Orbitally Degenerate Spin-1 Model for Insulating V_2O_3

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(Received 16 February 2000; revised manuscript received 17 May 2000)

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 twofold 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.

PACS numbers: 71.30.+h, 75.10.–b, 75.50.Ee

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 $S = 1$ model without an orbital degeneracy and the $S = 1/2$ orbitally degenerate model of Castellani *et al.* [4]. In this Letter we propose a new model for the antiferromagnetic-ordered insulating (AFI) phase based on the molecular orbitals of the c-axis V-V pairs, which combines features of both existing models and which reconciles the apparently conflicting experiments supporting each.

The V ions in the corundum structure of V_2O_3 sit in an O octahedron with a small trigonal distortion causing a small splitting in the nonbonding t_{2g} shell between the a_{1g} orbital oriented along the c axis and doublet planar e_g orbitals [5] (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 nearest neighbor (n.n.) exchange constants in the a-b plane (two antiferromagnetic, one ferromagnetic) [6–8]. Paolasini *et al.* [9] 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.* [10] showed a coexistence of both $(e_g e_g)$ and $(e_g a_{1g})$ configurations in roughly equal amounts. These led them to argue that Castellani's $S = 1/2$ picture is not valid and that V^{3+} has $S = 1$ character. This is favored by the atomic Hund's rule whose strength, as they point out, is not screened in the crystal. This was confirmed by local density approximation (LDA) calculations by Ezhov *et al.* [11], who argued for a $S = 1$ model with a $(e_g e_g)$ configuration and no orbital degeneracy. The differing planar exchange constants they attribute to the monoclinic distortion in the AFI phase. Yet general considerations of the phase diagram [12] and NMR investigations [13] 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 twofold 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 ferroarrangement 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 [14] are specified by a further index as $|e_{g1}\rangle = 1/\sqrt{2}\,(|d_{yz}\rangle - |d_{zx}\rangle)$ and $|e_{g2}\rangle = 1/\sqrt{6}\,(2|d_{xy}\rangle - |d_{yz}\rangle - |d_{zx}\rangle)$, while the a_{1g} orbital is

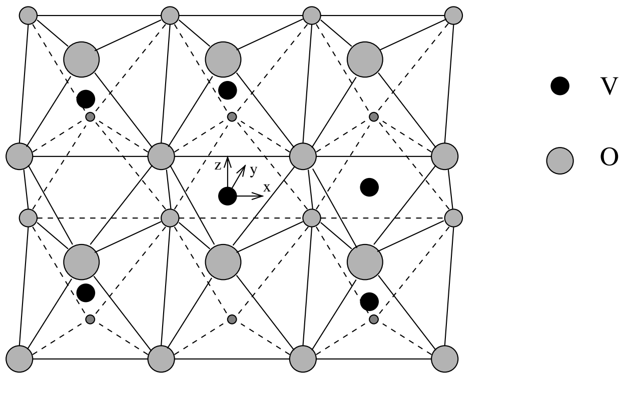

FIG. 1. Corundum structure of V_2O_3. The V ions are arranged in vertical V-V pairs in the z direction (c axis of the corundum structure) with face-sharing O octahedra. In the xy plane, they form a honeycomb lattice with edge-sharing O octahedra.

0031-9007/00/85(8)/1714(4)$15.00

given by $|a_{1g}\rangle = 1/\sqrt{3}(|d_{xy}\rangle + |d_{yz}\rangle + |d_{zx}\rangle)$. For each V ion, the d orbitals are defined in a local coordinate system whose axis points 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_{g1} and e_{g2} 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 (CF) induces an energy splitting Δ between the low-lying e_g orbitals and the excited a_{1g}. Finally, the hopping integrals are denoted by t_{ij}^{δ}, where $\delta = a, b, c, d$ stands for the direction of the bond (a, b, c: bonds inside the hexagonal planes, d: vertical bond) while $(i, j) = 1, 2, 3$ denote the orbitals (e_{g1}, e_{g2} and a_{1g}, respectively).

The main difference with Ref. [4] comes from the values of the interaction parameters. The values used in Ref. [4] ($U \simeq 2$ eV, $J = 0.2$ eV) are now believed to be much too small: Recent estimates based on LDA + U calculations [11] are in the range $U \simeq 3$–4 eV and $J \simeq 0.6$ 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 threefold degenerate, with three levels nearby. This corresponds to the limit of Ref. [4] where two electrons go into the bonding molecular orbital built out of a_{1g} orbitals, the other two electrons being described by a spin 1/2-pseudo spin 1/2 Kugel-Khomskii model [15]. At large U, however, the ground state is tenfold degenerate. It corresponds to a total spin 2 with a twofold degenerate orbital state. Since by symmetry $t_{ij}^{d} = 0$ if $i \neq j$, this orbital wave function can actually be written down explicitly:

$$|\pm\rangle = \frac{|e_g, a_{1g}\rangle \otimes |e_{g1}, e_{g2}\rangle + |e_{g1}, e_{g2}\rangle \otimes |e_g, a_{1g}\rangle}{\sqrt{2}}, \tag{1}$$

where e_g stands for e_{g1} (e_{g2}) in $|-\rangle$ ($|+\rangle$). This situation is generic for a large range of J/U and with the parameters proposed in Ref. [11], 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 nine low-lying states. In fact, there are 81 low-lying states, suggesting that if one wants to describe this system with a spin-1 operator, $\vec{S}$, at each site, one should also include a pseudospin-1 operator, $\vec{T}$, to describe the quasidegeneracy of the t_{2g} orbitals. This orbital degree of freedom is crucial since it is responsible for a factor of 2 in the tenfold ground state degeneracy.

These results suggest that, instead of starting from a spin-orbital model with a spin 1/2 and a pseudospin 1/2 at each V site, one should start from a spin-orbital model in which each vertical V-V pair is decribed by a spin 2 for the total spin, say $\vec{\sigma}$, and a pseudospin 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 $t_{23}^{a} \equiv t$, 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 [16]

$$\tilde{H}_{\rm eff}(a) = G\vec{\sigma}_l \cdot \vec{\sigma}_m + \frac{1}{4}G_3(\tau_l^z + \tau_m^z)\vec{\sigma}_l \cdot \vec{\sigma}_m, \tag{2}$$

with

$$G = -\frac{1}{3}G_1 + \frac{1}{3}G_2 + \frac{3}{4}G_3, \qquad G_1 = \frac{t^2}{4(U' - J)}, \qquad G_2 = \frac{t^2}{4(U' + 2J)}, \qquad G_3 = \frac{t^2}{4(U + J)}. \tag{3}$$

The effective Hamiltonians for n.n. along the b and c axes are easily obtained by the trigonal rotation of $\tilde{H}_{\rm eff}(a)$ equivalent to the following replacement of the orbital pseudospin $\tau^z \to -1/2\tau^z \pm \sqrt{3}/2\tau^x$. 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 [15]. 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 [17]. In this language, the realistic magnetic structure of V_2O_3 corresponds to the C-type arrangement in the pair sc lattice: One of three 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 $\langle\tau^\alpha\rangle$, $\langle\sigma^\alpha\rangle$, and $\langle\tau^\alpha\sigma^\beta\rangle$.

Details will be given in a forthcoming paper [18]. 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 favored [state $|-\rangle$ of Eq. (1)]. Such a ferromolecular 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 [19].

The physical picture that emerges from this model is very encouraging. First of all, the observed magnetic arrangement [6–8] 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 [10]. Third, there is an orbital degree of freedom whose ordering is consistent with the monoclinic distortion of the low-temperature phase [19]. 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.* [9]. In that experiment, resonant scattering was observed in the low-temperature phase at wave vector $q = (111)$ and at energies corresponding to the transition from $1s$ to unoccupied $3d$ states on V ions. Paolasini *et al.* [9] explained that pure magnetic scattering should lead to a vanishing intensity at that wave vector, and they interpreted this result in connection with 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 invoked by Paolasini *et al.,* is also consistent with the experimental results.

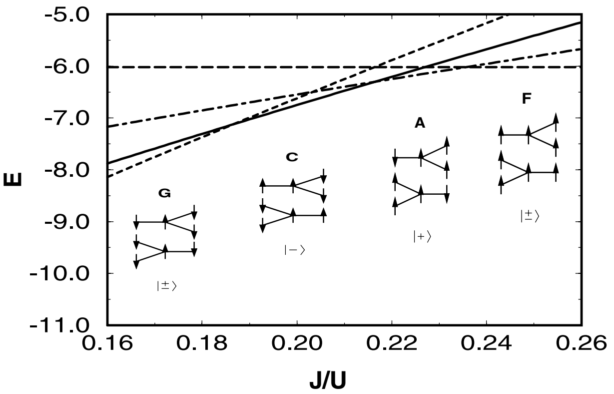

FIG. 2. Energy comparison of various magnetic patterns. The letters refer to the notations of Ref. [17] for the *sc* lattice. The pictures give the corresponding magnetic pattern for the corundum lattice. The symbols $|\pm\rangle$, $|+\rangle$, and $|-\rangle$ indicate which of the molecular orbitals of Eq. (1) is consistent with the magnetic pattern. The orbital degeneracy is lifted for states C and A, but not for states G and F.

The resonant scattering amplitude as a function of the energy ω and q of x rays for a crystal V_2O_3 is given by $F = \sum_{i=1}^{8} e^{i\vec{q}\cdot\vec{\rho}_i} f_i(\omega)$, where $f_i(\omega)$ is the amplitude contributed from the V atom at position $\vec{\rho}_i$ 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 α is a phase factor which depends on $\vec{\rho}_1 - \vec{\rho}_2$. $f_i(\omega)$ depends in general on the magnetic moment and orbital occupation [20]. 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 coordinate 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: $C_2(x, y, z) = (-x, y, -z)$ (the trigonal coordinate system is used here with the 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 spin-down magnetic states, we then have, e.g.,

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

Now $f(1,u) \neq f(1,d)$ and $f(2,u) \neq f(2,d)$ because of the magnetic moment of the V atom, while $f(1,u) \neq f(2,u)$ and $f(1,d) \neq f(2,d)$ because of the orbitals. Thus, our model gives nonzero F_{111} and is qualitatively

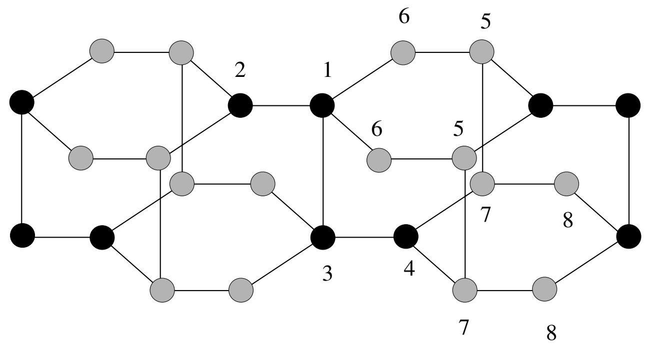

FIG. 3. The structure of the low-temperature monoclinic phase of V_2O_3. The gray and filled circles correspond to spin-up and spin-down orientations of the local magnetic moments on V ions.

consistent with the experimental observation of Paolasini *et al.* [9]. 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, in contrast to the explanation by Paolasini *et al.* [9] based on Ref. [4], where the form factor of Eq. (5) is nonzero because the orbitals occupied on the two V of a vertical pair are different linear combinations of eg_1 and eg_2. We believe that, within the $S = 1$ model, our explanation is the only one consistent with the low-temperature structure determined by Dernier and Marezio [19] for the following reasons. If one tries to come up with an orbital ordering similar to Castellani *et al.* but for $S = 1$, energetic considerations show that the only serious candidate is an orbital ordering in which one V of a vertical pair would be in the (ega_{1g}) configuration, while the other one would be in the $(egeg)$ configuration. It is indeed possible along these lines, and for reasonable parameters, to find a ground state with RS spin and an orbital ordering corresponding to the pattern reported by Paolasini *et al.* [9]. Details will be given in a forthcoming publication [21]. 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, and this is definitely inconsistent with the monoclinic structure reported by Dernier and Marezio [19], where all V are equivalent [22]. So we do not think that this kind of orbital ordering is realized in V_2O_3.

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 twofold degenerate, $S = 2$ model for the vertical pair is in progress.

We acknowledge useful discussions with W. Bao, B. Normand, P. M. Platzmann, G. Sawatzky, L. H. Tjeng, and C. Vettier, and the hospitality of the Center for Theoretical Studies of ETH Zürich. This work was in part supported by the DOE Grant No. DE/FG03-98ER45687, Russian Foundation for Basis Research Grants No. RFFI-98-02-17275 and No. RFFI-00-15-96575.

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