Origin of spin gap in CaV$_4$O$_9$: effect of frustration and lattice distortion

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We study the origin of spin-gap in recently discovered material CaV$_4$O$_9$. We analyze the spin-1/2 Heisenberg model on the 1/5 depleted square lattice with nearest neighbor (nn) and next nearest neighbor (nnn) interactions, in terms of the singlet and triplet states of the 4-spin plaquettes and 2-spin dimers. Phase diagram of the model is obtained within a linear “spin-wave”-like approximation, and is shown to agree well with the earlier results of QMC simulations for nn interactions. We further propose that the special lattice structure of CaV$_4$O$_9$ naturally leads to lattice distortions, which enhances the spin-gap via a spin-Peierls mechanism.

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Recent discovery$^1$ of a quantum disordered phase and spin-gap in the layered magnet CaV$_4$O$_9$ has attracted considerable interest$^2-^5$. The magnetic system has Neel order for$^6$ $T$ to the transition into the disordered phase.

However, a physically relevant choice of exchange parameters one needs to consider representations for spin operators in terms of both dimer and plaquette states. We generalize previous derivations of such representations$^6-^8$ for the two cases.

The starting point of these representations are non-interacting 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 $|t\rangle$, $\alpha = x, y, z$ ($E_t = \frac{1}{2}J_1$). All 16 states of a four spin plaquette can be found in Ref.$^9$. The lowest levels, once again, are a singlet with energy $E_s = -2J_0 + \frac{1}{2}J_2$, and a triplet with $E_t = -J_0 + \frac{1}{2}J_2$. In the bosonic representation for plaquette spins we will restrict ourselves to these four states only. This assumes that occupation numbers of all higher levels are small.

The site spins $S_i$ are expressed in terms of the basis block states as
\[ S_i = \langle \alpha | S_i | \beta \rangle Z^{\alpha \beta}, \]  
(2)

where \( Z^{\alpha \beta} \) is the projection operator \( |\alpha\rangle \langle \beta| \) and summation over repeated indices is assumed.

Consider first the matrix elements that occur in Eq. (2), in the subspace of one singlet and three triplet states. Using rotational invariance in spin space and time-reversal symmetry one gets

\[ \langle s | S_i^a | s \rangle = 0, \quad \langle s | S_i^a | t_{\beta} \rangle = \delta_{\alpha \beta} A_{i \xi}^a, \]

\[ \langle t_{\alpha} | S_i^a | t_{\beta} \rangle = \delta^{a \alpha \beta} A_{i \eta}^a, \]  
(3)

where \( e^{\alpha \beta \gamma} \) is the totally antisymmetric tensor and \( A_{i \xi}^a, A_{i \eta}^a \) are real. Let each spin of the block be decomposed as \( S_i = L_i + M_i \), where \( L_i \) has nonzero matrix elements between triplets and singlet, while \( M_i \) acts between triplets only. It is easy to see that \( M_i \) must be proportional to the total spin of the block, and, thus, is independent of \( i \), whereas \( L_i \propto (-1)^i \) for blocks consisting of equivalent spins. Further calculations using explicit forms of singlet and triplet states are straightforward and give \( A_{i \xi}^a = (-1)^i/2, A_{i \eta}^a = 1/2 \) for dimers, and \( A_{i \xi}^a = (-1)^i/\sqrt{6}, A_{i \eta}^a = 1/4 \) for plaquettes.

We define the vacuum \( |0\rangle \) and four boson operators that yield the four physical states \( |s\rangle = s^+ |0\rangle, |t_{\alpha}\rangle = t_{\alpha}^+ |0\rangle \). The projection operators are naturally expressed as \( Z^{st_{\alpha}} = s^+ t_{\alpha}, Z^{st_{\beta}} = t_{\alpha}^+ t_{\beta}, \) and so on. Block spins represented via these boson operators are

\[ S_i^a = (-1)^i(s^+ t_{\alpha} + t_{\alpha}^+ s) - \frac{2}{\sqrt{6}} e^{\alpha \beta \gamma} t_{\beta}^+ t_{\gamma}, \]  
(4)

for dimers, and

\[ S_i^a = (-1)^i(s^+ t_{\alpha} + t_{\alpha}^+ s) - \frac{2}{\sqrt{6}} e^{\alpha \beta \gamma} t_{\beta}^+ t_{\gamma}, \]  
(5)

for plaquettes.

Commutation relations between spins are satisfied as well. This approximation can be formulated for both types of block spin representations in the same way. It consists of replacing \( s \) and \( s^+ \) by 1, when calculating \( \langle S_i \cdot S_j \rangle \) 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 3-fold 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

\[ \omega_p^2(k) = J_0 \left[ J_0 + \frac{2}{3} (J_1 - 2J_2)(\cos k_x + \cos k_y) \right]. \]  
(6)

The minimum of the spectrum is at \( (\pi, \pi) \) for \( (J_1 - 2J_2) > 0 \) and at \( (0, 0) \) for \( (J_1 - 2J_2) < 0 \). From Eq. (6) 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 \( J_0/J_1|_{cr} = \frac{4}{7} \), which is not too far from the QMC estimate \( J_0/J_1|_{cr} = 1.1 \). The total energy of this phase, per spin, is

\[ E_{p.s.} = -\frac{1}{2} J_0 - \frac{5}{8} J_2 + \frac{3}{4N} \sum_k \omega_p(k) - J_0 \]  
(7)

It consists of the energy of noninteracting plaquette singlets and the energy of zero-point fluctuations.

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. This procedure is quite similar to performing a spin-wave expansion around the rotating quantization axis, as is often done in standard spin-wave theory. As a result, we obtain one triply degenerate excitation mode in the new Brillouin zone, which is twice the original one,

\[ \omega_d^2(k) = J_1 \left[ J_1 - (J_0 - J_2)(\cos k_x + \cos k_y) \right. \]

\[ \left. - J_2 \cos(k_x + k_y) \right]. \]  
(8)

The minimum of the spectrum is at \( k = (0, \pi) \) for \( J_2 < \frac{1}{7} J_0 \) and moves into the interior of the zone for larger \( J_2 \). At \( J_2 = 0 \), the dimer phase is unstable for \( J_0/J_1 > \frac{4}{7} \), while the corresponding critical ratio from QMC is \( J_0/J_1|_{cr} = 0.6 \pm 0.05 \). Note that the instabilities of the Néel phase at \( J_2 = 0 \), as predicted by our linear bosonic theory, coincide with the mean field cluster approach. However, the latter is not appropriate...
to study spin-liquid phases. The total energy per spin in the dimer phase is

\[ E_{\text{g.s.}}^d = -\frac{3}{8}J_1 + \frac{3}{4\pi} \sum_k [\omega_d(k) - J_1]. \] (10)

Phase diagram of the model follows from Eqs. (11) and (12). When frustration exceeds the critical value \( J_2^c = 0.25J_0 \), the Néel phase ceases to exist. A first order transition line separates plaquette and dimer phases since their symmetries are different. This line is found by comparing (13) and (14) and is shown in Fig. 2 (12).

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 (23). We have checked that this phase is not stable in the linear approximation for any values of the parameters. Another possible short-range RVB state is the plaquette-RVB on large squares 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 in the limit \( J_2 \gg J_0 \), \( J_1 \) 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 (13). We have presented in Fig. 2 transition line between this ordered state and disordered plaquette phase.

A theoretical comment is in order here. Calculations described above can be repeated within an alternative slave-boson treatment (1), which amounts to introducing a singlet condensate \( s^2 \neq 1 \) and a chemical potential \( \mu \), and finding their values self-consistently. Solving the self-consistent equations for the phase boundaries, we found, at \( J_2 = 0 \), that dimer phase is stable for \( J_0/J_1 \leq 0.874 \), whereas plaquette-RVB exists up to \( J_0/J_1 = 0.76 \). Thus, unlike linear approximation, mean-field slave-boson treatment predicts no ordered phase even at \( J_2 = 0 \), in striking contradiction with numerical simulations and linear approximation results. Situ-

ation is not improved even upon taking triplet-triplet interaction into account - its effect on the location of phase boundaries is ridiculously small, less than 1 percent. These findings clearly favor our linear approxima-
tion as the most suitable one for the problem at hand.

To make contact with experiments, let us first confine ourselves to \( J_0 = J_1 \). Note that only second terms of Eq. (14) contribute to the uniform susceptibility, leading to

\[ \chi \sim \frac{1}{N\mu^2} \sum_k n(\omega_k)(1 + n(\omega_k)), \]

where \( n(\omega) \) is the Bose factor. We can compare the Curie-Weiss relation \( \theta = \frac{1}{3}(J_0 + J_2) \) and the gap \( \Delta \), in Eq. (15) appropriate for the PRVB phase, with the experimental Curie Weiss constant and the gap determined from the T-dependence of the susceptibility. We find that the experimental numbers \( \Delta = 107 \text{K} \) and \( \theta = 220 \text{K} \) can arise from two sets of exchange constants (i) \( J_0 = 245 \text{K} \), \( J_2 = 48 \text{K} \) and (ii) \( J_0 = 193 \text{K} \), \( J_2 = 100 \text{K} \). Thus this theory, by itself, can provide a consistent description of the properties of CaV\(_4\)O\(_9\) observed so far.

However, we would now like to point out an additional aspect of this material which has so far gone unnoticed. Because of the special lattice structure, spin-phonon couplings will cause a gain in magnetic energy which is linear in the lattice distortion, whereas the loss in elastic energy is always quadratic. Thus there will always be a lattice distortion in this system which will cause the plaquette bonds to shrink and the dimer bonds to elongate. This will lead to \( J_0 > J_1 \). This spin-Peierls mechanism will enhance the stability of the PRVB phase and contribute to the spin-gap.

To get a quantitative estimate, let the shrinking of the plaquettes change the distance between the Vanadium ions from \( R \) to \( R + 2u \). Using the phenomenological relation \( J(R) \approx \text{const/}R^{10} \) (14), the exchange constants \( J_0 \) \( J_1 \) increase (decrease) by \( \delta J = 20u/J/R \). The magnetic energy gain per Vanadium atom is \( \epsilon_m = -\delta J(C_1 - 0.5C_2) \), where \( C_1 \) and \( C_2 \) are spin correlations on the plaquette and dimer bonds in the absence of distortion. It is sufficient to evaluate them on the Neel state, where they both are \(-1/4\). Thus the gain in magnetic energy per unit volume is \( E_m \sim (20u/J/8R)(1/R^2R_\perp) \), where \( R_\perp \) is the distance between magnetic layers. A rough estimate for the elastic energy per unit volume is \( E_{\text{ph}} \sim \frac{1}{2}B(u/R)^2 \), where \( B \) is a bulk modulus of the material. Minimizing the energies leads to a distortion \( u \sim (5J/2BR_{\perp}) \), which induces a variation of the exchange integrals by

\[ \delta J/J \approx (50J/R^2R_\perp B). \] (11)

Taking \( R = 3 \text{Å}, R_\perp = 5 \text{Å}, J = 300 \text{K}, B = 10^{12} \text{dynes/cm}^2 \), we get \( u/R \sim 10^{-3} \) and \( \delta J/J \sim 10^{-2} \sim 10^{-1} \). These values are similar to what is found in most of the spin-Peierls materials (14), 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 1D spin-\( \frac{1}{2} \) chain (10).

If \( J_2 \) was negligible, and the spin-Peierls mechanism was entirely responsible for the spin-gap, we would use Eq. (15) with \( J_2 = 0 \) and the Curie-Weiss relation \( \theta = \frac{1}{3}(2J_0 + J_1) \) to compare with experiments. This leads to estimates \( J_0 = 331 \text{K}, J_1 = 218 \text{K} \). The ratio \( J_0/J_1 \sim 1.5 \) corresponds to \( \delta J = 0.2J \), which is somewhat larger than our earlier back of the envelop estimate, suggesting that some \( J_2 \) is needed to explain the data.

We note that here the spin-Peierls mechanism does not lead to a spontaneous breaking of the lattice symmetry. Hence, we do not expect a sharp change in the lattice distortion with temperature. Instead, it
should follow short-range order and the spin-gap should be temperature-dependent. Finally, we point out that most known spin-Peierls materials have first order structural phase transition at high temperature [15]. This creates a soft phonon mode in the system, which in the end favors the spin-Peierls phenomena [17]. Curiously enough, a small discontinuous jump in $\chi(T)$ at 340 K was observed also in CaV$_4$O$_9$ [1], but was attributed to an admixture of the VO$_2$ phase. In view of our proposal this point should be studied more carefully.

Our discussion of possible spin-Peierls phenomena is only an order of magnitude estimate. Nevertheless it shows that spin-phonon coupling may successfully “cooperate” with intrinsic tendencies for forming a spin-gap due to the frustrating next-nearest-neighbor interaction present in CaV$_4$O$_9$.

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FIG. 1. Lattice structure of CaV$_4$O$_9$. Three types of exchange bonds are indicated by thick lines. The pattern of lattice distortion is shown schematically by thin dashed lines.

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