integrals. Assuming the phenomenological relation $J(R) \sim R^{-10}$, valid for most transition metal oxides [14], the distortion pattern shown in Fig. 1 produces the following variations of exchange constants: $\delta J_0/J_0 = \delta J_2/J_2 = -\delta J_1/J_1 = \frac{20u}{R}$, and $\delta J_2'/J_2 = -\frac{10u}{R}$. Here $J_i \equiv J_i(R)$ are (unknown) bare exchanges on the undistorted lattice with length of the plaquette bond R equal to that of the dimer bond. Note also that on the distorted lattice one should distinguish between nnn interaction inside the plaquette $(J_2 + \delta J_2)$, and between different plaquettes $(J_2' = J_2 + \delta J_2')$. It is J_2' that appears in Eq. (3) in the presence of distortion u. Repeating the analysis that led to Eq. (7) we find that spin gap is *enhanced* by the lattice distortion, $\Delta(u) = \sqrt{\Delta_0^2 + (20uJ_0/R)(2J_0 \pm \frac{4}{3}J_2)}$. We see that this enhancement may be quite large if the bare gap Δ_0 is relatively small. Note that this expression predicts mean-field scaling $\Delta(u) \sim u^{1/2}$ (compared to $u^{2/3}$ scaling in $d = 1$ spin-Peierls chain [15]) as one approaches the "bare" critical point. To find the equilibrium value of the distortion one has to minimize the free energy per spin on the distorted lattice [16], which is given by

$$F = \frac{3T}{4N}\sum_{\mathbf{k}} \ln(1 - e^{-\omega_p(\mathbf{k})/T}) + E^p_{\rm g.s.} + \frac{1}{2}Ku^2. \qquad (8)$$

Here $\omega_p(\mathbf{k})$ and $E^p_{\rm g.s.}$ are given by Eqs. (3) and (4) with renormalized exchange parameters $J_i(u)$, and $K = BR_\perp$ is the bulk modulus of the material normalized to one layer. Use of the "spin wave" approximation for the free energy makes sense as long as spin correlation length is bigger then a lattice spacing [17]. Minimization gives

$$u(T) = u_0 - \alpha T,$$
$$\alpha = \frac{3}{4KTN}\sum_{\mathbf{k}} \frac{\partial\omega_p(\mathbf{k})}{\partial u}\frac{1}{e^{\omega_p(\mathbf{k})/T} - 1}, \qquad (9)$$

where $u_0 \equiv u(T = 0)$ is determined by the derivative of $E^p_{\rm g.s.}$. An important point to observe is that α is exponentially suppressed by the spin gap for $T \le \Delta$, but saturates at some nonzero value at higher temperatures. At still higher temperatures the distortion must approach its equilibrium (lattice value) which we have taken to be zero [18]. T dependence of the distortion translates into that of the exchange integrals. We find that at high temperatures the uniform susceptibility has the form $\chi = 1/4[T(1 - a) + \theta]$, where a is directly proportional to α, and θ is renormalized from its bare value θ_0. This should be contrasted with the standard $1/4(T + \theta_0)$ behavior in the absence of lattice distortions. We believe that indirect

evidence for this behavior was observed in the recent high-T expansion study of Gelfand *et al.* [13]. It was found there that the "best fit" to the experimental $\chi(T)$ curve in terms of the Heisenberg models, which reproduces well the experimental data around the peak, deviates notably from it at high temperatures. We attribute this feature to the intrinsic T dependence of the exchange integrals discussed here.

To get estimates of these effects we concentrate on the case $J_0 = J_1, J_2 = J_0/2$ suggested by Ueda *et al.* [2]. As discussed before, the excitation spectrum is almost dispersionless at this point, and for simplicity we set $\omega_p(\mathbf{k}) = J_0$. Parameters of Eq. (9) are then found to be

$$u_0 = \frac{15J_0}{2KR}, \quad \alpha = \frac{2u_0}{J_0} f\left(\frac{J_0}{T}\right), \quad a = \frac{5J_0\alpha}{R}, \qquad (10)$$

where $f(x) = x/(e^x - 1)$. Taking $R = 3$ Å, $R_\perp = 5$ Å, $J = 200$ K, and $B = 10^{12}$ dyn/cm^2, we get $u_0/R \sim 5 \times 10^{-3}$, which leads to quite large variations of J's: $J_0(u)/J_1(u) \sim 1.2$ and $J_2(u)/J_2'(u) \sim 1.1$, and spin gap enhancement $\Delta(u) = 1.06\Delta_0$. These variations of exchanges are similar to one-dimensional spin-Peierls chains [19,20], where $J_0/J_1 \sim 1.3$. This similarity is not unexpected as the linear gain in magnetic energy is somewhat analogous to $u^{4/3}$ gain in a spin-$\frac{1}{2}$ chain [15].

Finally, we point out that first order phase transition observed in [1] at 340 K may signal the presoftening of the phonon mode we discuss here, as happens in $d = 1$ spin-Peierls materials [19]. In view of our proposal this question should be studied more carefully.

To summarize, one of the key findings in our paper is that CaV_4O_9 may represent a unique example of a two-dimensional "spin-Peierls" system, where the spin-phonon coupling may "cooperate" with intrinsic tendencies for forming a spin gap due to the frustrating next nearest neighbor interactions. We have made several experimental predictions including the temperature dependence of the lattice and exchange constants, as well as the behavior of the uniform susceptibility and the location of the spin gap in the Brillouin zone. We hope that further experimental work will help to clarify many of these issues.

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