Orbitally Degenerate Spin-1 Model for Insulating $V_2O_3$

F. Mila$^{(a)}$, R. Shiina$^{(b)*}$, F.-C. Zhang$^{(c)}$, A. Joshi$^{(c)}$, M. Ma$^{(c)}$, V. Anisimov$^{(d)}$, and T. M. Rice$^{(b)}$

$^{(a)}$ Laboratoire de Physique Quantique, Université Paul Sabatier, 31062 Toulouse, France
$^{(b)}$ Theoretische Physik, ETH-Hönggerberg, CH-8093 Zürich, Switzerland
$^{(c)}$ Department of Physics, University of Cincinnati, Cincinnati, Ohio 45221
$^{(d)}$ Institute of Metal Physics, Russian Academy of Sciences, 620219, Ekaterinburg, GSP-170, Russia

Motivated by recent neutron, X-ray absorption and resonant scattering experiments, we revisit the electronic structure of $V_2O_3$. We propose a model in which $S=1$ $V^{3+}$ ions are coupled in the vertical V-V pairs forming two-fold orbitally degenerate configurations with $S=2$. Ferro-orbital ordering of the V-V pairs gives a description which is consistent with all experiments in the antiferromagnetic insulating phase.

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Although the metal-insulator transition in $V_2O_3$ has long been studied as a classic Mott-transition [1–3], the detailed electronic structure remains open. Recently new experimental techniques have been applied but these have not resolved the issue. Rather they have reopened the long standing controversy between an antiferromagnetic (AF) [4] and a spin singlet covalent (solid circles) arrangement in V-V pairs along the c-axis and doublet planar (see Fig. 1). In their early work, Castellani et al. proposed that one electron of the $3d^2$ $V^{3+}$-ion entered a spin singlet covalent $a_{1g}$-bond in the V-V pair while the remaining electron was in the $e_g$-doublet. Orbital ordering of these $e_g$-doublets allowed them to explain the unusual magnetic structure of the AFI-phase with inequivalent $n.n.$ exchange constants in the $a - b$ plane (2 antiferromagnetic, 1 ferromagnetic) [5–7]. Paolasini et al. [8] interpreted their recent resonant x-ray experiments as a confirmation of this orbital ordering. On the other hand the polarized soft x-ray experiments by Park et al. [9] showed a coexistence of both ($e_g e_g$) and ($e_g a_{1g}$) configurations in roughly equal amounts and these led Ezhov et al. [10] to argue for a $S=1$ model with a ($e_g e_g$) configuration and no orbital degeneracy. This is favored by the atomic Hund’s Rule whose strength, as they point out, is not screened in the crystal. The differing planar exchange constants they attribute to the monoclinic distortion in the AFI-phase. Yet general considerations of the phase diagram [11] and NMR investigations [12] all point towards to the presence of an orbital degeneracy.

Here we take a different approach to the AFI-phase and start from an atomic limit but consider first the V-V pairs, since the intersite $a_{1g}$-hopping matrix elements are the largest [4]. Keeping a strong Hund’s Rule coupling, as proposed by Ezhov et al., leads us to molecular orbitals for a V-V pair consisting of a superposition of ($e_g e_g$) on one V-site and of ($e_g a_{1g}$) on the second site with a total spin $S=2$. This delocalized molecular orbital has also a two-fold degeneracy due to a choice in ($e_g a_{1g}$) among the $e_g$-doublet. Next we consider planar hopping processes and show that in a reasonable parameter range the real spin (RS) structure is the most stable. This state has a ferro-arrangement of the molecular orbitals which agrees with the monoclinic structure and, as we shall see, also with the x-ray experiments of Paolasini et al.

Let us start with a description of a vertical pair. Following Ref. [4], the two $e_g$ orbitals [13] are specified by a further index as $|e_g1⟩ = 1/\sqrt{2} (|d_{yz}⟩ − |d_{zx}⟩)$ and $|e_g2⟩ = 1/\sqrt{3} (|d_{xy}⟩ − |d_{yz}⟩ − |d_{zx}⟩)$, while the $a_{1g}$ orbital is given by $|a_{1g}⟩ = 1/\sqrt{3} (|d_{xy}⟩ + |d_{yz}⟩ + |d_{zx}⟩)$. For each V ion, the d-orbitals are defined in a local coordinate system whose axis point towards the surrounding O ions, and thus refer to different, symmetry related orbitals for
the different V ions in the unit cell. Consequently, the \( e_g \) and \( a_{1g} \) orbitals on the two V ions of a vertical pair are not identical. This will be important when we compare our results to that of resonant scattering experiments. The intra-atomic interaction is described by three parameters: \( U \), the Coulomb interaction in the same orbital, \( U' \), the Coulomb interaction in different orbitals, and \( J \), the Hund’s Rule coupling, which we assume satisfy the usual relation for \( t_{2g} \) orbitals: \( U = U' + 2J \). The trigonal crystal field induces an energy splitting \( \Delta \) between the low-lying \( e_g \) orbitals and the excited \( a_{1g} \). Finally, the hopping integrals are denoted by \( t_{ij}^\delta \), where \( \delta = a, b, c \), \( d \) stands for the direction of the bond \((a, b, c, \text{ bonds inside the hexagonal planes, } d; \text{ vertical bond})\) while \((i, j) = 1, 2, 3\) denote the orbitals \((e_g, e_g, a_{1g})\) respectively.

The main difference with Ref. [4] comes from the values of the interaction parameters. The values used in Ref. [4] \((U \approx 2eV, J = 0.2eV)\) are now believed to be much too small: Recent estimates based on LDA+U calculations [10] are in the range \( U \approx 5 eV \) and \( J \approx 1 eV \). It turns out that this makes a dramatic difference for the ground state of a V-V pair. To be specific, if we consider the same hopping and crystal field parameters as in Ref. [4], and if we fix the ratio \( J/U = 0.1 \) to the value they used, there is a level crossing as a function of \( U \) between two very different situations. At small \( U \), the ground state is 3-fold degenerate, with 3 levels nearby. This corresponds to the limit of Ref. [4] where two electrons go into the bonding molecular orbital built out of \( e_g \) orbitals, the other two electrons being described by a spin \( 1/2 \)- pseudo spin \( 1/2 \) Kugel-Khomskii model [14]. At large \( U \) however, the ground state is 10-fold degenerate. It corresponds to a total spin \( 2 \) with a two-fold degenerate orbital state. Since by symmetry \( t_{ij}^\delta = 0 \) if \( i \neq j \), this orbital wavefunction can actually be written down explicitly:

\[
|\pm\rangle = \frac{|e_g, a_{1g}\rangle \otimes |e_g, e_g\rangle + |e_g, e_g\rangle \otimes |e_g, a_{1g}\rangle}{\sqrt{2}}
\]  

where \( e_g \) stands for \( e_g(1) \) in \( (-) \) (\( |+\rangle \)). This situation is generic for a large range of \( J/U \) including \( J/U = 0.2 \), and with the parameters proposed in Ref. [10], we found that the ground state is clearly of this second type.

It is interesting to compare this state with the spin 1 picture of Ezhov et al.. When the Hund’s Rule coupling is large, all low-lying states can indeed be described by considering only the states with total spin 1 at each site. However, the resulting effective Hamiltonian for a pair of sites is not simply a Heisenberg Hamiltonian, since this would correspond to only 9 low-lying states. In fact there are 81 low-lying states, suggesting that it one wants to describe this system with a spin 1 operator, \( \vec{S} \), at each site, one should also include a pseudo-spin 1 operator, \( \vec{T} \), to describe the quasi-degeneracy of the \( t_{2g} \) orbitals. This orbital degree of freedom is crucial since it is responsible for a factor 2 in the 10-fold groundstate degeneracy.

These results suggest that, instead of starting from a spin-orbital model with a spin 1/2 and a pseudo-spin 1/2 at each V site, one should start from a spin-orbital model in which each vertical V-V pair is described by a spin 2 for the total spin, say \( \vec{\sigma} \), and a pseudo-spin 1/2 for the orbital degeneracy, say \( \vec{\tau} \), \( \tau^z = 1/2 \) (\( \tau^z = -1/2 \)) corresponding to \( |+\rangle \) (\( |-\rangle \)) in Eq.1. The low energy properties are then determined by the way the degeneracy is lifted when these pairs are coupled by the in-plane hopping integrals. Since these hopping parameters are small, we can treat them within second-order perturbation theory. For simplicity, we include only the largest hopping integral \( t_{2g} \equiv t \), and the corresponding hopping integrals for directions \( b \) and \( c \), in the present discussion. We have checked that the conclusions are unaffected by this simplification. The second order effective spin-orbital Hamiltonian for n.n. along the \( a \)-axis then reads [15]:

\[
\hat{H}_{\text{eff}}(a) = G\vec{\sigma} \cdot \vec{\sigma}_m + \frac{1}{4} G_3(\tau^1_m + \tau^2_m)\vec{\sigma}_l \cdot \vec{\sigma}_m,
\]  

with

\[
G = -\frac{1}{3} G_1^2 + \frac{2}{3} G_2^2 + \frac{4}{3} G_3^2, \quad G_1 = \frac{t^2}{4(U-J)}
\]

\[
G_2 = \frac{t^2}{4(U+2J)}, \quad G_3 = \frac{t^2}{4(U+J)}
\]  

The effective Hamiltonians for n.n. along the \( b \)- and \( c \)-axes are easily obtained by the trigonal rotation of \( \hat{H}_{\text{eff}}(a) \) equivalent to the following replacement of the orbital pseudo-spin \( \tau^z \to -1/2\tau^z \pm \sqrt{3}/2\tau^x \). While there is a strong anisotropy in orbital space, the interaction preserves \( SU(2) \) symmetry for the spin operator \( \vec{\sigma} \).

Remarkably enough, the symmetry properties of this model are quite similar to the Kugel-Khomskii model for the cubic perovskite [14]. In fact one can regard the corundum lattice as a distorted simple cubic (sc) lattice of the V-V pairs. This analogy is useful to give a systematic analysis for such a complicated system. Namely, it is promising that the stable magnetic phases of Kugel-Khomskii-type models are collinear two-sublattice orderings with associated orbital orderings. Within this criterion the possibility is naturally restricted into G, F, C, and A-type magnetic patterns [16]. In this language, the realistic magnetic structure of \( V_2O_5 \) corresponds to the \( C \)-type arrangement in the pair sc lattice: One of 3 in-plane bonds is ferromagnetic and other two bonds are antiferromagnetic.

Keeping in mind these relations, we have examined the stable phase in the molecular model by comparing the energies of all magnetic phases. This has been done, as for the Kugel-Khomskii model, within a mean-field decoupling based on the order parameters \( \langle \tau^x \rangle, \langle \sigma^x \rangle \), and \( \langle \tau^x \sigma^y \rangle \). Details will be given in a forthcoming paper [17]. The results are plotted in Fig.2 as a function of Hund’s Rule coupling \( J \). It turns out that the stable phase changes successively from G to F phase as \( J \) increases. In order to gain energy by the orbital-dependent \( G_3 \) term, the symmetry-broken C and A phases are stabilized in the intermediate-\( J \) region. In particular the realistic \( C \)-type phase is found to be the lowest for \( J/U \) around 0.2, which agrees with the estimates of Ezhov et
al., and which is consistent also with the stability region for the $S = 2$ degenerate molecular orbitals of a $V$-pair. For this phase, the orbital order parameter is ferromagnetic with $\tau^z < 0$, i.e. the $e_{g1}$ orbital is favoured (state $|−\rangle$ of Eq. 1). Such a ferro molecular orbital order will cause an effective uniaxial stress on the lattice degrees of freedom, leading to a uniform rotation of $V$-$V$ pairs. This is consistent with the monoclinic distortion proposed by Dernier and Marezio [20].

The physical picture that emerges from this model is very encouraging. First of all, the observed magnetic arrangement [5-7] is consistent with this model for reasonable values of the parameters. Second, the atomic configuration is a mixture of $(e_g e_g)$ and $(a_{1g} e_g)$, in agreement with X-ray absorption [9]. Third, there is an orbital degree of freedom whose ordering is consistent with the monoclinic distortion of the low-temperature phase [20]. It corresponds to choosing between $e_{g1}$ and $e_{g2}$ for the $V$-$V$ pairs.

The results of our model are also consistent with the resonant x-ray scattering experiment of Paolasini et al. [8]. In that experiment, resonant scattering was observed in the low temperature phase at wavevector $q = (111)$ and at energies corresponding to the transition from $1s$ to unoccupied $3d$ states on $V$-ions. Since this is forbidden by symmetry if all the orbital configurations on $V$-atoms are equal, this led Paolasini et al. [8] to conclude to the existence of orbital ordering. They further suggested that their experiment can be taken to confirm one of the orbital ordered phases previously proposed by Castellani et al [4]. We now show that the orbital ordering proposed in this paper for our model, while different from that interpreted by Paolasini et al., is also consistent with the experimental results.

The resonant scattering amplitude as a function of the energy $\omega$ and $q$ of x-rays for a crystal $V_2O_3$ is given by $F = \sum_{\alpha} e^{i\alpha} f_\alpha(\omega)$, where $f_\alpha(\omega)$ is the amplitude contributed from the $V$ atom at position $\vec{R}_i$ in the monoclinic unit cell of $V_2O_3$. The low-temperature monoclinic lattice of $V_2O_3$ has eight atoms in a unit cell (Fig.3). Atoms 1-4 have spin-up magnetic moments and atoms 5-8 have spin-down magnetic moments. $F$ at $q = (111)$ is given by

$$F_{111} = (f_1 - f_5 + f_8 - f_4) e^{i\alpha} + (f_2 - f_6 + f_7 - f_3) e^{-i\alpha}$$

where $\alpha$ is a phase factor which depends on $\vec{R}_1 - \vec{R}_2$. $f_\alpha(\omega)$ depends in general on the magnetic moment and orbital occupation [18]. The nonvanishing intensity of $(111)$ reflection for this energy implies that the combinations $(f_1 - f_5 + f_8 - f_4)$ and $(f_2 - f_6 + f_7 - f_3)$ are nonzero. The ferro-orbital phase in our model exhibits this feature for the following reasons. As discussed before, the $e_g$ orbitals are defined with respect to a local co-ordinate system on each $V$ ion. In particular, for the two $V$ ions on a vertical bond, they are related by a rotation around the $y$-axis: $C_e(x,y,z) = (x,y,−z)$ (the trigonal coordinate system is used here with $z$-axis directed perpendicular to the hexagonal plane) while for the $V$ ions in the same hexagonal plane local coordinate systems are identical. Thus, the ferro-orbital phase actually corresponds to having different orbitals on alternate hexagonal planes. Denoting these as 1 and 2 and denoting $u$ and $d$ for the spin up and down magnetic state, we then have e.g.

$$f_1 - f_5 + f_8 - f_4 = f(1, u) - f(1, d) + f(2, d) - f(2, u)$$

Since $f$ depends on both the orbital occupation and the magnetic moment of the $V$-atom, $f(1) \neq f(1)$. Thus, our model gives nonzero $F_{111}$, and is qualitatively consistent with the experimental observation of Paolasini et al. [8]. More work is needed to compare our theory with the observed polarization and the azimuthal dependences of the resonance intensity.

According to this explanation, the intensity of the $(111)$ reflection is not simply a direct consequence of the orbital order, but comes both from magnetic and orbital order. This should be contrasted to Paolasini et al.’s explanation based on Ref. [4], where the form factor of Eq. (5) is non zero because the orbitals occupied on the two $V$ of a vertical pair are different linear combinations of $e_g1$ and $e_g2$. While Castellani et al.’s picture is very specific to their $S=1/2$ model, there is room a priori within the $S=1$ model for a similar orbital ordering. Energetic considerations then show that the only serious candidate is an orbital ordering in which one $V$ of a vertical pair would be in the $(eg a_{1g})$ configuration, while the other one would be in the $(eg eg)$ configuration. To be more precise, the model considered thus far corresponds to having all interplane hopping amplitudes much larger than intraplane ones. If we maintain the limit of $t_{11}^2$ large, but allows $t_{11}^3$ and $t_{22}^3$ to be compatible to intraplane hoppings, it can be shown that the problem can then be mapped into a transverse field Ising model. Details will be given in a forthcoming publication [19]. Here we briefly summarize the main results.
In this mapping, there is an Ising spin associated with each V-V pair which corresponds to the orbital occupation of \((e_g e_g)\) and \((e_g a_{1g})\) on the two site. The transverse field strength \(h\) is given by the energy difference of the bonding and antibonding states of a V-V pair, a measure of the orbital quantum fluctuation in a V-V pair. The molecular orbital model corresponds to the large \(h\) limit. In the opposite limit \(h \rightarrow 0\), the spin and orbital ordering depends on the relative strengths of the intraplane hoppings. In a reasonable parameter range, we found a ground state with RS spin and an orbital ordering corresponding to the pattern reported by Paolasini et al [8]. However, since in this state the V ions of a vertical pair are in \((e_g e_g)\) and \((e_g a_{1g})\) configurations, the electronic densities are very different. This should lead to different local distortions of the O octahedra, which is inconsistent with the monoclinic structure reported by Dernier and Marezio [20], where all V are equivalent [21]. So we do not think that this kind of orbital ordering is realized in \(V_2O_3\).

FIG. 3. The structure of the low temperature monoclinic phase of \(V_2O_3\). The gray and filled circles correspond to spin-up and spin-down orientations of the local magnetic moments on V ions.

To summarize, we have proposed a model for the AF insulating phase of \(V_2O_3\). This model seems to be the only way to combine basic facts about the electronic structure (\(S=1\), orbital degeneracy, strong coupling along vertical pairs) into a coherent picture that agrees with all experiments. Further investigation of the resulting two-fold degenerate, \(S=2\) model for the vertical pair is in progress.

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