OPEN POINTS ON THE NATURE OF THE ANTIFERROMAGNETIC GROUND STATE OF V_2O_3*

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In the last three years, various theoretical interpretations have been proposed on the nature of the ground state in the antiferromagnetic (AFI) phase of V_2O_3. There are two main results on this subject: the idea of a correlated vertical molecule and that of a complex ground state. In spite of the results achieved, we show, with the present work, that the pictures proposed are still lacking and more work is needed for a unified description of the AFI phase of V_2O_3.

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1. Introduction

In spite of the big theoretical effort of the last three years [1–6] a unified picture describing the ground state properties of the AFI phase of V_2O_3 is still lacking. The new experimental data coming from X-ray non-resonant scattering [7] and $L_{2,3}$-edge linear dichroism [8], *i.e.*, showing evidence of spin $S = 1$ per vanadium site and an occupation of the a_{1g} orbitals between 18% and 25%, contributed to show the inadequacy of the old model by Castellani *et al.* [9] to explain the system. At the moment, there are two main ideas that seem to be well established and correctly determine two of the main features of the AFI ground state of V_2O_3.

The first was proposed by Mila *et al.* [2, 3] and, soon afterwards, by Di Matteo *et al.* [4,5]: these authors realized that an entangled state for the nearest neighbors vanadium pairs (vertical couple), with a finite presence of a_{1g} electrons, was by far the most stable, due to the strong correlations in

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the hopping processes. In this way they were able to exclude the previous model by Ezhov *et al.* [1] who supposed that each atom was populated by two e_g electrons in order to reduce the trigonal field energy.

The other important idea to be taken into account is that the orbital part of the ground state must be complex. This can be deduced from the non-resonant magnetic X-ray scattering experiments of Paolasini *et al.* [7], who measured a large orbital angular momentum $L = 0.5\mu_{\rm B}$ per site, and from resonant X-ray scattering [7, 10]. This was pointed out by Tanaka [6], who introduced a spin-orbit interaction in such a way as to split the molecular orbital degeneracy obtained for the ground stated in Refs. [2–5]. However, he did not develop a formalism to treat the whole crystal, but simply solved the molecule and stated that the experimentally observed magnetic structure (RS) is the one to be considered. But this poses some conceptual problems, because the energies neglected by Tanaka are the hopping terms, whose magnitude, $\simeq t^2/(U_2 - J) \simeq 20 \div 40$ meV, is of the same order, and even bigger than that of the spin-orbit term, that determines energy splittings of the order of $10 \div 20$ meV.

These considerations led us to re-examine the effective Hamiltonian derived from the Hubbard degenerate model in the atomic limit [4] when a spin-orbit interaction is added. We first evaluated exactly the action of the spin-orbit on the vertical molecule and then looked for a global description of the crystal ground state, using a variational procedure, in a similar way as done in our previous work [4].

If we include the spin–orbit interaction, the effective spin $S = 1$ Hamiltonian $H_{\rm eff}$ can be written as

$$H_{\rm eff} = -\frac{1}{3}\frac{1}{U_2 - J}\sum_{ij}\left[2 + \vec{S}_i \cdot \vec{S}_j\right] O_{ij}^{(1)} - \frac{1}{4}\frac{1}{U_2 + 4J}\sum_{ij}\left[1 - \vec{S}_i \cdot \vec{S}_j\right] O_{ij}^{(2)}$$

$$-\frac{1}{12}\frac{1}{U_2 + 2J}\sum_{ij}\left[1 - \vec{S}_i \cdot \vec{S}_j\right] O_{ij}^{(3)} + H_{\rm trig} + H_{LS}. \tag{1}$$

The $O_{ij}^{(k)}$ describe the orbital dependent exchange coupling and are given in the Appendix C of Ref. [4]. $H_{\rm trig}$ is the trigonal crystal field already taken into account in Ref. [4] and $H_{LS} = \xi \sum_{i,\alpha} \vec{l}_i^\alpha \vec{s}_i^\alpha$ is the spin-orbit interaction with coupling constant ξ. The terms l_i^α and s_i^α correspond to the orbital and the spin angular momentum of the electron at site i and orbital α.

As a first step, we solve exactly $H_{\rm eff}$ for the vertical molecule. In doing so, we follow the same procedure already used in Section V of Ref. [4]. The main difference lies in the presence of H_{LS}, which forces the eigenstates to be complex. We consider the Coulomb on-site inter-orbital repulsion U_2 and Hund's constant J in the same range as in Ref. [4] ($U_2 \simeq 2.5$ eV, $J \in [0.7, 1.0]$ eV).

Because of the high value of J the molecular states with global spin $S^M = 2$ become by far favourable. Their explicit expression is

$$|S = 2, \ S_z\rangle_{ab} \times \sqrt{2}(|\Psi^-\rangle_{ab} \pm \imath|\Psi^+\rangle_{ab}), \qquad (2)$$

where

$$|\Psi^-\rangle_{ab} = \frac{1}{\sqrt{2}} \left(|e_{1g}^a e_{2g}^a e_{1g}^b a_{1g}^b\rangle + |e_{1g}^a a_{1g}^a e_{1g}^b e_{2g}^b\rangle \right)$$

and

$$|\Psi^+\rangle_{ab} = \frac{1}{\sqrt{2}} \left(|e_{1g}^a e_{2g}^a e_{2g}^b a_{1g}^b\rangle + |e_{2g}^a a_{1g}^a e_{1g}^b e_{2g}^b\rangle \right)$$

are the orbital part (a and b refer to the two different sites of the vertical pair). The ten states (2) are degenerate in absence of spin–orbit interaction. Actually they form the degenerate manifold from which the crystal ground state is found in Refs. [2–5]. But the spin-orbit interaction splits this 10-fold degeneracy into five magnetic doublets, with a global splitting of the order of $\xi \sim 25$meV.

We follow Tanaka's idea and consider only the lowest magnetic doublet

$$
\begin{aligned}
|g^+\rangle_n &= \imath/\sqrt{2}(|\Psi^-\rangle_n + \imath|\Psi^+\rangle_n) \times |S_z = 2\rangle_n, \\
|g^-\rangle_n &= \imath/\sqrt{2}(|\Psi^-\rangle_n + \imath|\Psi^+\rangle_n) \times |S_z = -2\rangle_n.
\end{aligned}
\qquad (3)
$$

Note that the degeneracy does not involve anymore orbital degrees of freedom, as it was before taking into account the spin–orbit interaction, but it has now a pure magnetic origin. We used as a trial wave function a linear combination of $|g^+\rangle_n$ and $|g^-\rangle_n$ with a variational coefficient. Then we performed the numerical minimization of H_{eff}, as in Ref. [4], for various spin configurations. The results are presented in Fig. 1 where we have drawn the phase diagram in the plane α/τ versus J/U_2, where α is the hopping integral between the $e_g^{(1)}$ orbitals on the two vanadium ions along the in-plane ferromagnetic bond and τ is the hopping integral between the e_{2g} and a_{1g} orbitals along that same bond (Ref. [4]).

With respect to the minimization performed in the whole 10-fold degenerate space, without spin-orbit interaction (compare Section VI of Ref. [4]), in this case the RS phase disappears from the phase diagram and the transition occurs directly between the antiferromagnetic (AFM) and the ferromagnetic (FM) phases.

This means that, in order to retain the RS phase, it is not possible to consider only the lowest magnetic doublet (3), as Tanaka suggested. The minimization must be performed on the whole 10-fold subspace (2), and the spin-orbit interaction and the hopping terms must be treated on an equal footing, as was qualitatively deduced before.
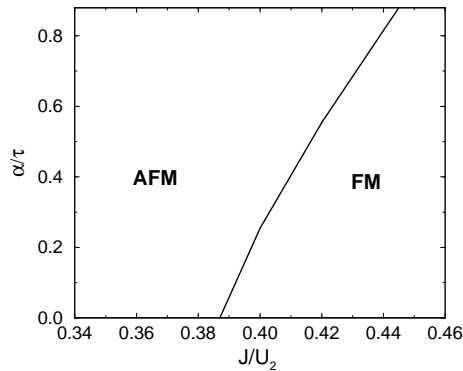
Fig. 1. Phase diagram in the $(\alpha/\tau,\ J/U_2)$ parameter plane. Here AFM and FM denote the corresponding type of magnetic order. The solid lines indicate the phase boundaries.

In conclusion, we stressed the importance of the vertical entangled molecule and of the complex ground state to describe the properties of V_2O_3 in the AFI phase. Nonetheless, our calculations show that the magnetic doublet proposed by Tanaka [6] as a ground state for the vertical molecule is insufficient to explain the RS magnetic structure of the crystal. This, in turn, implies that the solution to the problem must be probably looked for within the whole 10-fold subspace, as the second order hopping processes and the spin-orbit splittings in the molecular spectrum have a comparable magnitude.

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