Plaquette Resonating-Valence-Bond Ground State of CaV_4O_9

Kazuo Ueda and Hiroshi Kontani
Institute for Solid State Physics, University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan

Manfred Sigrist and Patrick A. Lee
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 6 September 1995)

A theoretical model is presented to explain the spin gap observed for CaV_4O_9. The underlying lattice of the 1/5-depleted square lattice favors a formation of the plaquette resonating-valence-bond state. Inclusion of the frustrating second neighbor interaction enhances this tendency, leading to a quantum disordered state of a two-dimensional spin-1/2 Heisenberg model with a sufficiently big spin gap compatible with experiments.

PACS numbers: 75.10.Jm, 75.30.–m, 75.40.–s

Quantum disordered phases with a spin gap are of great current interest. This topic has gained additional momentum by Anderson's proposal of the resonating-valence-bond (RVB) state in the undoped parent materials of a high temperature superconductivity [1]. Some typical examples with spin gaps are the spin-1 antiferromagnetic Heisenberg chain [2], the double chain spin-1/2 Heisenberg model [3], the spin-1/2 Heisenberg antiferromagnet on a kagomé lattice [4], and the Kondo spin liquid phase of the Kondo lattice model at half filling [5].

Recently a new system with a spin gap was found experimentally by Taniguchi *et al.* for CaV_4O_9[6]. The spin gap observed by magnetic susceptibility and nuclear magnetic resonance (NMR) measurements is $\Delta/k_B = 107$ K. In this paper we propose that the underlying lattice of the 1/5-depleted square lattice of CaV_4O_9, see Fig 1, favors a new type of spin disordered phase which may be called a plaquette resonating-valence-bond (PRVB) state.

Each vanadium ion occupies a crystallographically equivalent site and is surrounded by a pyramid of oxygens. First, let us discuss the electronic state of this cluster $(VO_5)^{2-}$. In this configuration the vanadium ion is in the V^{4+} state with one d electron. Since V^{4+} is surrounded by a pyramid of oxygen ions, the d electron is in either the d_{xz} or d_{yz} orbital. This twofold degeneracy is lifted by a small Jahn-Teller distortion whose existence was reported in [6], although its details are not yet clear [7]. However, for our discussion of the spin gap, the details are not important because V^{4+} has a magnetic moment of spin 1/2 for which single ion anisotropy is absent.

The couplings between the spins on the vanadium ions are mediated by superexchange via the oxygen orbitals. The nearest neighbor vanadium ions share an edge of the square of oxygens (edge sharing), while the next nearest neighbor pairs share an oxygen at a corner (corner sharing). Superexchanges between the spins are possible through hybridization with the p_z orbitals of these oxygens. Since the number of paths for edge sharing and corner sharing is two and one, respectively, we expect J_1 (edge sharing) $\cong 2J_2$(corner sharing). Thus an appropriate model for CaV_4O_9 is the spin-1/2 Heisenberg model on the 1/5-depleted square lattice

$$\mathcal{H} = J_1 \sum_{\mathrm{NN}} \mathbf{s}_i \cdot \mathbf{s}_j + J_2 \sum_{\mathrm{NNN}} \mathbf{s}_i \cdot \mathbf{s}_j . \qquad (1)$$

The magnitude of the exchange couplings may be estimated from the susceptibility data [6]. At high temperatures it is reasonable to assume a Curie-Weiss type behavior, and the Weiss constant is given by $k_B\theta = \frac{1}{3}s(s+1)(z_1J_1 + z_2J_2)$, where s is the spin quantum number, z_1 is the number of nearest neighbors, and z_2 is the number of next nearest neighbors. For the 1/5-depleted square lattice $z_1 = z_2 = 3$. From the intersect of the inverse susceptibility with the temperature axis it is estimated as $\theta = 220$ K [8]. Under the assumption of $J_1 = 2J_2$, we obtain $J_1/k_B \sim 200$ K.

To understand specific features of the 1/5-depleted square lattice let us consider a cluster of four spins on

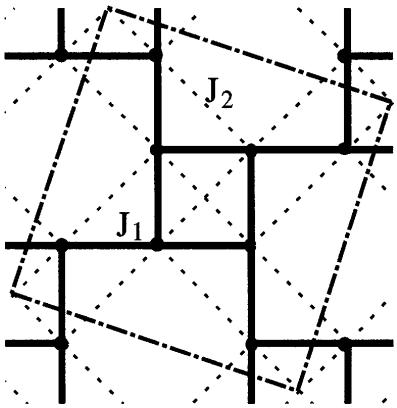

FIG. 1. A model for CaV_4O_9 of the spin-1/2 Heisenberg model with the nearest neighbor (solid lines) and the next nearest neighbor (broken lines) exchange interactions. The dot-dashed lines show the unit cell of the 1/5-depleted square lattice.

 0031-9007/96/76(11)/1932(4)$10.00

TABLE I. Eigenstates of a plaquette.

S_{13}	0	1	0	1		
S_{24}	0	0	1	1		
S	0	1	1	0	1	2
E_g	$-\frac{3}{2}J_2$	$-\frac{1}{2}J_2$	$-\frac{1}{2}J_2$	$-2J_1+\frac{1}{2}J_2$	$-J_1+\frac{1}{2}J_2$	$J_1+\frac{1}{2}J_2$

a plaquette. The Hamiltonian of this system is

$$\mathcal{H}_{\text{plaquette}} = J_1(\mathbf{s}_1 + \mathbf{s}_3)\cdot(\mathbf{s}_2 + \mathbf{s}_4) + J_2(\mathbf{s}_1\cdot\mathbf{s}_3 + \mathbf{s}_2\cdot\mathbf{s}_4). \quad (2)$$

This Hamiltonian is readily diagonalized as is shown in Table I, where S_{13} (S_{24}) is the spin quantum number of $\mathbf{s}_1 + \mathbf{s}_3$ ($\mathbf{s}_2 + \mathbf{s}_4$) and S is the total spin quantum number. It is seen that the ground state of the plaquette is a singlet, and the first excited state is a spin triplet with a spin gap of J_1 for $J_1/2 > J_2$. At $J_1 = 2J_2$ the spin neutral excitation crosses with the spin triplet excitation.

To proceed further let us first discuss a simplified Heisenberg model on the $1/5$-depleted square lattice with only nearest neighbor couplings ($J_2 = 0$). This model is very interesting in its own right, because the ground state of this model is probably disordered, having no long range order, or at least very close to a quantum phase transition, in spite of the fact that the lattice is bipartite and completely two dimensional. For this lattice structure, there are two topologically inequivalent bonds. One type of bonds, which will be called plaquette bonds hereafter, form a plaquette covering of all spins, see Fig. 2. We introduce an exchange coupling J for these types of bonds. The other type of bonds, dimer bonds, form a complete dimer covering of the lattice, and we use J' for the exchange coupling of this type. Although our final aim is to discuss the ground state of the model with $J = J'$, for the time being we consider J and J' as independent parameters. In comparison, all bonds are equivalent in the square lattice. A dimer or plaquette covering is possible in this case, too. However, in contrast to the above lattice, it is not unique and it is known that the square lattice favors an antiferromagnetically ordered ground state.

We begin our discussion from the limit $J \gg J'$. In this limit, as we have discussed (Table I with $J_1 = J$ and $J_2 = 0$), four spins on each plaquette form a singlet ground state which has resonating-valence-bond character [1]. The ground-state energy of this state per spin is $E_{\text{PRVB}} = -\frac{1}{2}J$. In the other limit, $J' \gg J$, the global ground state is a collection of dimer singlets, $E_{\text{dimer}} = -\frac{3}{8}J'$. For $J \approx J'$, another possible ground state is one with antiferromagnetic long-range order, since the lattice is bipartite. The energy of the classical Néel state is $E_{\text{Néel}} = -\frac{1}{8}J' - \frac{1}{4}J$. These energies are plotted in Fig. 3. The three states discussed here may be considered as the simplest variational states for three different phases.

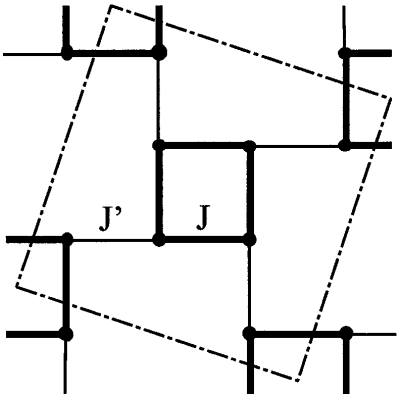

FIG. 2. Spin-1/2 Heisenberg model on the $1/5$-depleted square lattice with the nearest neighbor exchange interactions. Topologically there are two different types of bonds: plaquette bonds J and dimer bonds J'.

At this level, the spin disordered phase, either the dimer phase or the PRVB phase, has a lower energy than the Néel state. Concerning the two singlet phases, it should be mentioned that they are different phases although the global symmetry properties are the same for the two phases. It can be shown that the wave function of the dimer singlet state has no overlap with that of the PRVB state, based on the fact that the two wave functions have different transformation properties under reflection with respect to the dimer bonds: odd for the dimer singlet but

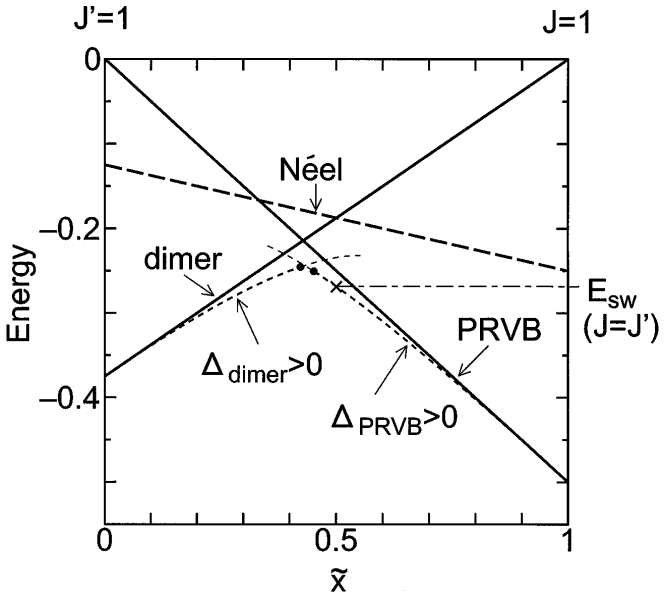

FIG. 3. Ground-state energies for the dimer singlet, the PRVB singlet, and the Néel ordered phase. The horizontal axis $\tilde{x}$ is defined by $J = \tilde{x}J$ and $J' = (1 - \tilde{x})J$, and energies are in units of J. The energies obtained by second order perturbation are shown by the dashed lines. The dots on the dashed lines are the points where the spin gap vanishes, see text. E_{SW} is the energy estimated by the linear spin wave theory at $J = J'$.

even for the PRVB singlet. Thus the two states cannot be continuously connected by tuning J and J' from one to the other limit.

It is necessary to improve the estimate of the ground-state energies for the three phases. For the singlet phases we can use perturbation theories. Let us take the example of the PRVB state. When a dimer bond is introduced, polarization processes from the singlets on both ends of the bond should be included. The polarization energy per bond may be calculated by second order perturbation as $-(43/576)J'^2/J$. A similar perturbation calculation is also possible from the other limit of the dimer singlet. The results are summarized as

$$E_{\mathrm{PRVB}} = -\frac{1}{2}J\left[1 + \frac{43}{576}\left(\frac{J'}{J}\right)^2\right], \tag{3}$$

$$E_{\mathrm{dimer}} = -\frac{3}{8}J'\left[1 + \frac{1}{4}\left(\frac{J}{J'}\right)^2\right]. \tag{4}$$

These energy are also plotted in Fig. 3.

For the Néel ordered phase a possible improvement is obtained by linear spin wave theory [9]. Extension of the linear spin wave theory to the present case is rather complicated but straightforward. The ground-state energy per spin in this approximation is

$$E_{\mathrm{Néel}}(J = J') = -J\left[\frac{3}{2}s^2 + 0.325\,248s\right], \tag{5}$$

where $s = 1/2$ for the present model. At $J = J'$ the energy obtained by the spin wave theory, $-0.5376J$, is very close to that of the PRVB state estimated by second order perturbation, $-0.5373J$. In the spin wave theory it is possible to calculate the reduction of the magnetic moment by the zero point fluctuations of the magnons, $\delta s = 0.288$, which is nearly 50% larger than the reduction for the square lattice, $\delta s = 0.197$, and amounts to 58% of the magnitude of spin. Linear spin wave theory shows that Néel order survives at this level but is on the verge of a quantum phase transition. In view of the fact that the linear spin wave theory has a tendency to favor Néel order [10], more careful treatments are necessary.

If there were a transition from the disordered phase to the Néel phase, it would probably be a second order transition. In this case the spin gap vanishes at the transition point. Therefore the critical point may be estimated by examining the spin gap in the disordered phases. A spin-triplet excitation in a plaquette is mobile. It can hop to a neighboring plaquette with an effective hopping matrix element $J'/6$, to a second neighbor plaquette with $-J'^2/36J$, and to a third neighbor plaquette with $-J'^2/216J$. The polarization energies for the bonds connected to the triplet are different from the polarization energy in the ground state, $-(289/3456)J'^2/J$. From these results the spin gap is calculated as

$$\Delta_{\mathrm{PRVB}} = J\left[1 - \frac{2}{3}\left(\frac{J'}{J}\right) - \frac{111}{864}\left(\frac{J'}{J}\right)^2\right]. \tag{6}$$

Similar second order perturbation gives the spin gap for the dimer phase,

$$\Delta_{\mathrm{dimer}} = J'\left[1 - \frac{J}{J'} - \frac{1}{2}\left(\frac{J}{J'}\right)^2\right]. \tag{7}$$

Within the second order perturbation theory, the spin gap vanishes at $(J'/J)_c = 1.215$ from the PRVB side and at $(J/J')_c = 0.732$ from the dimer side. These points are shown by the dots in Fig. 3. This result suggests that in the narrow region between these critical points antiferromagnetic long-range order would exist. However, the spin gap remains finite at $J = J'$ within the present perturbation theory.

An alternative way to estimate the critical points is a cluster mean field theory. We explain the method with a simple example. For the PRVB state we consider a cluster with four spins on a plaquette under the influence of molecular fields coming from the dimer bonds,

$$\mathcal{H}_{\mathrm{CMF}} = J(\mathbf{s}_1 + \mathbf{s}_3)\cdot(\mathbf{s}_2 + \mathbf{s}_4) - J'\sigma(s_1^z - s_2^z + s_3^z - s_4^z). \tag{8}$$

In the cluster mean field theory the average of a spin is determined by the self-consistency equation, $\sigma = \langle s_1^z\rangle$. This four-spin problem can be solved analytically, and the critical value is obtained as $(J'/J)_c = 3/4$. When a bigger cluster of 16 spins is used, the critical value increases to $(J'/J)_c = 0.8044$. One can use a similar cluster mean field approximation for the dimer singlet. The smallest cluster of two spins gives $(J/J')_c = 1/2$. The next smallest, 8-spin, cluster gives $(J/J')_c = 0.5378$. From both sides the critical value increases as the cluster size becomes larger. Therefore we may consider $(J'/J)_c = 3/4$ and $(J/J')_c = 1/2$ as the lower limits for the critical points, if any. However, unfortunately, the cluster size is not big enough to perform a reliable finite size scaling to determine the existence or absence of the Néel phase.

All treatments discussed above suggest that the spin-1/2 Heisenberg model on the 1/5-depleted lattice with only nearest neighbor couplings has a spin disordered ground state in a wide region of parameter space. Only in a narrow region around the crossing point between the PRVB phase and the dimer phase is there a possibility of antiferromagnetic long-range order. The recent quantum Monte Carlo simulations by Katoh and Imada [11] suggest that there is a spin gap of $\Delta = 0.11J$ for the model with $J = J'$, consistent with the perturbation results.

Let us return to the original model, Eq. (1), keeping the different exchanges for the dimer bonds and the plaquette bonds. It should be noted that the second nearest neighbor coupling is frustrating for Néel order. It may be best illustrated by considering the cluster mean field theory. Again we consider the smallest cluster for the PRVB singlet,

$$\mathcal{H}_{\mathrm{CMF}} = J(\mathbf{s}_1 + \mathbf{s}_3)\cdot(\mathbf{s}_2 + \mathbf{s}_4) + J''(\mathbf{s}_1\cdot\mathbf{s}_3 + \mathbf{s}_2\cdot\mathbf{s}_4) - (J' - 2J'')\sigma(s_1^z - s_2^z + s_3^z - s_4^z). \tag{9}$$

Since the eigenstates without the molecular field are completely determined by quantum numbers listed in Table I, the critical value is obtained analytically as $(\frac{J'-2J''}{J})_c = \frac{3}{4}$. Thus we may conclude that the model for CaV_4O_9 has the quantum disordered ground state with a safe margin.

We can extend the second order perturbation theory for the spin gap of the PRVB state with the frustrating exchange coupling, for which we obtain

$$\Delta_{\mathrm{PRVB}} = J\Big\{1 - \frac{2}{3}(x - 2y) - \frac{1}{54}(7x^2 - 10xy + 10y^2) - \frac{1}{12}\frac{2x^2 - 3xy + 4y^2}{2 - y} + \frac{7}{18}\frac{(x - y)^2 + y^2}{3 - y} - \frac{1}{12}\frac{x^2 + 2y^2}{3 - 2y} - \frac{5}{72}\frac{(x - y)^2 + y^2}{4 - y}\Big\}, \quad (10)$$

where $x = J'/J$ and $y = J''/J$. From this result it is seen that the gap increases as J'' increases. This behavior is illustrated in Fig. 4 for the case $J = J'$. A similar behavior is observed in the expansion around the dimer limit which gives

$$\Delta_{\mathrm{dimer}} = J'\Big\{1 - x^{-1}\Big(1 - \frac{3}{2}y\Big) - \frac{1}{8}x^{-2}(4 - 4y + 9y^2)\Big\}. \quad (11)$$

It is clear that the quantitative results of perturbation theory are questionable at $J = J' = J_1$; this is shown by the difference between the values of the spin gap for the model with only nearest neighbor coupling. $\Delta = 0.205J_1$ is obtained by the PRVB perturbation theory, on one hand, and $\Delta = 0.11J_1$ by quantum Monte Carlo simulations, on the other hand [11]. When we use the results of the quantum Monte Carlo simulations the magnitude of the spin gap is too small compared with the experimental value. The present perturbation result shows the tendency that the spin gap increases significantly when we include the frustrating next nearest neighbor exchange of the order of $J_2 = J_1/2$, which may lead to a reasonable value of the spin gap compared with the experiments.

In conclusion, the spin-1/2 Heisenberg model on the 1/5-depleted square lattice is presented as a theoretical model for the spin gap of CaV_4O_9. It is shown that the 1/5-depleted square lattice is favorable for the quantum spin disordered phase, which may be characterized as the PRVB singlet. When the frustrating exchange for the corner sharing bonds is included, it is possible to explain the large spin gap observed experimentally.

It is our great pleasure to acknowledge fruitful discussions with Masatoshi Sato, Hirokazu Tsunetsugu, Yoshio Kitaoka, and Maurice Rice. We thank N. Katoh and M. Imada for pointing out that some processes of second order perturbation were missing in the original manuscript of this paper. This work is financially supported by a Grant-in-Aid from the Ministry of Education, Science and Culture of Japan. We acknowledge financial support from Swiss Nationalfonds (M. S., 8220-037229) and from MIT Science Partnership Fund and from the NSF (P. L. and M. S., DMR-90-22933).

A significant part of this work was done during the stay at the Aspen Center for Physics of K. U. and M. S.

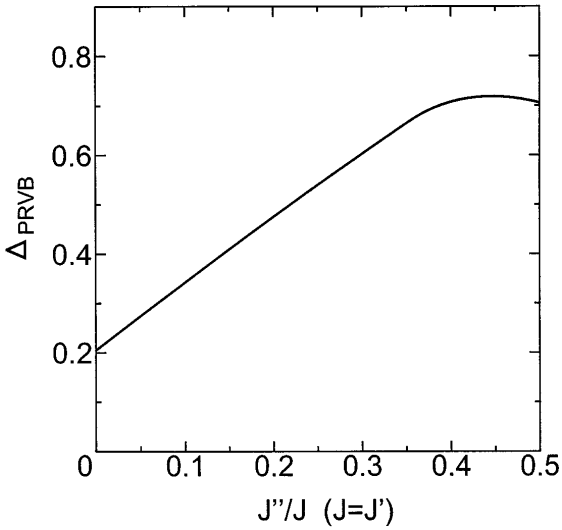

FIG. 4. The spin gap as a function of frustrating exchange coupling, $y = J''/J$. For $J''/J > 0.354$ the spin gap deviates from Eq. (10) because the minimum of the spectrum is different from (π, π).

[1] P. W. Anderson, Science **235**, 1196 (1987).
[2] F. D. M. Haldane, Phys. Lett. **93A**, 464 (1983); Phys. Rev. Lett. **50**, 1153 (1983).
[3] S. P. Strong and A. J. Millis, Phys. Rev. Lett. **69**, 2419 (1992).
[4] C. Zeng and V. Elser, Phys. Rev. B **42**, 8436 (1990).
[5] H. Tsunetsugu, Y. Hatsugai, K. Ueda, and M. Sigrist, Phys. Rev. B **46**, 3175 (1992).
[6] S. Taniguchi, T. Nishikawa, Y. Yasui, Y. Kobayashi, M. Sato, T. Nishioka, M. Kontani, and K. Sano, J. Phys. Soc. Jpn. **64**, 2758 (1995).
[7] Another possibility is the d_{xy} orbital since the vanadium ion is shifted from the basal plane towards the inside of the pyramid of oxygens. If this is the case, estimation of the exchange couplings may be done only through detailed comparison with experiments.
[8] M. Sato (private communication).
[9] P. W. Anderson, Phys. Rev. **86**, 694 (1952); R. Kubo, *ibid.* **87**, 568 (1952).
[10] One typical example is the Heisenberg model; T. Matsuda and K. Hida, J. Phys. Soc. Jpn. **59**, 2223 (1990); K. Hida, *ibid.* **61**, 1013 (1992).
[11] N. Katoh and M. Imada (private communication).