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LETTER TO THE EDITOR

Ground-state electronic properties of V_2O_3 **S Di Matteo^{1,2}, N B Perkins³ and C R Natoli⁴**¹ ESRF, BP 220, F-38043 Grenoble Cedex 9, France² Dipartimento di Scienze Fisiche 'E R Caianiello', Università di Salerno, 84081, Baronissi (SA), Italy³ BLTP, JINR, Dubna, 141980, Russia⁴ Laboratori Nazionali di Frascati, INFN, Casella Postale 13, I-00044 Frascati, Italy

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Online at stacks.iop.org/JPhysCM/14/L37**Abstract**

We analyse the problem of the electronic correlations in V_2O_3 , focusing on its low-temperature antiferromagnetic phase, in the light of recent experimental findings. In fact, the implications of the vanadium K-edge linear dichroism data demand further theoretical investigations to explain the consequences of the non-reciprocal gyrotropic effect, which has not been considered by previous theoretical models. The analysis of all the available experimental data indicates $\underline{2}/m$ as a magnetic space group for the ground state, instead of $C_{2h} \otimes \hat{\Theta}$. Such a reduction of the symmetry can be given by the onset of an orbital ordering in the system. We illustrate the merits and drawbacks of the proposed solution.

The purpose of this letter is to re-examine the problem of the electronic correlations in V_2O_3 and to analyse the implications of the vanadium K-edge linear dichroism data [1]. As is well known [2], V_2O_3 is considered to be the prototype of the Mott–Hubbard systems, showing a metal–insulator transition from a paramagnetic metallic (PM) phase to a paramagnetic insulating (PI) phase at high temperatures (≈ 500 K), due to the interplay between band formation and electron Coulomb correlation. Actually it is the only known example among transition-metal oxides to show a PM to PI transition [3], without including magnetic degrees of freedom. Another phase transition is present at a lower temperature (≈ 150 K) from the PM to an antiferromagnetic insulating (AFI) phase.

The observations by Paolasini *et al* [4] in the AFI phase, interpreted as evidence for the existence of an orbital ordering with the periodicity predicted by Castellani *et al* [5] seem to provide a nice confirmation of their model. However, the latter is based on the assumption that there is only one magnetic electron in the doubly degenerate e_g band, and that therefore each V atom is substantially in a state of spin $S = 1/2$. There is now definite evidence based on the non-resonant magnetic scattering [4] that $\langle L \rangle / (2\langle S \rangle) = -0.3$, which, together with the value of the magnetic moment $\langle L \rangle + 2\langle S \rangle = 1.2 \mu_B$ seen by neutrons [6], gives $2\langle S \rangle = 1.7$, is compatible with a spin $S = 1$ state of the V atoms. Another indication for a spin $S = 1$ state of the vanadium ions comes from the interpretation of the linear dichroism experiment at the

vanadium $L_{2,3}$ -edge absorption spectra [7]. These are strong indications that in the AFI phase of V_2O_3 intra-atomic correlations prevail over band delocalization, contrary to the assumption made by Castellani *et al* [5].

An attempt to go beyond this model was first made by Ezhov *et al* [8] whose LDA + U method [9] is very similar to the Hartree–Fock (HF) + U method used by Castellani *et al* [10] in the second work of their series. However, their solution, with no orbital ordering (OO) and spin $S \approx 1$ on each V atom, presents stability problems. Moreover, it underestimates the exchange integrals by about one order of magnitude, the explanation for the forbidden $(111)_m$ reflection observed by Paolasini *et al* [4] is lacking [11, 12], and it is unable to reproduce the results of the linear dichroism experiment performed by Goulon *et al* [1].

The fact that the spin $S = 1$ solution seems to point to a lack of OO must be an artefact of the HF approximation. Indeed, an examination of the electronic states of the V^{3+} ion leads again to an orbital degeneracy: out of the three one-electron states $|e_g^1\rangle$, $|e_g^2\rangle$ and $|a_{1g}\rangle$ in octahedral symmetry, one can form three degenerate two-electron states, $|e_g^1 e_g^2\rangle \equiv |0\rangle$, $|a_{1g} e_g^1\rangle \equiv | - 1\rangle$, $|a_{1g} e_g^2\rangle \equiv |1\rangle$ (these constitute the spin and orbital triplet ground state of a two-electron system in a strong cubic crystal field [13]). In the presence of a trigonal distortion $\Delta_t > 0$, the singlet state $|0\rangle$ would lie lowest, followed by the doublet $| + 1\rangle$, $| - 1\rangle$. Nonetheless, putting the two atoms belonging to a vertical pair in the same $|e_g^1 e_g^2\rangle$ state to gain Δ_t , as suggested by Ezhov *et al* [8], would lose the much larger gain coming from the allowed hopping processes in a configuration in which one atom is in the state $|e_g^1 e_g^2\rangle$ and the other in $|a_{1g} e_g^{1,2}\rangle$, and vice versa. This situation has been realized by Mila *et al* [14] who have taken up an old suggestion by Allen [15] that ‘the magnetic and optical properties of all the phases of V_2O_3 show a loss of V^{3+} -ion identity’. These findings, together with the results by inelastic neutron scattering quoted above [3], indicate that the vertical bond is quite stable and coupled to total spin $S = 2$ with the non polar part of the wavefunction given by $|\psi_{\pm 1}\rangle = (|0\rangle_a | \pm 1\rangle_b + | \pm 1\rangle_a |0\rangle_b) / \sqrt{2}$ (where a and b indicate the two V centres). This state is clearly doubly degenerate, due to the freedom in the choice of the two degenerate states $| \pm 1\rangle$. As a consequence of this, Mila *et al* have proposed a simple spin–orbital Hamiltonian [16] and found a (small) region in the parameter space where the observed spin structure (called C) for the AFI phase of V_2O_3 was stabilized by a ferro-orbital order, i.e. with all the molecules in the same electronic state. But, apart from problems of stabilization, this solution is not compatible with the more recent x-ray gyrotropy data obtained by Goulon *et al* [1], as shown below.

We have, therefore, been led to study [11] the atomic limit of the Hubbard Hamiltonian with three bands and two electrons per site coupled to spin $S = 1$, along the patterns developed by Castellani *et al* [5] for spin $S = 1/2$. We hope that by starting from the fundamental Hamiltonian, we can enlarge the set of solutions found by Mila *et al* [14]. The result is a spin $S = 1$ Heisenberg Hamiltonian (H_{eff})

$$H_{\text{eff}} = -\frac{1}{U_2 - J} \sum_{ij} (2 + \vec{S}_i \cdot \vec{S}_j) f_1(\vec{\tau}_i, \vec{\tau}_j) - \frac{1}{U_2 + 2J} \sum_{ij} (1 - \vec{S}_i \cdot \vec{S}_j) f_2(\vec{\tau}_i, \vec{\tau}_j) - \frac{1}{U_2 + 4J} \sum_{ij} (1 - \vec{S}_i \cdot \vec{S}_j) f_3(\vec{\tau}_i, \vec{\tau}_j) \quad (1)$$

with exchange integrals $f_k(\vec{\tau}_i, \vec{\tau}_j) / U_{\text{eff}}$ ($k = 1, 2, 3$) depending on the orbital occupancy, described by a pseudo spin $\tau = 1$. Here, $(2 + \vec{S}_i \cdot \vec{S}_j)$ and $(1 - \vec{S}_i \cdot \vec{S}_j)$ project onto ferromagnetic (F) and antiferromagnetic (AF) bonds, respectively. J is the intra-atomic exchange and U_2 is the Coulomb repulsion integral between different t_{2g} orbitals. The expressions for $f_k(\vec{\tau}_i, \vec{\tau}_j)$ contain each $3^4 = 81$ terms arising from double hopping in second-order perturbation theory. Even though some regrouping is possible, these contain so many terms that, due to limitation

of space, they will be given elsewhere [11]. As to the tight binding parameters, we adopt as standard the values given by Mattheiss [17], after correction for oxygen interference. These values, which are listed in [11], are very similar to those used by Castellani *et al* [10] and are appropriate for corundum symmetry. Finally we take $U_2 = 2.5$ eV, as suggested by Mila *et al* [14] in order to have a check with this latter work. Note that there is not much agreement in the literature about a realistic value of the two parameters J and U_2 . For example, Tanabe and Sugano [18] evaluated the Racah parameters B and C for the free ion V^{3+} and found $B = 0.107$ eV and $C = 0.473$ eV. Using the relation, valid for a t_{2g}^2 configuration, $J = 3B + C$, we obtain $J = 0.79$ eV. In that same paper, Tanabe and Sugano performed a fit with optical spectra and this time found $B = 0.080$ eV and $C = 0.352$ eV, thus obtaining the value $J = 0.59$ eV. Mizokawa and Fujimori [19] have provided the intermediate value $J = 0.68$ eV. In contrast, the Auger experiment in the PI phase of V_2O_3 by Sawatzky and Post [20] gives $J = 1.0$ eV, which is consistent with the LDA + U *ab initio* estimates by Solovyev *et al* [21], who also found $J \simeq 1$ eV. The same uncertainty is present for the value of U_2 , for which we have estimates that vary from $U_2 \simeq 2.0$ eV [22, 23] to $U_2 \approx 4.0$ – 4.5 eV [19, 24]. Moreover, another origin of possible incomprehension comes from the fact that in all the cited works a d -averaged Coulomb interaction U is given. This is sometimes confused with the Coulomb repulsion integral between electrons on the same orbital, U_1 , which is such that, for t_{2g} electrons, $U_1 = U_2 + 2J$. Instead, for a d^2 configuration, U can be expressed [24] in terms of the Racah parameters A , B and C as $U = A - \frac{14}{9}B + \frac{7}{9}C$. It is easy to check that such a U , even if conceptually different, is numerically very close to U_2 . In fact, for t_{2g} electrons, we have $U_2 = A - 2B + C$, leading to $U_2 - U = \frac{2}{9}(C - 2B) \leq 0.06$ eV, for any estimate of B and C present in the literature. This justifies our numerical identification between U_2 and U .

As a preliminary to a variational study of H_{eff} we analyse the energetic of the vertical pair. It is found that the competition is always between a doubly degenerate F $S_{\text{tot}} = 2$ state and singlet AF $S_{\text{tot}} = 0$, the latter lying lower in energy for $J/U_2 \leq 0.29$. As appropriate in C_3 symmetry, we assume that the only hopping integrals different from zero are ρ (between a_{1g} electrons) and μ (between e_g^1 or e_g^2 electrons), in the notation of Castellani *et al* [5, 10]. The energy lowering of the F state with respect to the atomic on-site energy is easily derived analytically to be $\Delta E_F = -(\rho - \mu)^2/(U_2 - J)$, where ρ and μ have opposite signs. In the F regime, the HF approximation to the state has an energy lowering of $\Delta E_{\text{HF}} = -(\rho^2 + \mu^2)/(U_2 - J)$ so that if the difference $\Delta E_F - \Delta E_{\text{HF}} = 2\rho\mu/(U_2 - J)$ cannot be recuperated by interaction in the basal plane, the most appropriate variational wavefunction for the whole H_{eff} must be constructed in terms of molecular units with the wavefunction $|\psi_{\pm 1}\rangle$.

Therefore we write a molecular variational wavefunction

$$|\Psi\rangle = \Pi_j (\cos \theta_j |\psi_{+1}\rangle + \sin \theta_j |\psi_{-1}\rangle) \quad (2)$$

for the orbital part (the spin part giving +3 and +2 for the F and AF bonds, respectively). We minimize H_{eff} with respect to the variational parameters θ_j . As anticipated, in this approach the vertical pairs are treated exactly, whereas the three bonds in the basal plane ($\delta_1, \delta_2, \delta_3$) are treated in the HF approximation. The in-plane variational minimization proceeds then exactly as in Castellani *et al* [5] with the following results:

- (a) If we set all the hopping integrals in the basal plane equal to zero, except $t_{\delta_1}^{23} = -\tau = 0.27$, in order to mimic the model of Mila *et al* [14] we find the same phase diagram as in their figure (2). However, the stabilizing energy gap for the C phase is exceedingly small (≈ 3 meV). Although it scales like τ^2/U_2 there is not enough room for increase by a reasonable variation of the parameters.
- (b) If we search for minimizing solutions with the set of parameters of Mattheiss, the phase space for the C phase is even smaller than in the previous case.

Table 1. Orbital orderings for the eight vanadium atoms of the monoclinic cell, compatible with the magnetic space group C_{2h} .

Atom							
V ₁	V ₂	V ₃	V ₄	V ₅	V ₆	V ₇	V ₈
$e_{g\alpha}^+$	$e_{g\alpha}^-$	$e_{g\alpha}^+$	$e_{g\beta}^-$	$e_{g\beta}^+$	$e_{g\beta}^-$	$e_{g\alpha}^-$	$e_{g\beta}^+$
$e_{g\alpha}^1$	$e_{g\alpha}^2$	$e_{g\alpha}^1$	$e_{g\beta}^1$	$e_{g\beta}^2$	$e_{g\beta}^1$	$e_{g\alpha}^2$	$e_{g\beta}^2$

On the contrary, if we assume that the in-plane stabilization energy prevails over the vertical pair binding energy, the appropriate trial wavefunction should be $|\Psi\rangle = \prod_j [\cos\theta_j|0\rangle + \sin\theta_j(\cos\phi|+1\rangle + \sin\phi|-1\rangle)]$. Even in this case we have obtained a phase diagram with a C phase whose stability region is exceedingly small (≈ 3 meV).

The above findings indicate that this model has serious problems in describing the AFI of V_2O_3 . Even in the assumption of a strong vertical bond, the phase space occupied by the C configuration is very limited, in contrast with the spin $S = 1/2$ case. Moreover, it does not correctly take into account the value obtained by Park *et al* [7] for the average occupation of the a_{1g} orbitals (18% versus 25%). Finally, the ferro-orbital order is not compatible with the presence of the non-reciprocal gyrotropy tensor found by Goulon *et al* [1]. However this model, with suitable values of parameters, seems to be more appropriate for describing the short-range magnetic correlations in the PM and PI phases, as indicated by the inelastic neutron measurements of Wei Bao *et al* [3]. It correctly shows an incipient tendency to break the original trigonal symmetry, which might be increased by other mechanisms [11], for example by some mixing of molecular spin $S = 0, 1$ with the spin $S = 2$. This latter mechanism could also be responsible for the reduction of the a_{1g} occupation below the value of 25% [11].

To discriminate among the possible ground states, the magnetic space group must be known. From the preceding discussion, the importance of the x-ray linear dichroism data on any theory of V_2O_3 is unquestionable. From the neutron [3, 6] and x-ray [25] scattering experiments, one can infer that this group is given by $C_{2h} \times \hat{\Theta}$, where $\hat{\Theta}$ is the time reversal operator and C_{2h} contains the identity \hat{E} , the inversion \hat{I} , the twofold \hat{C}_2 rotation about the monoclinic b axis and the reflection with respect to the vertical glide plane \hat{C}_s perpendicular to it. The appropriate translation is associated to each of these operators, as described in section IV of [11]. But the observation of non-reciprocal x-ray gyrotropy implies that neither $\hat{\Theta}$ nor \hat{I} are separate symmetry elements and, therefore, there should be some electronic degrees of freedom which lower the symmetry $C_{2h} \times \hat{\Theta}$. There are only two subgroups of the magnetic space group $C_{2h} \otimes \hat{\Theta}$ compatible with this constraint, apart from two-element subgroups: group $C_{2h}(\hat{C}_s)$ with elements $\hat{E}, \hat{C}_s, \hat{\Theta}\hat{I}, \hat{\Theta}\hat{C}_2$ and group $C_{2h}(\hat{C}_2)$ with elements $\hat{E}, \hat{C}_2, \hat{\Theta}\hat{I}, \hat{\Theta}\hat{C}_s$ (respectively $\underline{2}/m$ and $\underline{2}/\underline{m}$ in international notation). Both are magnetoelectric (ME) [26], but while in the latter the ME tensor is diagonal, in the former it is off-diagonal. This could explain the failure of Al'shin and Astrov [27] to find a ME effect in V_2O_3 , since this experiment was set up to look for diagonal components of the ME tensor. This observation leads us to indicate the group $C_{2h}(\hat{C}_s)$ as the ground-state space magnetic group of V_2O_3 . The breakdown of the time-reversal and inversion symmetries can be explained as due to some anisotropy in the charge distribution on the sites otherwise linked by these symmetries; this is just what is usually called OO. There are only two orbital orderings that preserve the molecular structure of the vertical pair and are compatible with the group $C_{2h}(\hat{C}_s)$. These are summarized in table 1, for the eight vanadium atoms of the monoclinic cell, numbered as in [5, 11]. The Greek indices indicate the different definitions of the e_g orbitals (see [10]) and $e_g^\pm \equiv e_g^1 \pm e_g^2$. Note that not one of the OO relative to the $C_{2h}(\hat{C}_s)$ group is the same as that suggested by Paolasini *et al* [4].

Thus the experimental data give a striking indication of what the ground state of V_2O_3 should be and that something is missing in the descriptions of the system given by Mila *et al* [14] and by Di Matteo *et al* [11]. It is worth noticing that, by varying the hopping parameters given by Mattheiss [17], we can find a region where a ME solution is present only 0.4 meV above the ground state. We infer that this solution might be stabilized by coupling with the lattice. In fact, in the ME phase the stresses arising from the magnetostrictive forces and that originating from the orbital coupling to the lattice, presenting the same pattern of broken symmetry, act along the same axis, in contrast to the ferro-orbital phase.

In conclusion, we have analysed the AFI phase of V_2O_3 in the light of recent experiments and we have found that none of the proposed theoretical models [8, 14, 28] is able to explain all the experimental data. Then, on the basis of simple considerations about the magnetic space group of the system, we have discussed the features that the ground state of V_2O_3 must possess in order to be compatible with the experiments. We have also speculated on the possible degrees of freedom, neglected by previous works, that can lead to this solution.

Of course, more work in this sense has to be done and the last word on the properties of this fascinating system has not been written, yet.

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