Structural Aspects of Magnetic Coupling in CaV$_4$O$_9$

W. E. Pickett
Complex Systems Theory Branch, Naval Research Laboratory, Washington DC 20375
(March 23, 2022)

The strong corrugation of the V$_4$O$_9$ layer in the spin gap system CaV$_4$O$_9$ is examined for its impact on the exchange coupling constants between the spin $\frac{1}{2}$ V ions. Local spin density (LSD) calculations show that the V spin occupies a $d_{z^2}$ orbital ($\hat{x}$ and $\hat{y}$ are the V-V directions). The Kanamori-Goodenough superexchange rules, and the degeneracy of ferromagnetic and antiferromagnetic alignments within LSD, suggest that 2nd neighbor couplings dominate over nearest neighbor, resulting in two coupled S=$\frac{1}{2}$ metaplaquette systems.

From its vanishing susceptibility $\chi(T \to 0)$ and related NMR properties, CaV$_4$O$_9$ is known to enter a quantum disordered phase with a spin gap. This behavior has stimulated theoretical investigation of the exchange couplings between the S=$\frac{1}{2}$ spins on the V lattice, using a Heisenberg model with nearest ($J_{nn}$) and next-nearest ($J_{nna}$) exchange couplings. The $\frac{1}{2}$-depleted lattice (described below) has been viewed as an array of square "plaquettes" of V ions tending toward singlet formation. Isolated plaquettes have a singlet ground state; structural chemistry however suggests intra- and inter-plaquette V-V coupling ($J$ and $J'$) should be very similar, so the limit of isolated plaquettes is not realistic.

Depletion alone does not destroy Néel order, and although competing interactions lead to $\chi(T \to 0)$, they do not account quantitatively for the $\chi(T)$ data. Yet the "plaquette phase" of incipient singlets provides an attractive framework for accounting for the lack of magnetic ordering and the spin gap behavior. In this paper we take into account all complications of the crystal structure, and find that the orbital character of the occupied V $d$ spin orbital is different than previously anticipated. For this spin orbital, nn exchange coupling exceeds nn coupling. The resulting coupling leads to a picture of two coupled metaplaquette systems that may preserve the tendency toward local singlet formation while enhancing frustration of ordering.

The crystal structure of CaV$_4$O$_9$ has been idealized in most previous theoretical treatments to the consideration of VO layers with periodic V vacancies. The actual structure is much more interesting. The space group is simple tetragonal P4/n (#85 in the International Tables), with $a = 8.333\AA$, $c = 5.008\AA$, and two formula units per cell. The low crystal symmetry is reflected in the fact that ten of the 15 internal structural parameters (for five sites) are not fixed by symmetry. Conceptually, one may start from a VO square lattice with cations and anions arranged as on a checkerboard. Each V ion along a V-O axis has an apical oxygen above (say) the layer, with V ions along neighboring V-O lines having their apical oxygen below the plane. V ions are removed in a pattern corresponding to a left-moving (or right-moving, giving the chiral partner) knight on a chessboard that lies at a 45° angle derived only from the V ions: from one V vacancy, go two V ions along a line of V ions, and one to the left to locate a neighboring vacancy. The resulting pattern, shown in Fig. 1, is a $\sqrt{5} \times \sqrt{5}$ enlargement with respect to the V sublattice, which is itself $\sqrt{2} \times \sqrt{2}$ larger than the VO square lattice. Ca ions arrange themselves either above or below the V vacancies.

Superimposed on this superstructure is a severe corrugation of the plane, with V ions displaced alternately ±0.625 Å perpendicular to the plane in the direction of their apical O ion. The entire structure is shown in Fig. 2. V ions, as well as apical ions (O2), remain equivalent by symmetry, but there are two other O sites. O1 sites are near (±0.12Å) the plane and are coordinated with three V ions, two on one plaquette and the third on a neighboring plaquette, all at 1.95-1.96 Å. O3 sites remain in the plane at positions at the plaquette center, and are four-fold coordinated with V ions at 2.04 Å. The compound can be written descriptively as [CaV$_4$O$_1$O$_2$O$_3$]$_2$. The V, O1, and O2 sites have no symmetry. The V ion lies within a tilted square pyramid of O ions ('square' of O1, O2, O3, with O2 apex), not far from the center of mass.

FIG. 1. Top view of the V$_4$O$_9$ layer, with Ca and O2 atoms not displayed. A plaquette of V ions is labelled by 'V'. Two metaplaquettes, formed by the V ions above the layer, are shown by the solid lines.
of the five O ions (Fig. 3). Each V$_4$ plaquette is boat-shaped, with two corner V ions up and the other two down. Due to the corrugation, the V-V-V angle that would be 180° for a plane is reduced to 130°.

![FIG. 2. Structure of CaV$_4$O$_9$, from Bouloux and Galy, illustrating the severe corrugation of the V-O layer. Unit cells in two successive layers are shown.](image)

We have applied the full potential linearized augmented plane wave (FLAPW) method used in previous studies of magnetic transition metal oxide compounds. The sphere radii used in fixing the FLAPW basis were chosen to be 2.0, 2.0, 1.60, 1.45, and 1.60 a.u. for Ca, V, O1, O2, and O3, respectively. Local orbitals were added to the basis set for extra flexibility and to allow semicore states to be treated within the same energy window as the band states. For the V atoms, s, p, and d local orbitals were used, while for Ca and the O atoms s and p local orbitals were added. The plane wave cutoff corresponded to an energy of 19 Ry. The total basis set size is 3350 LAPWs and local orbitals.

An initial calculation without spin polarization found the O 2p states to be centered 6-7 eV below the center of the V 3d bands, and separated from them by a gap of 2 eV. The lowest Ca-derived band bands arise from the 3d states, but lie above the V d bands and are inactive. The Fermi level $E_F$ lies low in V d bands, corresponding to a $d^1$ configuration. Thus the conventional ionic picture is well respected in this compound.

To interrogate magnetic interactions, ferromagnetic (FM) and antiferromagnetic (AFM) alignments of the V moments were studied. The energy gain from polarization is 0.12 eV/V ion. For FM ordering, an insulating state is obtained, as shown in Fig. 4, so the moment obtained is precisely 1 $\mu_B$ per V. An insulating result was not anticipated from the non-polarized calculation: there was no gap in the d bands, so a rigid Stoner splitting of majority and minority bands would leave a metallic result. The lowest lying V d orbital in the majority bands, which we show below to be the $d_{x^2-y^2}$ orbital, upon polarization becomes separated from the remaining 4 d orbitals, due to an exchange splitting $\Delta_{ex}$ that is strongly orbital dependent. $\Delta_{ex}(d_{x^2-y^2}) \approx 1.3$ eV is an unusually large value (LSDA exchange forces usually are less than 1 eV/$\mu_B$), reflecting a weakly hybridized (and therefore more confined) $d_{x^2-y^2}$ orbital. $\Delta_{ex}$ is only about 0.6 eV in the center of the d bands and decreases to 0.4 eV at the top. The calculated gap in the majority bands is 0.7 eV, and the gap between occupied majority and unoccupied minority bands is of the order of 0.1 eV. Correlations effects can only increase these gap values, perhaps substantially.

![FIG. 3. Side view of the VO$_5$ “pyramid.” The V ion actually lies above the center of mass of the five O ions. V-O bond lengths (Å) are shown. The three V-O1 lengths are inequivalent but nearly equal.](image)

![FIG. 4. Majority (left) and minority (right) bands along high symmetry directions for FM aligned CaV$_4$O$_9$. The majority $d_{x^2-y^2}$ is disconnected from other d states, leading to an insulating result.](image)

The spin density for this FM state, shown in Fig. 5, is clearly that due to occupation of a single spin-orbital of V $d_{x^2-y^2}$ character, where $\hat{x}$ and $\hat{y}$ refer to the lines of V ions. Due to the low V ion site symmetry the lobes do not point precisely in the direction of neighboring V ions nor lie exactly in the crystallographic $\hat{x} - \hat{y}$ plane, but these ‘misalignments’ are only a few degrees. These spin-orbitals are non-bonding with respect to the neighboring O ions, a point we return to below. This occupied orbital
is not of the type \(d_{xy}, d_{yz}, d_{zx}\) anticipated in previous work, \(\text{[3]}\) or used by Marini and Khomskii for orbital ordering \((d_{xz} \text{ or } d_{yz})\). \(\text{[4]}\) Note that this orientation is determined by the crystal field, and is unrelated (at least for this narrow band system) to the FM order.

The chosen AFM order was of the Néel type: each V spin is antiparallel to its two neighbors on a plaquette and to the neighbor on the next plaquette. This type of order breaks inversion symmetry, and all V ions on one side of the (idealized V-O) plane have the same spin direction. This ordered state is essentially degenerate with the FM alignment. \(\text{[4]}\) The resulting state is also insulating, and as expected the occupied bandwidth is smaller (20\%) than for FM alignment.

The effective V \(d_{x^2-y^2} - d_{x^2-y^2}\) transfer integrals \(t_{ij}\) are thought to be mediated via virtual hopping processes through the intervening O ions, with amplitudes \(t_{d\sigma\sigma}\) and \(t_{d\pi\pi}\). In the idealized VO parent layer the O ions lie at 45° angles to the V-V nn direction. In terms of hopping processes, the nn V ion is no more distant than the nn V ions, which are at the same height, there is a single path. Within a plaquette, the angles for nn V ions are 100° (V-O1-V) and 95° (V-O3-V), and is 144° (V-O3-V) across the diagonal. Between plaquettes, nn V are connected by two identical 100° angles (V-O1-V), while the diagonal nn angle is 130° (V-O1-V). These angular variations, coupled with the fact that the O ions are not coplanar with the lobes of the \(d_{x^2-y^2}\) spin orbital and that direct V-V exchange may not be negligible, make it very difficult to estimate realistic net exchange couplings.

The direct V-V separations are 3.00±0.01 Å, which can be compared to the bondlength in V metal of 2.73 Å. This difference of less than 10% suggests that direct V-V hopping might be appreciable. The less extended nature of the \(V^{4+}\) orbitals compared to neutral V orbitals will reduce the overlap, however. Since nn V ions do not lie in the plane of the \(d_{x^2-y^2}\) orbital, the orbital must be rotated by \(\theta = \sin^{-1}(\frac{1.25}{2.73}) = 25°\) on both atoms before the overlap can be expressed in terms of the usual \(t_{dd\sigma}, t_{dd\pi}, t_{dd\delta}\) hopping amplitudes. Neglecting the latter two, which at this distance should be much smaller than \(t_{dd\pi}\), the effective hopping between the non-aligned \(d_{x^2-y^2}\) spin-orbitals will go as \(t_{dd\pi} \cos^2 \theta\), a reduction by \(\cos^2 \theta \approx 0.8\).

It is not a straightforward matter to determine the relative importance of direct V-V hopping and V-O-V mixing that gives the dispersion pictured in Fig. 4. The effect on the \(dd\) bandwidth of the V-O-V coupling was probed by moving the O2 ions from \(\pm \frac{7}{2}\) to \(\pm 0.75\). This distortion brings the O2 ion nearer one V but much farther from the other (2.6 Å), essentially eliminated V-
O1-V coupling of neighboring plaquettes. The resulting occupied \( d \) bandwidth of \( W_d = 0.4 \) eV, compared to 1.3 eV for the real structure, can be ascribed to direct V-V coupling. This result suggests that coupling through the O1 ions is responsible for roughly \( \frac{2}{3} \) of the bandwidth, with direct V-V interactions providing the remaining \( \frac{1}{3} \); i.e. direct V-V coupling is not negligible. This complexity arises specifically from the fact that the spin-orbital is \( d_{x^2-y^2} \) character, which greatly hinders coupling to O ions and maximizes V-V interaction. Using a coordination number \( z_c = 3 \), the V-V bandwidth translates to a hopping amplitude \( t_{dd} = W_d/(2z_c \cos^2 \theta) = 80 \) meV.

The hybridization leading to magnetic coupling is reflected in the spin density distribution on O ions neighboring V. The primary feature, in both FM and AFM alignments studied, is an antiparallel polarization of the apical O2 by perhaps as much as 0.2 \( \mu_B \) (the spin density attributable to a given ion is not precisely defined). The O2 ion, however, is not involved in exchange coupling. The O1 ions have moments about \( \frac{1}{3} \) as large, aligned parallel, while the O3 ion’s moment is even smaller (zero by symmetry for AFM case). Thus the O1 site should be more important in the exchange coupling process than is the O3 site.

These results – the occupied spin orbital of \( d_{x^2-y^2} \) character, \( J_{nnn} > J_{nn}, J_{V-V} \neq 0 \), degenerate FM and AFM alignments – suggest a picture of coupled two metaplaquette system. Each metaplaquette is comprised solely of V ions either above the plane, or below the plane; the upper metaplaquette is highlighted in Fig. 1. The two metaplaquette systems, each topologically equivalent to the original, are coupled by at least three, possibly competing, exchange couplings \( J_{nn}, J'_{nn}, \) and \( J'_{V-V} \), but their values will not be easy to ascertain. The degeneracy of the FM and AFM alignments, in which the two ferromagnetic metaplaquette systems are aligned and antialigned respectively, suggests relatively weak net coupling between the two metaplaquette systems.

There is one particularly interesting difference between the original plaquette system and (either one of) the metaplaquette systems. As was noted in the introduction, V-O-V couplings within a plaquette, or between neighboring plaquettes, are very similar from the structural chemistry point of view. The metaplaquette system is different: intra-metaplaquette coupling proceeds through the O1 site, while inter-metaplaquette coupling proceeds through the O3 site. Not only is the V-O3 distance 4\% longer than the V-O1 distance (Fig. 3) resulting in weaker coupling, but the environments are different and the LSD calculation indicates substantially less hybridization through the O3 site, as reflected in the much lower induced O3 spin density (somewhat visible in Fig. 3). This O1-O3 site distinction provides a mechanism whereby the tendency to form singlets on each metaplaquette is not disrupted by equally strong inter-metaplaquette coupling, which was the case for the original plaquette model.

To summarize, it has been found that consideration of the full low symmetry structure of CaV\(_4\)O\(_9\) indicates that five unequal exchange couplings \( (J_{nn}, J_{nnn}, J'_{nn}, J'_{nnn}) \) from superexchange, and direct \( J_{V-V} \) are present. The orbital character of the spin, together with the topology of the V-O layer, suggest that a coupled two metaplaquette system may provide a realistic way to interpret the spin gap behavior.

I thank R. R. P. Singh for stimulating my interest in this compound. This work was supported in part by the Office of Naval Research. Computation was done at the Arctic Region Supercomputing Center and at the DoD Major Shared Resource Center at NAVOCEANO.

[1] S. Taniguchi et al., J. Phys. Soc. Japan 64, 2758 (1995).
[2] T. Ohama et al., J. Phys. Soc. Japan 66, 23 (1997).
[3] K. Ueda et al., Phys. Rev. Lett. 76, 1932 (1996).
[4] K. Sano and K. Takano, J. Phys. Soc. Jpn. 65, 46 (1996).
[5] M. Troyer et al., Phys. Rev. Lett. 76, 3822 (1996).
[6] O. A. Staryk et al., Phys. Rev. Lett. 77, 2558 (1996).
[7] M. Albrecht et al., Phys. Rev. B 54, 15856 (1996).
[8] N. Katoh and M. Imada, J. Phys. Soc. Jpn. 64, 4105 (1995).
[9] M. P. Gelfand et al., Phys. Rev. Lett. 77, 2794 (1996).
[10] J.-C. Bouloux and J. Galy, Acta Cryst. B 29, 1335 (1973).
[11] S. Marini and D. I. Khomskii, [cond-mat/9703130].
[12] S. H. Wei and H. Krakauer, Phys. Rev. Lett. 55, 1200 (1985); D. J. Singh, Phys. Rev. B 43, 6388 (1991).
[13] D. J. Singh, Planewaves, Pseudopotentials, and the LAPW Method (Kluwer Academic, Boston, 1994).
[14] The AFM alignment had 1.5 meV/V ion higher energy than the FM alignment, probably within the convergence of the calculation.
[15] J. B. Goodenough, Magnetism and the Chemical Bond (Wiley, New York, 1963), Chap. IIIC.