Orbital occupation, local spin and exchange interactions in $V_2O_3$

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We present the results of an LDA and LDA+U band structure study of the monoclinic and the corundum phases of $V_2O_3$ and argue that the most prominent (spin $\frac{1}{2}$) models used to describe the semiconductor metal transition are not valid. Contrary to the generally accepted assumptions we find that the large on site Coulomb and exchange interactions result in a total local spin of 1 rather than $\frac{1}{2}$ and especially an orbital occupation which removes the orbital degeneracies and the freedom for orbital ordering. The calculated exchange interaction parameters lead to a magnetic structure consistent with experiment again without the need of orbital ordering. While the low-temperature monoclinic distortion of the corundum crystal structure produces a very small effect on electronic structure of $V_2O_3$, the change of magnetic order leads to drastic differences in band widths and band gaps. The low temperature monoclinic phase clearly favors the experimentally observed magnetic structure, but calculations for corundum crystal structure gave two consistent sets of exchange interaction parameters with nearly degenerate total energies suggesting a kind of frustration in the paramagnetic phase. These results strongly suggest that the phase transitions in $V_2O_3$ which is so often quoted as the example of a $S=\frac{1}{2}$ Mott Hubbard system have a different origin. So back to the drawing board!

The $V_2O_3$ system has been a topic of intense study for over more than fifty years by both theoreticians and experimentalists because of it’s “rich” phase diagram. It undergoes a first order metal-insulator transition with a seven orders of the magnitude change in the electrical conductivity §, which can be induced by temperature, pressure, alloying or by nonstoichiometry. It also exhibits an antiferromagnetic insulator to paramagnetic insulator transition which also is first order and a first order paramagnetic insulator to paramagnetic metal transition. Many theoretical models have been put forward to understand the electronic and magnetic behavior of this compound. Goodenough proposed a model involving both itinerant and localized 3$d$ orbitals § to describe the the $V_2O_3$ electronic structure. Various models have been suggested and worked out in some detail using mainly the Mott-Hubbard picture §. 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.) 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 § and revived recently § to explain new neutron scattering results §. 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 §. 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 § 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. In this letter we present the study of the electronic structure of $V_2O_3$ in LDA § and LDA+U § approximations. In contrast to the standard LDA, in LDA+U method the influence of the on-site $d-d$ Coulomb interaction is included in Hamiltonian, as an effective potential which is different for electron removal than for electron addition which has been shown to be crucial to describe strongly correlated materials.

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 definitions of notations used for the superexchange interactions along the various paths are also shown.

The crystal structure in the low temperature AFI phase is monoclinic § above $T_c$ this changes to the corundum structure, ($T_c \approx 150K$ §). The calculated densities of states for both structures are very similar showing that the electronic structure itself is little influenced by the lattice distortions so that the strong change in properties must be a rather subtle effect with respect...
to the electronic structure. In Fig.2 the partial densities of states (DOS) obtained in the LDA calculation for the monoclinic crystal structure of V₂O₅ are shown. They are very similar to those found by Mattheis’s [20] for the corundum lattice. As the monoclinic distortion of the lattice is not very strong, we can plot DOS’s assuming approximate trigonal symmetry. The V ions are somewhat off center in a slightly trigonally distorted octahedron of O ions. This distortion causes the otherwise 3 fold degenerate $t_{2g}$ 3d orbitals to split into a non-degenerate $A_{1g}$ 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 $z$ axis along $c$ direction (V-V pairs), and $E_g$ orbitals are directed more towards the V ions in the basal plane.

![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.](image)

At first glance the LDA picture looks very simple and one may conclude that the conventionally used ideas concerning the splitting of the $A_{1g}$ orbitals into bonding and antibonding partners because of a hopping integral between the V ions in the pairs along the $c$ axis with two electrons per pair in the bonding orbital are confirmed. However upon closer examination a different picture emerges which is further supported by the LDA+U calculations below as well as the recent experimental XAS results [13]. First we see indeed a rather broad $A_{1g}$ band with a total width of a little more than 2 eV and an about $\frac{1}{2}$ eV narrower $E_g$ band both straddling the Fermi energy and resulting in a metallic state. The $A_{1g}$ band, although it shows some structure that might be interpreted as a bonding-antibonding pseudo gap, 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 if dimer hopping integrals were dominating the problem. We also note that the total $A_{1g}$ band width is only 2.5 eV which is considerably smaller than the expected value of the Hubbard $U$ of about 3 eV including the screening due to the strongly bonding $e_g$ electrons [21] or about 4-5 eV without this screening channel [22]. Such a small band width would invalidate a molecular orbital like approach also for the $A_{1g}$ orbitals. So even these results already cast doubt on the validity of the most commonly used starting point with a strong bonding-antibonding splitting of the $A_{1g}$ orbitals, with the $E_g$ orbitals in this gap ending up with two spin-antiparallel electrons per $c$-axis pair in the $A_{1g}$ bonding state leaving only one electron in an assumed narrow doubly degenerate $E_g$ band [21]. It was this starting point which led to the now very much used one electron per site Hubbard model for V₂O₅.

The total occupation number of the $A_{1g}$ band is only 0.5 electrons per V atom. Another very important point, which can be derived from the LDA result is that the $E_g$-$A_{1g}$ actual splitting due to the trigonal crystal field is as large as ~0.4 eV with the $E_g$ band center of gravity lower than the $A_{1g}$ band center of gravity. This large splitting makes the $E_gE_g$ configuration for the localized AFI phase more favorable than the $A_{1g}E_g$ configuration removing the orbital degeneracy. We can clearly see at this point that if we switch on the on-site Coulomb interaction $U$ in our LDA+U calculations the $A_{1g}$ states will be pushed up above the Fermi level and the resulting ground state will be $E_gE_g$. This implies that the ground state (AFI phase) will not be degenerate leaving no place for any orbital ordering in the usual sense.

The above LDA results give us rough ideas which should be further checked. The LDA+U calculations can provide us with some more details about the electronic structure of V₂O₅. 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 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. These values of $U$ and $J$ were calculated by Solovyev et. al., taking into account the screening of $t_{2g}$ interactions by $e_g$ electrons [21]. 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 Fermi level indicating the very strong sensitivity of the electronic structure to the spin structure. However, the occupation numbers for all magnetic structures are $\sim 0.95$
for each of $E_g$ orbital, and $\sim 0.25$ for $A_{1g}$, which formally corresponds to $E_gE_g$ configuration. In the present calculation there is no sign of any orbital ordering at all. We have calculated quadrupole moment tensor for d-shell of V ion and have found that while 3-fold symmetry is broken for “real” AFM structure, the quadrupole moment tensor is the same on all V ions. We should mention that we did not include the spin orbit coupling in these calculations and these could have appreciable effects for V$^{3+}$. For example the crystal structure allows for a Dzyaloshinsky-Moria coupling which could result in a small non collinear spin alignment. This could in the end increase the unit cell and could be visible in an anomalous scattering experiment.

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 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 1/2 and secondly that the orbital occupation is consistent with a $E_gE_g$ configuration of the ground state, which is in-plane symmetric and orbitally nondegenerate, but still with the complex ”Real” magnetic structure of the AF1 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 ($J_\alpha$) and the other two — antiferromagnetically ($J_{\beta_1}$ and $J_{\beta_2}$), and also there is one neighbor along the hexagonal c axis which is ferromagnetically aligned ($J_\gamma$)(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 23. We calculated EIP’s for both crystal structures: monoclinic and corundum. It was found that according to EIP calculation 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 $E_gE_g$ 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$_2$O$_3$ as only nearest neighbor Heisenberg exchange. This is most probably connected with the fact that V$_2$O$_3$ 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 LDA+U calculation. The polarized neutron scattering experiments 24 show the qualitative change of magnetic interactions in the transition from the antiferromagnetic insulator with the monoclinic crystal structure to both the metallic phase and paramagnetic insulator with the corundum structure. Instead of a peak in reciprocal space corresponding to AFI magnetic structure (“real” AF) it has a peak corresponding to a magnetic structure with all three V-V interactions in basal plane antiferromagnetic (“layered” AF). Another peculiarity of the neutron scattering results is a very large width of the peak.

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. Transition to the corundum crystal structure leads to the coexistence of the two well defined sets of exchange interaction parameters with nearly degenerate values of total energy for those two magnetic configurations, the symmetric in basal plane “layered” AF structure being slightly lower in energy. That would result, in reciprocal space, in a peak centered at the corresponding Q-vector but this peak will be strongly broadened due to the transitions to the excited state and corresponding fluctuations in the magnetic structure.

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 $\mu$ 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 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 \( E_gE_g \) 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 degeneracy left and correspondingly no orbital ordering of the kind which was invoked previously to explain magnetic properties of \( V_2O_3 \). Despite that we are able to obtain the correct magnetic structure of \( V_2O_3 \): the signs of the exchange constants in the monoclinic phase are consistent with the observed antiferromagnetic structure. The calculated values of the energy gap \( \sim 0.6 \text{ eV} \) and the magnitude of the magnetic moment per \( V \sim 1.7\mu_B \) also agree with the experiment. Strong change of magnetic correlations through \( T_N \) is ascribed to the near degeneracy of different magnetic structures in the corundum magnetic structure of \( V_2O_3 \), the state with antiferromagnetic correlations in all three directions in a basal plane having slightly lower energy. Thus orbital ordering is not required to explain the physical properties of \( V_2O_3 \) in the antiferromagnetic and in the paramagnetic insulating phases. The LDA+U results also demonstrate that a spin 1/2 Hubbard model is not the correct starting point but that one should use a spin 1 model with very strong hunds rule exchange. Within such a model with two electrons \( S=1 \) in \( E_g \) orbitals on each site the hopping would have to involve both the minority spin \( E_g \) orbitals as well as the \( A_{1g} \) orbitals which are close in energy. Having found this it is also not so surprising any more 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.

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![FIG. 3. Partial densities of states for \( d \) states of \( V \) obtained in LDA+U calculation. a) "Real" antiferromagnetic structure; b) "simple" antiferromagnetic structure; c) ferromagnetic structure.](image)

[1] M. Foex and 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] 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. Raninger, Phys. Rev. B 18, 4945 (1978).
[8] C. Castellani, C. R. Natoli, and J. Raninger, Phys. Rev. B 18, 4967 (1978).
[9] C. Castellani, C. R. Natoli, and J. Raninger, Phys. Rev. B 18, 5001 (1978).
[10] T. M. Rice, in Spectroscopy of Mott Insulators and Correlated Metals, edited by A. Fujimori and Y. Tokura (Springer, Berlin, 1995), pp. 221–229.
[11] G. Aeppli et al., in Spectroscopy of Mott Insulators and Correlated Metals, edited by A. Fujimori and Y. Tokura (Springer, Berlin, 1995).
[12] M.J. Rozenberg et al., Phys. Rev. Lett. 75, 105 (1995).
[13] J.-H. Park et al. (unpublished).
[14] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
[15] W. Kohn and L. Sham, Phys. Rev. 140, A1133 (1965).
[16] V.I. Anisimov, J. Zaanen, and O.K. Andersen, Phys. Rev. B 44, 943 (1991).
[17] V. Anisimov, F. Aryasetiawan, and A. Lichtenstein, J. Phys.: Condens. Matter 9, 767 (1997).
[18] P. D. Dernier and M. Marezio, Phys. Rev. B 2, 3771 (1970).
[19] Dernier, J. Chem. Phys. 31, 2569 (1970).
[20] L. F. Mattheis, J. Phys. Condens. Matter 6, 6477 (1994).
[21] I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev. B 53, 7158 (1996).
[22] A. T. Mizokawa and A. Fujimori, Phys. Rev. B 48, 14150 (1993).
[23] A.I. Lichtenstein, V.I. Anisimov, and J. Zaanen, Phys. Rev. B 52, R5467 (1995).
[24] W. Bao et al., Phys. Rev. Lett. 78, 507 (1997).