Structural, Orbital, and Magnetic Order in Vanadium Spinels

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Vanadium spinels (ZnV_2O_4, MgV_2O_4, and CdV_2O_4) exhibit a sequence of structural and magnetic phase transitions, reflecting the interplay of lattice, orbital, and spin degrees of freedom. We offer a theoretical model taking into account the relativistic spin-orbit interaction, collective Jahn-Teller effect, and spin frustration. Below the structural transition, vanadium ions exhibit ferro-orbital order and the magnet is best viewed as two sets of antiferromagnetic chains with a single-ion Ising anisotropy. Magnetic order, parametrized by two Ising variables, appears at a tetracritical point.

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Frustrated magnetic systems have generated interest among researchers for more than a decade [1–3]. Frustration refers to the inability of spins to satisfy conflicting interactions resulting in a large degeneracy of the ground state at the classical level. The effect is particularly strong for spins with antiferromagnetic interactions on the three-dimensional network of corner-sharing tetrahedra, known as the pyrochlore lattice [4]. Magnets of this kind have rather unusual properties. For example, spinels containing magnetic ions Cr^{3+} ($ZnCr_2O_4$, $MgCr_2O_4$, and $CdCr_2O_4$) undergo a magnetoelastic phase transition [5,6], even though they have no spin chains commonly associated with the spin-Peierls effect [7].

In this Letter I discuss magnetic and structural properties of another remarkable group of magnetic spinels containing V^{3+} ions (ZnV_2O_4, MgV_2O_4, and CdV_2O_4). These compounds represent a step up in complexity from their chromium counterparts because vanadium ions have an orbital degree of freedom—*in addition to* lattice vibrations and spin. The interplay of orbital, spin, and vibrational motion against the backdrop of a high spatial symmetry leads to a sequence of phase transitions involving changes in structural and magnetic properties. The physics involves the relativistic spin-orbit interaction, collective Jahn-Teller effect, and spin frustration.

The vanadium spinels undergo a structural phase transition at a temperature T_s and a magnetic ordering at a lower temperature T_N. The structural distortion lowers the crystal symmetry from cubic $Fd\bar{3}m$ to tetragonal $I4_1/amd$ [8,9], with a slightly shorter lattice period along the c axis. The Néel temperature T_N is rather small compared to the Curie-Weiss scale Θ_{CW}, a sure sign of strong spin frustration. Ordered magnetic moments point along the c axis and have the length $\langle\mu\rangle < \mu_B$ at helium temperatures. Magnetic susceptibility is history dependent both below and above T_N [9,10]. The numbers for ZnV_2O_4 are representative of the entire family: $c/a = 0.994$, $T_s = 51$ K [10], $T_N = 42$ K [11], $\Theta_{CW} = 420$ K [12], and $\langle\mu\rangle = 0.63\mu_B$ [9].

The main difference between Cr^{3+} and V^{3+} ions is the number of electrons in the partially filled $3d$ shell. The crystal field splits the $3d$ quintet into a low-energy triplet t_{2g} and a high-energy doublet e_g, separated by a gap of roughly 2 eV. In accordance with Hund's rules, the three d electrons of Cr^{3+} have spin $S = 3/2$ and occupy all three triplet levels. The ion has a spin degree of freedom only. In contrast, the two d electrons of V^{3+} have spin $S = 1$ and occupy two out of three t_{2g} orbitals.

Tsunetsugu and Motome [13] have recently developed a model explaining structural and magnetic properties of the vanadium spinels. Following the approach of Kugel and Khomskii [14], they focus on Coulomb and exchange interactions between magnetic ions. However, their model is at odds with experimental observations: the orbital order predicted by the theory is incompatible with the spatial symmetry of the tetragonal phase, identified as $I4_1/amd$ [8,9]. The staggering of ions with empty yz and zx orbitals would break reflections m in the planes (110) and $(1\bar{1}0)$ and diamond glides d in the planes (100) and (010), lowering the symmetry to $I4_1/a$ [Fig. 1(a)].

I propose an alternative theory that is compatible with the structural data and predicts rather nontrivial magnetic behavior. In the new model, the structural order arises from simple single-ion physics: the interplay of the Jahn-Teller (JT) effect and relativistic spin-orbit interaction.

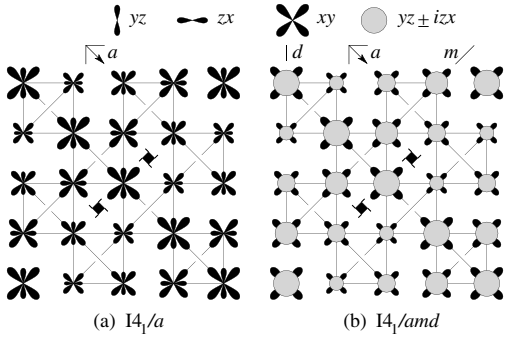

FIG. 1. Orbital order of vanadium ions below the structural phase transition. A view down the [001] direction. Smaller symbols are farther away. (a) The result of Tsunetsugu and Motome [13]. (b) This work.

The t_{2g} orbitals are *partially* ordered: their occupation numbers satisfy $n_{yz} = n_{zx} < n_{xy}$ [Fig. 1(b)]. The distorted magnet is best described as a collection of antiferromagnetic chains, running in the directions [110] and [1$\bar{1}$0], with an effective spin $J = 2$ and a single-ion anisotropy of the Ising type. Parallel chains are weakly coupled; the coupling of orthogonal chains is frustrated by symmetry. As a result, the Néel phase is characterized by two independent Ising order parameters; the magnetic transition occurs at a *tetracritical* point. Two nearby magnetic phases exist in which only one half of the chains order. Finally, memory effects in magnetic susceptibility are tied to the spontaneous breaking of the lattice symmetry.

Choice of the model.—The main difficulty in obtaining a consistent theoretical picture of the vanadium spinels is a poor separation of energy scales. The t_{2g} orbitals of a B site in spinels point away from the oxygen ligands and thus have a relatively weak JT coupling [15] comparable in magnitude to the relativistic spin-orbit coupling. (A recent estimate [16] puts the JT energy in YVO_3 at 20–60 meV. The spin-orbit splitting of the $^3F_2$ and $^3F_3$ levels in a free V^{3+} equals 39 meV [17].) Furthermore, the effective interaction of spin and orbital degrees of freedom on adjacent vanadium ions has a similar energy scale [13]. It is not at all obvious which of the three interactions plays the dominant role.

To make progress, one can adopt a phenomenological approach and investigate three simple limits, in which the dominant interactions are, respectively, (I) the JT coupling, (II) the spin-orbit coupling, (III) the Kugel-Khomskii interaction. Model III [13] yields orbital order incompatible with the observed symmetry of the tetragonal phase [8,9]. We therefore explore limits I and II.

Basis states and notation.—If the energy difference between the ^3P and ^3F electronic terms of the $3d^2$ configuration (≈ 1 eV) is neglected in comparison with its crystal-field splitting in a VO_6 octahedron (≈ 2 eV), the $3T_{1g}$ ground state of a V^{3+} ion has the $t_{2g}^2 e_g^0$ configuration. Its orbital part is triply degenerate and has the following basis:

$$\begin{aligned} |X\rangle &= (|zx\rangle|xy\rangle - |xy\rangle|zx\rangle)/\sqrt{2}, \\ |Y\rangle &= (|xy\rangle|yz\rangle - |yz\rangle|xy\rangle)/\sqrt{2}, \\ |Z\rangle &= (|yz\rangle|zx\rangle - |zx\rangle|yz\rangle)/\sqrt{2}. \end{aligned} \tag{1}$$

In this Hilbert space, the operator of orbital momentum $\mathbf{L}$ can be expressed in terms of an effective angular momentum $\mathbf{L}'$ of length $L' = 1$ such that

$$L'_z|X\rangle = i|Y\rangle, \qquad L'_z|Y\rangle = -i|X\rangle, \qquad L'_z|Z\rangle = 0, \tag{2}$$

etc. It can be verified that $\mathbf{L} = -\alpha\mathbf{L}'$, where $\alpha = 1$ in the approximation made (1). Inclusion of electronic correlations mixes in the states $t_{2g}^1 e_g^1$ and $t_{2g}^0 e_g^2$ and puts α somewhere in the range between 1 and 3/2 [18].

Model I.—A tetragonal distortion of a VO_6 octahedron along the c axis splits the $^3T_{1g}$ state into a doublet and a singlet. The splitting can be mimicked by the traceless operator

$$V_{\mathrm{JT}} = \delta[L_z'^2 - L'(L'+1)/3], \tag{3}$$

where δ is the tetragonal strain expressed in energy units. For a $3d^2$ ion, $\delta > 0$ for an elongated octahedron [15]. The lowest-energy state is $|Z\rangle$, in which the xy orbital is empty and the energy is $-2\delta/3$. In the opposite case (a flattened octahedron, $\delta < 0$), the orbital ground state is doubly degenerate and has a higher energy $-|\delta|/3$. Inclusion of the elastic energy $\mathcal{O}(\delta^2)$ and minimization with respect to δ yields a ground state with $\delta > 0$. Thus Model I, dominated by the JT coupling, predicts an elongation of VO_6 tetrahedra contrary to the data [8–11,19].

Model II.—The relativistic spin-orbit coupling in V^{3+}

$$V_{LS} = \lambda(\mathbf{L}\cdot\mathbf{S}) = -\alpha\lambda(\mathbf{L}'\cdot\mathbf{S}) \tag{4}$$

has the strength $\lambda \approx +20$ meV [16]. The "total angular momentum" $\mathbf{J}' = \mathbf{L}' + \mathbf{S}$ is a conserved quantity. The lowest-energy state is the $J' = 2$ quintuplet separated by the energy gap $2\alpha\lambda$ from the $J' = 1$ levels.

Inclusion of the JT interaction (3) as a perturbation ($\delta \ll \lambda$) splits the $J' = 2$ quintuplet into three levels. With the aid of the Wigner-Eckart theorem, one finds

$$V_{\mathrm{JT}} = (\delta/2)[J_z'^2 - J'(J'+1)/3]. \tag{5}$$

Remarkably, the ground state has the same energy $-|\delta|$ regardless of the sign of the δ. In an elongated VO_6 octahedron ($\delta > 0$), the ground state is nondegenerate and has $J_z = 0$; its magnetic moment $-\mu_B(-\alpha\mathbf{L}' + 2\mathbf{S})$ is quenched. In a flattened octahedron ($\delta < 0$), the ground state is a non-Kramers doublet $J'_z = L'_z + S_z = \pm 2$. Inclusion of the elastic energy $\mathcal{O}(\delta^2)$ fails to determine the sign of the tetragonal JT distortion. It will be determined by several competing perturbations, such as higher-order JT terms, Coulomb and spin-exchange interactions between vanadium ions.

The effect of Coulomb interaction can be crudely estimated by counting the number of filled t_{2g} orbitals with the largest overlap. For example, the Coulomb energy of a [110] V-V bond is raised if the xy orbitals are occupied in both ions [13]. In a state with uniform orbital order, the average occupations of the orbitals are as follows:

$$\begin{aligned} J'_z = \pm 2:&\ \langle n_{yz}\rangle = \langle n_{zx}\rangle = 1/2, \qquad \langle n_{xy}\rangle = 1, \\ J'_z = 0:&\ \langle n_{yz}\rangle = \langle n_{zx}\rangle = 5/6, \qquad \langle n_{xy}\rangle = 1/3. \end{aligned} \tag{6}$$

The expectation value of the Coulomb energy, summed over nearest-neighbor V-V pairs, will be proportional to $\langle n_{yz}\rangle^2 + \langle n_{zx}\rangle^2 + \langle n_{xy}\rangle^2$. This expression evaluates to 3/2 for both $J'_z = 0$ and $J'_z = \pm 2$ ground states. Thus the Coulomb repulsion between V^{3+} ions is the same in the elongated and flattened ground states of VO_6 octahedra and does not influence the outcome of their competition.

[The accidental degeneracy of the Coulomb term can be traced to the degeneracy of the flattened and elongated JT

states for $J' = 2$. Both the Coulomb and JT energies can be expressed in terms of the operators $J_z'^2 - J'(J'+1)/3$ and $J_x'^2 - J_y'^2$. It is therefore likely that the conclusion reached in the previous paragraph is not sensitive to the approximations made in this Letter.]

Exchange energy, on the other hand, clearly favors the magnetic ground states $J_z' = \pm 2$ because it can be made negative by an appropriate choice of spin orientations. In contrast, exchange energy is zero if the ions are in the nonmagnetic state $J_z' = 0$. Anharmonic terms of the JT energy $\mathcal{O}(\delta^3)$ can favor either sign of δ. Therefore, one cannot deduce the sign of the distortion on general theoretical grounds. Nonetheless, experimental observation of antiferromagnetic order in ZnV_2O_4 at low temperatures points to the magnetically active states $J_z' = \pm 2$ characterized by a flattening of the VO_6 octahedra along the c axis. For a given direction of the spin, $S_z = \pm 1$, one of the electrons occupies the xy orbital, whereas the other is in the state $|yz\rangle \pm i|zx\rangle$, whose actual orbital moment $L_z = -\alpha L_z' = \mp\alpha$ points opposite to the spin. Equal occupation of the yz and zx orbitals in such a state is in agreement with the observed spatial symmetry of the crystal ($I4_1/amd$). Magnetic moments of length $(2-\alpha)\mu_B$, where $1 \le \alpha < 3/2$, point along the c axis, as found experimentally. Thus phenomenological Model II, with strong relativistic spin-orbit coupling, a moderate JT distortion, and weak V-V interactions, is compatible with experimental observations.

Structural order and symmetry-breaking fields.—Below T_s the VO_6 octahedra flatten along one of the three major axes. From the symmetry viewpoint, the long-range order is similar to that of the 3-state Potts ferromagnet. A two-component order parameter $\mathbf{f} = (f_1, f_2)$ can be constructed, e.g., from the lattice constants

$$f_1 = (a + b - 2c)/\sqrt{6}, \qquad f_2 = (a - b)/\sqrt{2}. \tag{7a}$$

Other observables can be used to define the order parameter. The lattice constants (a, b, c) can be replaced with orbital populations $(\langle n_{yz}\rangle, \langle n_{zx}\rangle, \langle n_{xy}\rangle)$, or with magnetic susceptibilities $\chi_{ij} = \partial M_j/\partial H_i$

$$f_1 = (\chi_{xx} + \chi_{yy} - 2\chi_{zz})/\sqrt{6}, \qquad f_2 = (\chi_{xx} - \chi_{yy})/\sqrt{2}. \tag{7b}$$

Explicit construction of the order parameter allows us to identify symmetry-breaking fields that can be applied to select a particular phase with broken symmetry. The most obvious among these is the two-component (tetragonal and orthorombic) stress $\mathbf{h} = (h_1, h_2)$

$$h_1 = (e_{xx} + e_{yy} - 2e_{zz})/\sqrt{6}, \qquad h_2 = (e_{xx} - e_{yy})/\sqrt{2}. \tag{8a}$$

Cooling under a weak uniaxial stress applied along the c axis will produce an ordered phase with $a = b > c$.

A less obvious symmetry-breaking perturbation is magnetic field $\mathbf{H}$. The magnetic energy density of a sample can be written as $-(\chi_{xx}H_x^2 + \chi_{yy}H_y^2 + \chi_{zz}H_z^2)/2$. Unless the field is parallel to a $\langle 111\rangle$ direction, it lowers the energies of different ordered phases by different amounts. The symmetry-breaking field is

$$h_1 = (H_x^2 + H_y^2 - 2H_z^2)/\sqrt{6}, \qquad h_2 = (H_x^2 - H_y^2)/\sqrt{2}. \tag{8b}$$

These considerations could explain memory effects in magnetic susceptibility of ZnV_2O_4 above the Néel temperature T_N [9,10]. A crystal cooled through the structural transition in magnetic field chooses the distorted phase with the lowest magnetic energy. The difference between χ_{FC} and χ_{ZFC} in powder samples may simply reflect the presence of the order parameter (7b) below T_s and its sensitivity to the symmetry-breaking field (8b). It would be highly desirable to study these memory effects in single crystals.

Aniferromagnetic Ising chains with frustrated coupling.—In the distorted state, the magnetic system, comprising spins and orbital moments, can be thought of as a collection of chains running in the $[110]$ and $[1\bar{1}0]$ directions (Fig. 2). Because the xy orbitals are always occupied, the largest exchange coupling takes place along the chains. Exchange coupling along the other $\langle 110\rangle$ directions is expected to be substantially weaker because the relevant orbitals (yz and zx) are only half filled. Onoda and Hasegawa [8] have extracted the values of $J_{[110]} \approx 5$ meV and $J_{[011]} = J_{[101]} \approx 3$ meV for CdV_2O_4. In addition to the single-ion Ising anisotropy (5), which is a product of orbital order and spin-orbit coupling, the exchange interactions are likely anisotropic as well.

As the distorted magnet is cooled further, spin correlations develop first along the chains, as indeed observed [19]. If the interchain coupling is weak, long-range magnetic order will set in at a low temperature, when each chain already has a large correlation length. In that case, the magnetic transition will have almost no effect on the energetics of the spins. Indeed, measurements of specific heat in MgV_2O_4 reveal a very weak singularity at the magnetic transition [11].

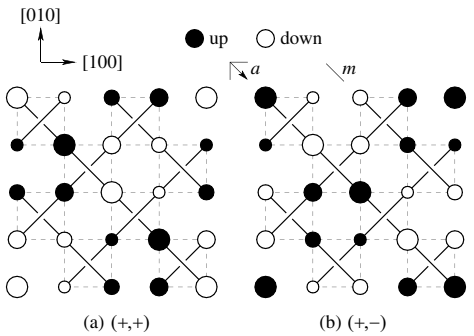

FIG. 2. Two of the four magnetically ordered states. The signs refer to the two Ising order parameters ($\sigma_{[110]}$, $\sigma_{[1\bar{1}0]}$). Ground states (a) and (b) are related by a (110) reflection m or by a (110) glide a in a (001) plane.

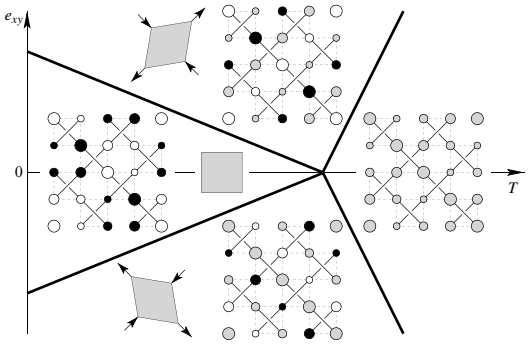

FIG. 3. The temperature-strain phase diagram in the vicinity of the tetracritical point $T = T_N$, $e_{xy} = 0$. Gray symbols correspond to disordered spins. Thick solid lines are phase boundaries. Other notations are same as in Fig. 2.

While magnetic interactions between parallel chains are expected to be weak because they are well separated in space, the coupling between crossing chains may be substantial: four of their spins are nearest neighbors forming a tetrahedron (Fig. 2). However, in this case the coupling is frustrated by the lattice symmetry: a (110) reflection m (or a glide a) changes the sign of staggered magnetization on the chain running in the direction $[1\bar{1}0]$ but preserves staggered magnetization on the [110] chain. Therefore, even if the crossing-chain coupling is numerically comparable to the intrachain coupling, it is still rendered weak by geometrical frustration.

Magnetic order.—Neutron scattering indicates that adjacent parallel chains have equal values of staggered magnetization (Fig. 2). Because of the geometrical frustration, the system has *four* ground states: those shown in Fig. 2 and their time-reversed copies. These ground states can be characterized by two independent Ising order parameters: one staggered magnetization for each set of chains, $\sigma_{[110]}$ and $\sigma_{[1\bar{1}0]}$ [20].

Magnetic tetracritical point.—Both sets of chains appear to be ordered at the lowest temperatures [9]. In the simplest scenario, both Ising order parameters develop continuously at the magnetic transition temperature T_N, which is characteristic of a tetracritical point [21,22]. One should be able to observe two additional phases in the vicinity of the tetracritical point, in which only one set of chains is ordered, while the other is not. This may be achieved by creating an orthorhombic strain e_{xy} in the vicinity of the magnetic transition. Doing so will violate the equivalence of the [110] and $[1\bar{1}0]$ chains while still preserving the geometrical frustration. A temperature scan under a uniaxial [110] stress should reveal two separate magnetic transitions for each set of chains. The temperature-strain phase diagram in the vicinity of the tetracritical point is shown in Fig. 3.

Outlook.—A phenomenological approach taken in this Letter is justified by the complexity of vanadium spinels: the relevant degrees of freedom include lattice vibrations, orbital motion, and spin. It is desirable to put these considerations on a quantitative footing with the aid of a microscopic theory. Nonetheless, the qualitative predictions of this work—a spin gap due to single-ion anisotropy, a magnetic tetracritical point, and a potential relation between magnetic memory effects and broken lattice symmetry—can be tested experimentally.

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Note added.—Upon completion of this work I learned that a similar model had been considered by D. I. Khomskii.

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