Theory for Phase Transitions in Insulating $V_2O_3$

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We show that the recently proposed $S = 2$ bond model with orbital degrees of freedom for insulating $V_2O_3$ not only explains the anomalous magnetic ordering, but also other mysteries of the magnetic phase transition. The model contains an additional orbital degree of freedom that exhibits a zero temperature quantum phase transition in the Ising universality class.

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The metal-insulator transition in vanadium oxide ($V_2O_3$) has long been hailed as a physical realization of the Mott transition. However, the insulating phase displays essential deviations from the standard Mott insulator with only spin degrees of freedom. For example, while it undergoes a transition from paramagnetic to antiferromagnetic (AF) insulator with decreasing temperature, the magnetic ordering pattern observed (hitherto called RS) is not that of the simplest two-sublattice Heisenberg model. They showed that within certain parameter regime, the ground state exhibits the RS magnetic ordering pattern together with orbital ordering. Recently, resonant x-ray scattering experiments have observed orbital ordering in $V_2O_3$ with an ordering wavevector consistent with one of the ordered state (so-called RO state) obtained by CNR.

The CNR model relies on one out of the two electrons on a V ion forming a spin singlet bond with its counterpart on the neighboring V ion along the c-axis, leaving one electron occupying doubly degenerate orbitals on each V ion. This has recently been criticized for not respecting the strong on-site coulomb repulsion and Hund’s rule coupling. This criticism is supported by polarized soft x-ray experiments, and strongly suggests that the effective spin on a V ion should have $S = 1$ instead of $S = 1/2$. Recently, a $S = 1$ model incorporating the orbital degree of freedom has been introduced. In this model V-V pair along c-axis is locked ferromagnetically into a total spin 2 “bond” with a double orbital degeneracy. These bonds occupy a lattice that is topologically equivalent to a cubic lattice (Fig. 1). Virtual in-plane hopping in the honeycomb planes couple such bonds to their neighbors. For Hund’s rule coupling and hopping constants consistent with reported/expected values, it was shown that the ground state has RS magnetic and ferro-orbital (FO) order. The FO ordering was shown to be also consistent with the resonant x-ray experiments.

In addition to the anomalous RS magnetic order, there are other mysteries associated with the $V_2O_3$ insulator. I) the magnetic and orbital ordering occur at the same transition temperature in contrast to the Jahn-Teller transitions observed in other transition metal oxides like MnO; II) the transition is strongly first order; and III) above the transition temperature, neutron scattering observes a relatively broad peak in the susceptibility for wavevector of AS ordering but no features for the RS ordering wavevector.

In this letter, we will show that the $S = 2$ bond model gives satisfactory explanation for the three mysteries above. In addition, we will elucidate on a new orbital degree of freedom, which can lead to a second orbital transition at a lower temperature. The critical temperature of this second orbital transition goes to zero as the intraplane hopping approaches some critical value, giving rise to a zero temperature quantum phase transition. This second transition is well described by the transverse field Ising model.

We begin by briefly recalling the steps leading to the effective $S = 2$ bond Hamiltonian. The large on-site, same-orbital coulomb repulsion ($U \approx 5 eV$) and Hund’s coupling ($J \approx 0.6 - 1 eV$) constrains the Hilbert space of each V ion to that of 2 electrons with total spin $S = 1$, hence singly occupying two of the lower three $t_{2g}$ d-orbitals favored by crystal field. The remaining 9-fold degeneracy of a single ion is then lifted due to virtual hopping. Let $t_{ij}$ be the various hopping integrals between
nearest neighbor (nn) V ions, where \( \delta = a, b, c, d \) stands for the direction of the bond (Fig. 1) and \( (i, j) = 1, 2, 3 \) for the orbitals \( e_{g1}, e_{g2}, a_{1g} \) respectively. Since \( t^z_{\delta} \) is by far the largest, the strongest effect is due to virtual hopping between vertical pairs of V ions. When combined with \( J \) large, this further reduces the Hilbert space of a single pair to that of total spin \( S = 2 \), with an occupation of \( (e_{g1}, e_{g2}) \) by the two electrons on one V ion and \( (e_g, a_{1g}) \) on the other. The orbital configuration proposed here is qualitatively consistent with the polarized x-ray absorption spectra of V_2O_5. The basis for such a V-ion pair can then be written as \(| \sigma \tau \mu \rangle \). Here \( \sigma = -2, -1, ... 2 \) is the spin state, \( \tau = +1 \) \((-1)\) if \( e_{g1} \) \( (e_{g2}) \) is occupied on the ion with \( (e_g, a_{1g}) \) occupation, and \( \mu = +1 \) \((-1)\) denotes whether the top V ion has the \( (e_{g1}, e_{g2}) \) or \( (e_g, a_{1g}) \) occupation.

Within this restricted Hilbert space, we can now obtain the effective Hamiltonian by considering the lifting of the degeneracies due to the effects of the other \( t^z_{\delta} \)'s. The effective Hamiltonian is expressed by defining on each vertical pair a spin 2 operator \( \sigma \), a pseudospin 1/2 operator \( \tau \), and yet another pseudospin operator \( \mu \), which act on the \( \sigma, \tau, \mu \) degrees of freedom respectively. The effective Hamiltonian must respect global SU(2) symmetry in spin space, \( Z_3 \) symmetry in \( \tau \) space, and \( Z_2 \) symmetry in \( \mu \) space. The \( Z_3 \) Potts symmetry in \( \tau \) reflects the \( C_3 \) rotational symmetry of the corundum lattice about the \( c \)-axis while the Ising \( Z_2 \) symmetry in \( \mu \) reflects the global “top-bottom” inversion symmetry of the V-ion pairs. We consider only processes where after two (virtual) hops, the system is restored into the restricted Hilbert space. With no loss of generality, we assume for \( t^z_{ij} \) that only \( t_{11} \) and \( t_{22} \) are non-negligible.

At temperature \( \approx 155K \), x-ray experiment has shown that all V ions remain equivalent in the AF phase, implying no symmetry breaking of the \( Z_2 \) \( \mu \) symmetry at the magnetic transition. If we further neglect fluctuation effects, effectively setting \( \mu = 0 \) in the effective Hamiltonian, \( \mu \) becomes decoupled from the \( \sigma \) and \( \tau \) degrees of freedom, and the Hamiltonian is simplified to

\[
H = a_0 \sum_{\langle ij \rangle} S_i \cdot S_j + a_1 \sum_{\langle ij \rangle} S_i \cdot S_j (\tau_i \cdot \hat{n}_{ij} + \tau_j \cdot \hat{n}_{ij}) \\
+ a_2 \sum_{\langle ij \rangle} \tau_i \cdot \hat{n}_{ij} \tau_j \cdot \hat{n}_{ij} + b_2 \sum_{\langle ij \rangle} S_i \cdot S_j (\tau_i \cdot \hat{n}_{ij} \tau_j \cdot \hat{n}_{ij})
\]

where \( \hat{n}_{ij} = \hat{n}_i \cdot \hat{n}_j \) for \( i, j \) nn in the \( x, y, z \) directions respectively. The \( \hat{n}_i \)'s are unit vectors in the \( x - z \) plane of the \( \tau \) space, with \( \hat{n}_3 = \hat{z} \), while \( \hat{n}_1 \) and \( \hat{n}_2 \) are rotated from \( \hat{n}_3 \) by \( 120^\circ \) and \( 240^\circ \). The coupling constants \( a_0 \) etc. depend on \( J \) and \( \gamma = (t_{11}/t_{22})^z \). The model contains three types of local order parameters: a vector order parameter \( M_i = < S_i > \), a Pott’s type order parameter \( r^z_i = < \tau_i \cdot \hat{n}_i > \), and a tensor order parameter \( Q_i^{z} = < S_i \tau_i \cdot \hat{n}_i > \). Assuming up to four sublattice ordering in these three order parameters on the equivalent cubic lattice with wavevectors \( k_x = k_y = 0, \pi, k_z = 0, \pi \), we approximate \( H \) by a single-site Hamiltonian using usual mean field theory (MFT) to find the values of \( M_i, r_i^z, \) and \( Q_i^z \) that minimizes the free energy. The phase diagram for zero temperature thus obtained is shown in Fig. 2.

[FIG. 2. \( T = 0 \) phase diagram of the \( S = 2 \) bond model. \( U' = U - 2J \). Phases are 1) FORS, 2) AOFS, 3) FORS', 4) AOAS, 5) AO_RS, and 6) AO_RS' (subscripts after AO indicate direction of AO ordering in \( \tau \) space). Dashed line shows where \( a_0 = 0 \). Dotted line shows the boundary between first order (below the line) and second order transitions for the FORS phase.]

The phase diagram can be understood qualitatively as follows. The key dependences of the various coupling constants on \( J \) and \( \gamma \) are that \( a_0 \) changes from \( > 0 \) to \( < 0 \) as \( J \) is increased, \( a_1 < 0 \) everywhere, and \( a_2, b_2 = 0 \) for \( \gamma = 0 \) and \( > 0 \) otherwise, with \( a_2 \geq 4b_2 \). The \( a_0 \) term favors AS or ferromagnetic spin (FS) ordering while the \( a_2 \) and \( b_2 \) terms combined favor antiferro-orbital (AO) ordering. The \( a_1 \) term in \( H \) appears as an explicit symmetry breaking field on \( \tau \). However, for the AS or FS states or any other state whose spin correlations \( < S_i \cdot S_j > \) do not break the lattice \( C_3 \) symmetry, this field equals zero when summed over all bonds, and the \( a_1 \) term gives no contribution to the energy. Thus, close to the boundary where \( a_0 \) changes sign, the spins should order magnetically in a way to break the \( C_3 \) symmetry to take advantage of the \( a_1 \) term. This accounts for the states RS and RS' which differ from each other by having 1 ferromagnetic bond and 2 antiferromagnetic bonds on the honeycomb plane for the RS and vice versa for RS'. Choosing the ferromagnetic bond for RS and antiferromagnetic bond for RS' to be along the \( a \) direction of the honeycomb planes, these magnetic orderings set up an uniform field on \( \tau \) in the \( +z \) and \( -z \) directions respectively, thus for small \( \gamma \) causing \( < \tau_{\pi} > \) to become uniformly non-zero (FO phase).

Of these phases, the one that is consistent with the magnetic and orbital ordering observed by neutron scattering and resonant x-ray scattering experiments is the FORS phase. Below we shall focus on this phase and study the finite temperature phase transition of the model to explain the three mysteries of insulating V_2O_3.

1) In V_2O_3, the magnetic transition is accompanied by
orbital ordering. In our MFT, we indeed find the spin and orbital to order at the same temperature. This result is robust, and can be explained more generally as a consequence of the form of the Hamiltonian together with FORS type ordering. Since the RS ordering produces a symmetry breaking field on $\tau$, any RS ordering must necessarily be accompanied by non-zero $\langle \tau \rangle$'s. The converse of this is not true, and orbitals can in principle produce a symmetry breaking field on $\tau$. Thus, we conclude that for FORS (or FORS') ordering, magnetic and orbital ordering must occur together. This is not true for the other ground states. For AOAS or AOFS, as $T$ is lowered, magnetic ordering can first occur without orbital ordering or vice versa. For AORS and AORS', magnetic ordering must be accompanied or preceded by orbital ordering, but orbital ordering can occur without magnetic ordering.

We should note that the observed monoclinic distortion below $T_c$ plays no role in our theory. Indeed, we believe it to be a by-product of the FORS transition breaking the $C_3$ rotation symmetry of the honeycomb planes.

II) The magnetic transition is strongly first order, with an entropy jump of $\approx k_B \ln 2$ per V ion. The size of entropy jump suggests that the first order transition should not be induced by critical fluctuations, but should be mean field in origin. Indeed, our MFT shows a first order transition for the paramagnetic-FORS transition for small $\gamma$ (Fig. 2). It should be remarked that while the symmetry of $H$ allows third order invariants in the Landau-Ginzburg free energy functional of the form $r^3$ and $M Q r$, they are not the cause of the first order transition. This is because the FO susceptibility at $T_c$ is small since the FO ordering is not favored by the bare orbital-orbital coupling of $H$. Indeed, for values of $\gamma$ such that the transition into FORS phase is continuous, $r \sim M Q$ below but close to the transition. Instead, the first order transition is due to the presence of a negative $M^2 Q^2$ quartic term.

While MFT gives a first order transition, the calculated entropy jump and maximum value of $\gamma$ are rather small, especially when compared to the actual experimental value of $\approx k_B \ln 2$ per V ion. We believe this to be a result of ignoring nn AF correlation in the paramagnetic state in a MFT for the FORS transition. This correlation is seen to be sizeable experimentally (see III below), and serves to stabilize the paramagnetic state. We estimate the nn correlation using high temperature expansion to second order in $a_0$ and find the entropy jump and maximum $\gamma$ to be significantly increased without much reduction in $T_c$. A schematic of the free energy functional without and with nn AF correlations included is shown in Fig. 3.

III) Given the magnetic RS ordering below $T_c$, one might expect peaks at the three symmetry related RS wavevectors above $T_c$, and that these peaks would sharpen as the temperature is lowered towards $T_c$. Neutron scattering above $T_c$, however, shows a broad peak in AS wavevector but no feature in the RS wavevectors. Moreover, as $T$ decreases, the broad peak increases in intensity but does not sharpen appreciably, indicating that nn spins are increasingly AF correlated but the correlation length remains of order of nn. This seemingly surprising feature can be explained qualitatively as follows in our theory. Above $T_c$, there are fluctuations in both the AS and RS states. The nn spin correlation of AS is of course AF. While the correlation of RS for a particular symmetry broken state has a pattern with ferromagnetic in one nn bond and AF in other two nn bonds in the honeycomb plane, the nn correlation when averaged over the three RS states also is AF. For long distance correlations, however, the signs of correlations due to fluctuations of AS and RS states can be competing. As a result, these spin correlations remain weak.

FO ordering exists only for RS or RS' ordering. Also, the simultaneity of magnetic and orbital ordering, and the first order phase transition depend crucially on FORS ordering. Thus, the phase transition phenomenology can be changed by changing the type of magnetic ordering. This can be achieved by applying an uniform magnetic field which with increasing strength will change the preferred magnetic ordering from RS to FS. This will in turn change the orbital ordering and the phase transition properties. This can be observed by performing resonant X-ray scattering in the presence of a magnetic field.

Let us now return to the $\mu$ degree of freedom. At temperature significantly lower than $T_c$, the FORS ordering will be approximately saturated and frozen out, and $\mu$ becomes the only relevant degree of freedom. The effective Hamiltonian thus becomes

$$H_\mu = -\Delta \sum_i \mu_i x + \sum_{\langle ij \rangle} J_{ij} \mu_i \mu_j$$
where $\Delta = 2t_{11}^d t_{22}^d / (U - 3J)$, $J_{ij} = J_1$ for ferromagnetically aligned nn, and $J_{ij} = J_2$ for antiferromagnetic ones. $J_1$ and $J_2$ are given by

$$J_1 = \frac{t_{23}^d}{U - 3J},$$

$$J_2 = \left( \frac{2}{(U - 3J)} + \frac{1}{U} - \frac{3}{U + 2J} \right) \frac{t_{23}^d}{24} (1 - \frac{9}{8} \gamma).$$

We recognize this Hamiltonian as the transverse field Ising model (TFIM). At $T = 0$, this model has a quantum phase transition from a disordered state for large $\Delta$ to an ordered one for small $\Delta$. The ordering pattern depends on the signs of $J_1$ and $J_2$. We see that $J_1 > 0$ always, while $J_2$ changes sign as $\gamma$ is decreased. For $J_2 < 0$, $\mu$ ordering does not lead to further reduction of translational invariance from the FORS state, and no new wavevector $q$ will be observed in resonant x-ray diffraction, only intensity change. For $J_2 > 0$, there will be further change in Bravais lattice symmetry, and peaks at new $q$'s will be observed. The value of $\gamma$ necessary for FORS ordering and in particular to have a first order transition for estimated value of $J$ suggests that $J_2 > 0$.

For the 3D TFIM, its finite temperature transition is in the same universality class as the 3D Ising model and its $T=0$ transition in that of the 4D Ising model respectively. However, if $J_2$ is close to zero, then the system behaves like a quasi-1D one. Therefore, as $J_2$ varies, it may be possible to observe a dimensional crossover. If $J_2$ is not too small, the critical value of $\Delta$ for LRO may be obtained by MFT as $2J_1 + 4|J_2| = \Delta / \tanh(\Delta / k_B T)$. This implies the critical temperature $T_\mu$ rises sharply from 0 as $\Delta$ is reduced from its $T = 0$ critical value. The MF value of $T_\mu$ should be accurate provided $\Delta$ is neither too close to $\Delta_c$ nor too small. For $\Delta$ close to $\Delta_c$, $T_\mu$ is governed by quantum critical phenomena, and scales as the inverse correlation time, so that up to logarithmic corrections $T_\mu \sim \xi^{-1} \sim (\Delta_c - \Delta)$. For small enough $\Delta$, $T_\mu$ can become comparable to $T_c$, and the assumption of saturated FORS ordering will not be valid.

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16 Details of the $T = 0$ phase diagram using a similar calculation has been previously reported.\[17\]
17 Beyond mean field, there is also the possibility of orbital ordering along with RS spin correlations but not ordering, in effect an orbital driven spin Peierls transition.