Orbital Occupation, Local Spin, and Exchange Interactions in V_2O_3

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A local-density-approximation (LDA) and LDA $+ U$ band structure study of various phases of V_2O_3 shows that the most prominent (spin-$\frac{1}{2}$) models used to describe the semiconductor-metal transition are not valid. We find that the large on-site Coulomb and exchange interactions result in a total spin of 1 rather than $\frac{1}{2}$ and especially an orbital occupation which largely removes the orbital degeneracy. The calculated magnetic structure is consistent with experiment, again without the need for orbital ordering. These results strongly suggest that the phase transition in V_2O_3 which is so often quoted as the example of a spin-$\frac{1}{2}$ Mott-Hubbard system have a different origin.

The V_2O_3 system has been a topic of intense study for more than 50 years by both theoreticians and experimentalists because of its rich phase diagram. It undergoes a first order metal-insulator transition with a 7 orders of the magnitude change in the electrical conductivity [1], which can be induced by temperature, pressure, alloying, or non-stoichiometry. It also exhibits an antiferromagnetic insulator (AFI) to paramagnetic insulator (PI) transition which also is first order and a first order paramagnetic insulator to paramagnetic metal (PM) transition. Many theoretical models have been put forward to describe these properties based mainly on the Mott-Hubbard model [2–6]. In fact V_2O_3 is nowadays used as the best studied example of a Mott-Hubbard system with a semiconductor to metal transition. To explain the peculiar antiferromagnetic order (Fig. 1) in the low temperature insulating phase (AFI) with pairs of parallel spins coupled antiferromagnetically in the basal plane the intriguing idea of orbital ordering in the presumably doubly degenerate E_g orbitals was suggested [7] and revived recently [8] to explain new neutron scattering results [9]. Also within the context of infinite dimension calculations to describe strongly correlated systems V_2O_3 is now used as a good example of the success of this approximation [10]. However, the character of the phase transition and the nature of the ground state is still very controversial. Recent photoemission and x-ray absorption results [11] strongly suggest that the AFI ground state should not be described as a spin-$\frac{1}{2}$ antiferromagnetic Mott-Hubbard insulator as assumed in the above theories and, related to this, that the d orbital occupation is quite different from that conventionally assumed.

Also the very recent anomalous x-ray scattering [12], although showing the inequivalent orbital occupation at different sites, resulted in an orbital structure different from the most plausible one which followed from [7].

The commonly used picture assumes that out of two d-electrons of each V^{3+}, one forms a bonding orbital with the corresponding electron in a pair along the c axis, so that this bonding level is filled by the singlet pair. As a result

we are left in the low energy scale with the one electron in the remaining doubly degenerate orbital at each V. Our calculations and the physical arguments however lead to a completely different picture.

First we give some general arguments. The molecular orbital picture [7] could be valid only if the hopping t_c between a c pair is bigger than the Hubbard U. As we will see later it is definitely not the case in V_2O_3. However even if the singlet pair could be formed on this bond, it will be a Heitler-London pair with binding energy of $\sim t_c^2/U$ rather than $\sim t_c$. But the Hund's rule interaction J_H with the remaining t_{2g} electron will break this pair for $J_H > t_c^2/U$ which is definitely the case here, resulting in the formation of a spin-1 state at each V, and not spin-$\frac{1}{2}$ as in the picture usually adopted. Thus the very starting point of conventional treatment [7] is not valid for realistic values of parameters. Actually Castelani *et al.* realized this themselves, see especially their discussion on p. 4990 of their second paper.

Below we confirm these general arguments by the actual calculations and show that despite the fact that it is still possible to explain the main properties of the low-temperature phase of V_2O_3 starting from a completely different picture.
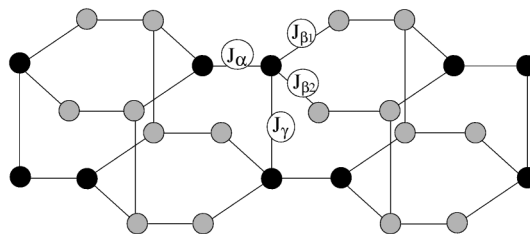

FIG. 1. The AF structure of the low temperature AFI phase of V_2O_3. The gray and filled circles correspond to spin-up and spin-down orientations of the local magnetic moments on V ions. The definition of notations used for the superexchange interactions along the various paths is also shown.

We carried out the study of the electronic structure of V_2O_3 in local-density approximation (LDA) [13,14] and LDA + U [15,16]. In LDA + U the Hubbard U is included as an effective potential, different for electron addition and removal.

The crystal structure in the low temperature AFI phase is monoclinic [17]; above T_c this changes to the corundum structure ($T_c \simeq 150$ K [18]). The calculated densities of states for both structures are very similar showing that the electronic structure itself is little influenced by the lattice distortions. In Fig. 2 the partial densities of states (DOS) obtained in the LDA calculation for the monoclinic crystal structure of V_2O_3 are shown. They are very similar to those found by Mattheis [19] for the corundum lattice. The trigonal distortion causes the otherwise threefold degenerate t_{2g} $3d$ orbitals to split into a nondegenerate A_{1g} and double degenerate E_g levels. In this representation the A_{1g} orbital has $3z^2 - r^2$ symmetry in a hexagonal coordinate system, i.e., with the z axis along the c direction (V-V pairs), and E_g orbitals are directed more towards the V ions in the basal plane.

In Fig. 2 we see a rather broad A_{1g} band with a total width of about 2.5 eV and a 2 eV E_g band both straddling the Fermi energy and resulting in a metallic state. The A_{1g} band actually exhibits a strong peaking above E_f and only relatively little weight below E_f. This looks very different from a bonding-antibonding splitting which should have exhibited a more symmetric structure about the center of gravity occupied by 1 electron per V atom. The total calculated occupation number of the A_{1g} band is only 0.5 electrons per V atom. We also note that the total A_{1g} bandwidth is only 2.5 eV which is smaller than the expected value of the Hubbard U of about 3 eV including the screening due to the strongly bonding e_g electrons [20] or about 4–5 eV without this screening

channel [21]. Such a small bandwidth would invalidate a molecular orbital-like approach.

Another important point is that the E_g-A_{1g} splitting due to the trigonal field is as large as ~0.4 eV with the E_g band center below that of the A_{1g} band. This large splitting makes the $E_g E_g$ configuration for the AFI phase more favorable than the $A_{1g} E_g$ configuration. This implies that the ground state AFI phase will not be degenerate leaving no place for any orbital ordering in the usual sense.

We performed LDA + U calculations for different magnetic structures, namely, the "real" AF (Fig. 1), a "simple" AF (all the nearest neighbors are antiferromagnetically coupled), a "layered" AF (all the nearest neighbors in basal plane are antiferromagnetically coupled and the neighbor along the hexagonal c axis is coupled ferromagnetically), and FM structure. In Fig. 3 the LDA + U partial DOS are plotted. Here the results for $U = 2.8$ eV and $J = 0.93$ eV are presented [20]. The striking point of the LDA + U result is that the electronic structure strongly depends on the magnetic structure. The band gap for instance in the real AF magnetic structure is 0.6 eV close to the experimental value [Fig. 3(a)], while in the FM structure we find a half-metal [Fig. 3(c)]. The nature of the DOS changes strongly even far below and above the Fermi level indicating the very strong sensitivity of the electronic structure to the spin structure. However, the occupation numbers for all magnetic structures are ~0.95 for each E_g orbital, and ~0.25 for A_{1g}, which formally corresponds to $E_g E_g$ configuration with a rather small admixture of $E_g A_{1g}$. The robustness of the $E_g E_g$ ground state is not only demonstrated by a very rapid convergence to this state independent of how we start the calculation but also by the very large difference of 0.5 eV per V atom between this lowest energy state and the energy of the $E_g A_{1g}$ state if the latter is kept frozen.

In this calculation there is no sign of the most commonly accepted orbital ordering. However, the A-E admixture has different phases, $E_g \pm \alpha A_{1g}$, for neighboring planes, consistent with the existence of a screw axis in the crystal structure of V_2O_3. We have calculated the quadrupole moment tensor for d shells of V ions and have found that while threefold symmetry is broken for the real AFM structure, the quadrupolar moment tensor is the same on all V ions in a given plane. Because of different signs of the A_{1g} admixture there is small tilting of the quadrupolar axes in opposite directions for atoms in a c pair; this can explain the superstructure observed in [12].

We should stress here that the total energy difference between different magnetic structures is really small. For the monoclinic crystal structure the real AF state has the lowest total energy followed by the simple AF state, which is higher by 80 K. In the case of the corundum crystal structure the simple AF state has the lowest energy, but the energy difference with the real AF state was only 5 K. Thus in the corundum phase these two magnetic structures (real and simple) turned out to be

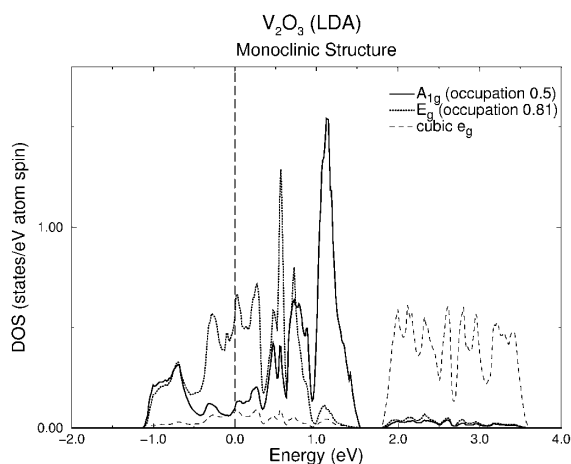V$_2$O$_3$ (LDA)
Monoclinic Structure

FIG. 2. Partial densities of state for $3d$ states of V obtained in the LDA calculation. Occupation numbers are given per one orbital (and both spins); i.e., each of the E_g orbitals has occupation of 0.81 electrons. The Fermi level is at zero energy.
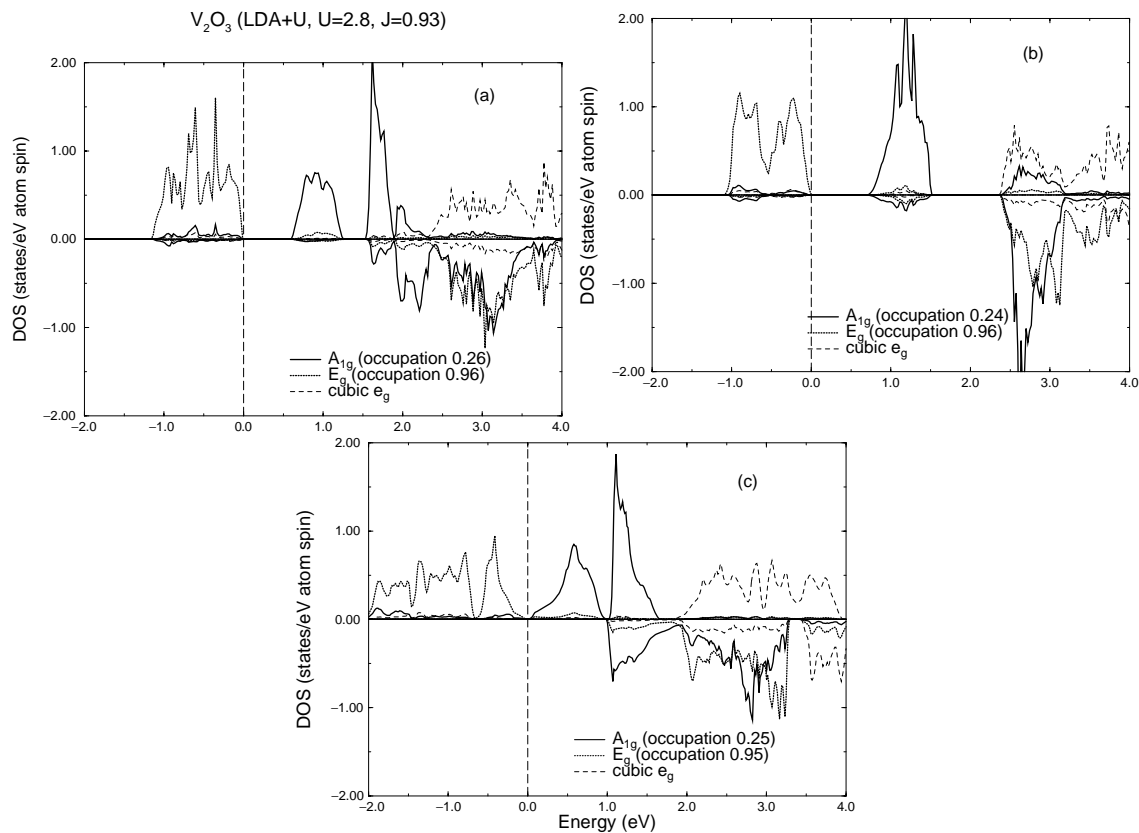
FIG. 3.   Partial densities of states for d states of V obtained in the LDA + U calculation. (a) Real antiferromagnetic structure; (b) simple antiferromagnetic structure; (c) ferromagnetic structure

almost degenerate. In short, the LDA + U results show us how important the small monoclinic distortions are for the magnetic structure and how low energy scale excitations, involving only spin reorientation, can effectively change large energy scale values such as band gaps.

There are two problems arising from the present results. First the spin should be considered to be 1 per V atom rather than $\frac{1}{2}$ and, second, that the orbital occupation is consistent with a predominantly $E_g E_g$ configuration of the ground state, which is in-plane symmetric and orbitally nondegenerate, but still with the complex real magnetic structure of the AFI phase. In this magnetic structure shown in Fig. 1, every atom has three closest neighbors in the basal plane, one of which is ferromagnetically aligned (J_α) and the other two—antiferromagnetically (J_{β_1} and J_{β_2}), and also there is one neighbor along the hexagonal c axis which is ferromagnetically aligned (J_γ) (see Fig. 1 for definitions of exchange interaction parameters). To check the above mentioned consistency we calculated the exchange interaction parameters (EIP) using a well tested method described in [22]. It was found that only one stable magnetic structure exists in the monoclinic phase. ("Stable" or "consistent" means that if in the EIP calculations the certain pair of spin was parallel, the corresponding exchange parameter came out as ferromagnetic, and if antiparallel, as antiferromagnetic.)

It is the real AF magnetic structure with the following values of EIP's: $J_\alpha = 48$ K (ferromagnetic), $J_{\beta_1} = -214$ K, $J_{\beta_2} = -90$ K, $J_\gamma = 47$ K. For the corundum crystal structure we obtained two stable magnetic configurations from the EIP calculation point of view: real AF ($J_\alpha = 55$, $J_{\beta_1} = J_{\beta_2} = -120$, $J_\gamma = 44$) and magnetic structure with uniform AF exchange in the basal plane ($J_\alpha = J_{\beta_1} = J_{\beta_2} = -65$) and small frustrated exchange along the hexagonal c axis ($J_\gamma \simeq 0$). From these results we can say that indeed the monoclinic distortion of the crystal structure stabilizes the real AF magnetic structure, and the $E_g E_g$ configuration of the d electrons is consistent with this magnetic structure. The values of EIP's depend strongly on the magnetic structure, which tells us that one cannot adequately model the magnetic interactions in V_2O_3 as only nearest neighbor Heisenberg exchange. This is most probably connected with the fact that V_2O_3 is close to being metallic which is also reflected in the strong dependence of the electronic structure on the magnetic one (and vice versa) which we saw in the LDA + U calculation. The polarized neutron scattering experiments [23] show the strong dependence of the magnetic interactions on the crystal structure.

Another factor may be that because of the specific crystal structure of V_2O_3 the exchange interactions with nnn in neighboring planes can be comparable with the

nn one; this *nnn* interaction occurs via the V-O-V superexchange path with the angle $\sim 135°$, whereas the *nn* exchange goes over via the V-O-V angle close to 90° which strongly reduces it and can even make it ferromagnetic [24]. All this shows that one should not try to explain the magnetic structure of V_2O_3 by only the nearest neighbor Heisenberg model.

Our results show that for the distorted monoclinic crystal structure the real AF magnetic structure is the lowest one and the only one which gives a consistent set of exchange interaction parameters. Our calculations also give a value of the magnetic moment per V $\sim 1.7\mu_B$, nearly the same in all the structures studied. This value is somewhat larger than the value of $1.2\mu_B$, obtained from neutron scattering for the antiferromagnetic phase, but is consistent with the value ($1.7\mu_B$) obtained from the high-temperature susceptibility. This relatively large value of μ is evidently a consequence of a strong Coulomb interaction on V^{3+} which tends to destroy the formation of the molecular orbital singlet state on A_{1g} orbitals of the V-V pair, which was assumed in most previous studies. The fact that this is independent of the magnetic or crystal structure suggests that this should be treated as a high energy scale parameter in any model.

Summarizing, we have carried out LDA $+ U$ calculations of the electronic structure and exchange constants of V_2O_3 in both the monoclinic and corundum structures and obtained a consistent description of the main properties of the antiferromagnetic insulating phase and of the paramagnetic insulating one. In contrast to the previous assumptions, in both these phases the electronic configuration is predominantly a $E_g E_g$ one; i.e., two d-electrons of V^{3+} occupy the doubly degenerate E_g orbitals. In addition the spins of the two electrons are parallel leading to a high spin $S = 1$ local moment. As a result there is no orbital ordering of the kind which was invoked previously to explain magnetic properties of V_2O_3 [7,8]. Despite that, we are able to obtain the correct magnetic structure of V_2O_3.

The calculated values of the energy gap ~ 0.6 eV and the magnitude of the magnetic moment per V $\sim 1.7\mu_B$ also agree with the experiment. The admixture of E_g and A_{1g} orbitals with opposite phases on neighboring planes can explain the superstructure recently observed by the anomalous x-ray scattering. Having found this it is also not so surprising anymore that the electronic structure and especially the d-band widths and splittings are strongly dependent on the nearest neighbor spin-spin correlation functions and that there may be a redistribution of electrons between the E_g and A_{1g} states on going

into the PI or metallic phase as found in recent electron spectroscopic studies [11].

[1] M. Foex, C. R. Acad. Sci. **223**, 1126 (1946).
[2] J. B. Goodenough, in *Proceedings of the Tenth International Conference of the Physics of Semiconductors* (U.S. Atomic Energy Commission, Oak Ridge, 1970), p. 304.
[3] J. B. Goodenough, Prog. Solid State Chem. **5**, 145 (1972).
[4] D. B. McWhan, T. M. Rice, and J. P. Remeika, Phys. Rev. Lett. **23**, 1384 (1969).
[5] H. Zeiger, Phys. Rev. B **11**, 5132 (1975).
[6] J. Spalek, A. Datta, and J. M. Honig, Phys. Rev. Lett. **59**, 728 (1987).
[7] C. Castellani, C. R. Natoli, and J. Ranninger, Phys. Rev. B **18**, 4945 (1978); **18**, 4967 (1978); **18**, 5001 (1978).
[8] T. M. Rice, in *Spectroscopy of Mott Insulators and Correlated Metals,* edited by A. Fujimori and Y. Tokura (Springer, Berlin, 1995), pp. 221–229.
[9] G. Aeppli *et al.,* in *Spectroscopy of Mott Insulators and Correlated Metals,* edited by A. Fujimori and Y. Tokura (Springer, Berlin, 1995).
[10] M. J. Rozenberg *et al.,* Phys. Rev. Lett. **75**, 105 (1995).
[11] J.-H. Park *et al.* (unpublished).
[12] L. Paolasini *et al.,* Phys. Rev. Lett. **82**, 4719 (1999).
[13] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[14] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[15] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).
[16] V. Anisimov, F. Aryasetiawan, and A. Lichtenstein, J. Phys. Condens. Matter **9**, 767 (1997).
[17] P. D. Dernier and M. Marezio, Phys. Rev. B **2**, 3771 (1970).
[18] P. Dernier, J. Chem. Phys. **31**, 2569 (1970).
[19] L. F. Mattheis, J. Phys. Condens. Matter **6**, 6477 (1994).
[20] I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev. B **53**, 7158 (1996).
[21] A. T. Mizokawa and A. Fujimori, Phys. Rev. B **48**, 14 150 (1993).
[22] A. I. Liechtenstein, V. I. Anisimov, and J. Zaanen, Phys. Rev. B **52**, R5467 (1995).
[23] W. Bao *et al.,* Phys. Rev. Lett. **78**, 507 (1997).
[24] W. Geertsma, Universidad de Valladolid, Valladolid, Spain (unpublished).