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Spin and orbital occupation and phase transitions in V_2O_3

J.-H. Park*
Randall Laboratory, University of Michigan, Ann Arbor, Michigan 48109;
AT&T Bell Laboratories, Murray Hill, New Jersey 07974;
and National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973

L. H. Tjeng
Randall Laboratory, University of Michigan, Ann Arbor, Michigan 48109
and Solid State Physics Laboratory, Materials Science Centre, University of Groningen, Nijenborgh 4,
9747 AG Groningen, The Netherlands

A. Tanaka
Department of Materials Science, Faculty of Science, Hiroshima University, Higashi-Hiroshima 724, Japan

J. W. Allen
Randall Laboratory, University of Michigan, Ann Arbor, Michigan 48109

C. T. Chen†
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

P. Metcalf and J. M. Honig
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

F. M. F. de Groot and G. A. Sawatzky
Solid State Physics Laboratory, Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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Polarization dependent x-ray-absorption measurements were performed on pure and Cr-doped V_2O_3 single crystals in the antiferromagnetic insulating, paramagnetic insulating, and metallic phases. The orbital occupation of the V $3d^2$ ion is found to depend appreciably on the phase, but always with the $S=1$ character, requiring an explanation which is beyond the elegant simplicity of the pure one-band Hubbard model or of models in which the a_{1g} orbital is projected out by means of a simple dimerization. The results reveal the critical role of the spin and orbital dependence of the on-site $3d$-$3d$ Coulomb energy, and a mechanism is proposed to explain the closing or opening of the band gaps which are of much higher energy scale than the transition temperatures.

The V_2O_3 system displays a very rich phase diagram which involves antiferromagnetic insulating (AFI), paramagnetic metallic (PM), and paramagnetic insulating (PI) regimes.[1,2] The crystal structure in the PM and PI phases is rhombohedral (corundum), while in the AFI phase it becomes monoclinic[1,3–5] with an unusual magnetic structure.[6] The metal-insulator transitions, from PM to AFI at low temperatures and from PM to PI at higher temperatures, are considered to be classical examples of Mott transitions,[7,8] in which changes in the interplay between band formation and electron correlation causes a crossover between the metallic and insulating regimes. Many models[9–15] have been proposed to explain these metal-insulator transitions and the AFI magnetic structure, mostly using the Mott-Hubbard picture,[7,8] with some of them also involving orbital ordering[12,15] or band crossing[9] phenomena.

Despite the large body of work on the V_2O_3 system, two fundamental and possibly related issues have been neglected. First, the V $3d$ orbital occupations for the various phases have never been directly established, even though these occupations are starting assumptions that distinguish the various models mentioned above. Second, for both the PM to AFI and PM to PI transitions, the transition temperatures, about 150 K and 200–300 K, respectively, are smaller by factors of 40 and ≈ 20 than the conductivity gaps of the insulating phases, around 0.66 eV (Ref. 16) and 0.3–0.5 eV.[2,17,18] None of the models provide a satisfactory explanation, at best predicting a gap of the same energy scale as the transition temperature.

In this paper we present a polarization-dependent x-ray-absorption spectroscopy (XAS) study on pure and Cr-doped V_2O_3 single crystals at the V $L_{2,3}(2p \rightarrow 3d)$ edges. XAS is a well-established technique to determine the orbital[19] and spin[20] character of the ground state of an ion, since the spectra can be understood in a straightforward manner in terms of transitions to multiplet-split final states subjected to dipole selection rules. The V ion in the V_2O_3 system is in the $3d^2$ configuration, where the two electrons occupy the t_{2g} orbitals in the near-octahedral VO_6 cluster. Due to the presence of a trigonal distortion associated with the corundum structure,

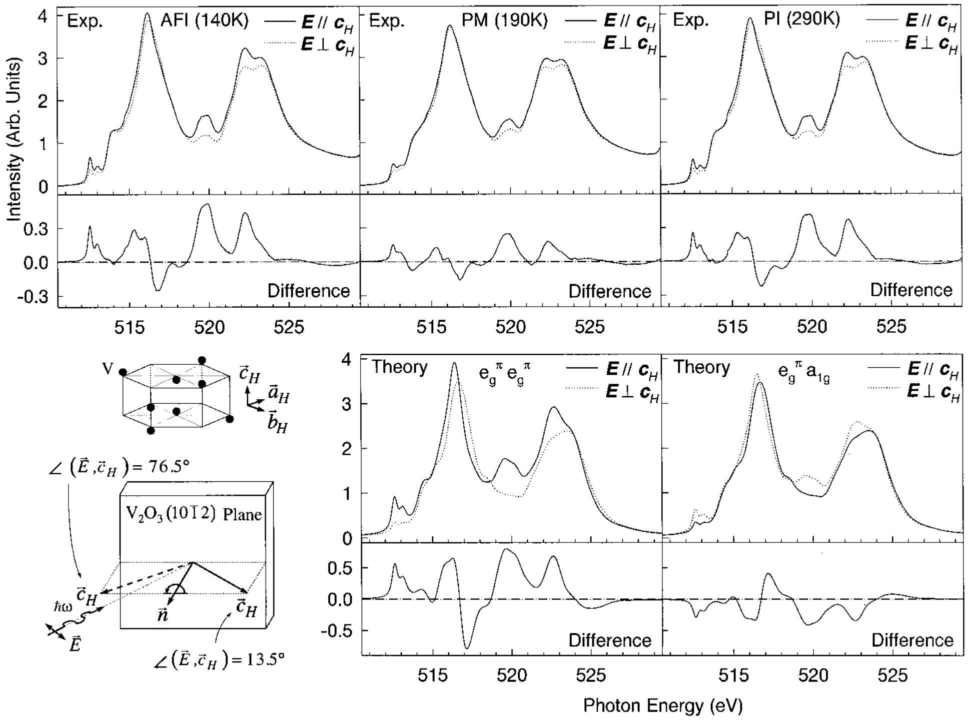

FIG. 1. Polarization-dependent V $L_{2,3}$ x-ray-absorption spectra. The top panels show the experimental spectra of $(V_{0.988}Cr_{0.012})_2O_3$ in the AFI, PM, and PI phases taken at 140, 190, and 290 K, respectively. The bottom-middle and right panels depict the theoretical spectra starting from the *pure* $e_g^\pi e_g^\pi$ and $e_g^\pi a_{1g}$ initial states, respectively. The spectra are given for the polarization vector $\boldsymbol{E}$ of the light parallel and perpendicular to the hexagonal $\boldsymbol{c}_H$ basis vector. The difference spectra are also included. The bottom-left panel shows the experimental geometry, where the surface normal $\boldsymbol{n}$ is 58.5° off from $\boldsymbol{c}_H$.

the t_{2g} orbital splits into a nondegenerate a_{1g} and a doubly degenerate e_g^π orbital. The a_{1g} orbital has lobes directed along the $\boldsymbol{c}_H$ vector of the hexagonal basis, while the e_g^π lobes are more within the $(\boldsymbol{a}_H, \boldsymbol{b}_H)$ basal plane. The XAS transition probability to an empty a_{1g} or e_g^π orbital depends strongly on whether the polarization vector $\boldsymbol{E}$ of the light is parallel or perpendicular to $\boldsymbol{c}_H$. In this way we have found out that the various phases have different orbital occupations, from which we deduce that a pure one-band Hubbard model is not adequate, and that the spin and orbital dependence of the on-site $3d$-$3d$ Coulomb energy need to be considered to explain the dramatic differences in the effective band widths[16–18] and intersite exchange interactions.[21]

The measurements were performed at the Dragon beamline at the National Synchrotron Light Source,[22] using the total electron yield mode. The light has a degree of linear polarization of $\approx 98\%$ and an energy resolution of ≈ 0.16 eV. Well annealed $(V_{1-x}Cr_x)_2O_3$ single-crystal samples with $x = 0.0\%, 0.4\%, 1.2\%$, and 1.8% were cleaved to expose a hexagonal $(10\bar{1}2)$ cleavage plane[23] in a vacuum better than 2×10^{-10} Torr. The surface normal $\boldsymbol{n}$ is 58.5° off from $\boldsymbol{c}_H$ as determined from Laue measurements. To eliminate optical path and surface sensitivity variations, an azimuthal rotation method was used as shown in Fig. 1. The angle between $\boldsymbol{E}$ and $\boldsymbol{c}_H$ can be varied between 13.5° and 76.5°. With a $\cos^2$ value of 0.95 and 0.05, respectively, the setup can almost reach the perfect $\boldsymbol{E}\|\boldsymbol{c}_H$ and $\boldsymbol{E}\perp\boldsymbol{c}_H$ alignments.

XAS results at the V $L_{2,3}$ edge are shown in the top panels of Fig. 1 for the $(V_{1-x}Cr_x)_2O_3$ sample with $x = 1.2\%$, measured at 140 K (AFI), 190 K (PM) and 290 K (PI). The spectra are dominated by the $2p$ core hole spin-orbit coupling, which divides them into roughly the L_3 ($h\nu \approx 512$–518 eV) and L_2(518–528 eV) regions, and are strongly influenced by the multiplet structure given by the $2p$-$3d$ Coulomb interactions and crystal fields. The $\boldsymbol{E}\|\boldsymbol{c}_H$ spectra are clearly different from the $\boldsymbol{E}\perp\boldsymbol{c}_H$ ones. The difference is much larger for the AFI than for the PM, and is intermediate for the PI. The presence of polarization dependence in the spectra has also been reported recently by others.[24]

The bottom panels of Fig. 1 show the results of a VO_6 cluster multiplet calculations[25–28] in which the V $3d^2$ ion is in various possible high spin $(S=1)$ states. Hybridization between the V ion and the O ligands is included, and values for the model parameters are taken from recent photoemission studies.[29,30] In addition to the octahedral crystal field of 10 Dq = 1.0 eV, the calculations include a small trigonal crystal field (0.05 eV), positive to get a pure $e_g^\pi a_{1g}$ initial state and negative for a pure $e_g^\pi e_g^\pi$. The figure includes not only the individual $\boldsymbol{E}\|\boldsymbol{c}_H$ and $\boldsymbol{E}\perp\boldsymbol{c}_H$ spectra, but also their differences. An important result is that the difference spectrum for the $e_g^\pi a_{1g}$ initial state has a sign which is opposite to that for the $e_g^\pi e_g^\pi$. Apart from this and a factor of close to 2, the difference spectra have a similar line shape.[31]

A comparison of the measured spectra with the calculations shows that there is a good general agreement. We can safely conclude that the V $3d^2$ ions are indeed in the high spin $(S=1)$ state, since the spectrum for a low spin $(S=0)$ $3d^2$ is completely different.[20] A more careful inspec-

TABLE I. Linear dichroism and orbital occupation in the AFI, PM, and PI phases of the V_2O_3 system. The dichroism is defined as the difference divided by the sum of the $\boldsymbol{E}\|\boldsymbol{c}_H$ and $\boldsymbol{E}\perp\boldsymbol{c}_H$ intensities of the lowest peak of the V $L_{2,3}$ x-ray absorption spectrum, and the temperature of the measurement is indicated between parentheses.

Phase	V_2O_3	$(V_{0.996}Cr_{0.004})_2O_3$	$(V_{0.988}Cr_{0.012})_2O_3$	$(V_{0.982}Cr_{0.018})_2O_3$	Average	$e_g^\pi e_g^\pi : e_g^\pi a_{1g}$ occupation
AFI	34% (140 K)	30% (145 K)	32% (140 K)	35% (150 K)	33%	2:1
PM	18% (170 K)	19% (180 K)	18% (190 K)		18%	1:1
PI			27% (290 K)	27% (190 K)	27%	3:2

tion of the experimental $\boldsymbol{E}\|\boldsymbol{c}_H$ minus $\boldsymbol{E}\perp\boldsymbol{c}_H$ difference spectra, shows that the initial state in all the phases considered cannot be $e_g^\pi a_{1g}$, since for this the calculated difference spectrum has the wrong sign. Although all the line shapes are very well reproduced, the initial state also cannot have the pure $e_g^\pi e_g^\pi$ symmetry, since the measured difference spectra have a smaller amplitude than the one calculated for the pure state. To be quantitative, it is most reliable to take the lowest peak in the XAS spectra ($h\nu = 512.6$ eV) as a benchmark, since its intensity is hardly affected by the background and solid-state broadening. Defining the dichroism at this peak as the difference divided by the sum of the intensities measured in the $\boldsymbol{E}\|\boldsymbol{c}_H$ and $\boldsymbol{E}\perp\boldsymbol{c}_H$ geometries, we find 32% for the AFI phase, 18% for the PM and 27% for the PI.[32] The multiplet calculations give 57% for a pure $e_g^\pi e_g^\pi$ initial state and -41% for a pure $e_g^\pi a_{1g}$. We then deduce that the $e_g^\pi e_g^\pi$ to $e_g^\pi a_{1g}$ occupation ratio is about 2:1 in the AFI, 1:1 in the PM and 3:2 in the PI phase. These results are summarized in Table. I, together with those from the $x = 0.0\%, 0.4\%$, and 1.8% samples.

One of the most important results of our experiment is that the different phases have different orbital occupations. This indicates that the V_2O_3 problem cannot be mapped onto a single-band Hubbard model. It also shows that the a_{1g} orbital should not be projected out as is done in a more involved model which includes orbital degeneracy.[12,15] In fact, the pure $e_g^\pi a_{1g}$ *ansatz* used in this model to explain the AFI magnetic structure, is not supported by our data, and the proposed a_{1g} molecular orbital singlet formation in the V-V dimer along the $\boldsymbol{c}_H$ axis to project out the a_{1g}, is adverse to the observed ferromagnetic spin alignment within the dimer[6] given that each V ion is in the $S = 1$ state. Remarkably, the AFI occupation ratio in the early model by Goodenough[9] is close to our experimental value. However, the proposed reduction of the a_{1g} occupation in the transition to the PM phase, is in disagreement with the data.

The observation of the high-spin state and the dramatic orbital occupation changes, indicates that the correlated motion of the electrons cannot be accounted for by a single parameter U, i.e., the spin and orbital dependence of the on-site $3d$-$3d$ Coulomb energy, such as the Hund's rule exchange, cannot be neglected as is often done. In fact, it has been determined that the resulting energy splittings of the different $3d$ configurations are large and hardly reduced from the atomic values by solid-state screening.[33] To illustrate that this spin and orbital dependence naturally connects the measured occupation changes with the observed changes in the intersite exchange interactions,[21] we consider a pair of ions (labeled A and B), with an idealized set of orbitals $\{a, e_x, e_y\}$, in which the only nonzero hopping integral t is between $(e_x)_A$ and $(e_x)_B$. Starting with a high spin $(e_x e_y)$ occupation for both ions, the total energy of the pair is lowered by $2t^2/U_0$ if the ions are antiferromagnetically aligned, allowing for the virtual process $(e_x^\uparrow e_y^\uparrow)_A + (e_x^\downarrow e_y^\downarrow)_B \rightarrow (e_y^\uparrow)_A + (e_x^\uparrow e_x^\downarrow e_y^\downarrow)_B$. Changing now the orbital occupation of B to $(a e_y)$, causes the exchange interaction between the two ions to become ferromagnetic: with the $(e_x)_B$ completely empty, the process $(e_x^\uparrow e_y^\uparrow)_A + (a^\uparrow e_y^\uparrow)_B \rightarrow (e_y^\uparrow)_A + (a^\uparrow e_x^\uparrow e_y^\uparrow)_B$ now becomes possible and gives an energy lowering of t^2/U_1, which is more than the $t^2/(U_1 + 2J_H)$ lowering in an antiferromagnetic alignment, where J_H is the Hund's rule exchange.

It is important to note that the orbital occupation determines not only the sign of the intersite exchange interaction but also the U that need to be used to estimate its strength. U_0 in the above example is quite different from U_1: for V_2O_3 we estimate that U_0 is about 3.5–4.0 eV, while U_1 is only 1.5 eV.[27,29,30,34,35]

Another consequence of the spin and orbital dependence of the on-site $3d$-$3d$ Coulomb energy is that changes in the orbital occupation can result in drastic changes of the band gap and effective band width as is observed.[16–18] Consider the pair as described above. If the orbital occupation is such that the exchange interaction is ferromagnetic within the pair, then the energy cost to separately remove and add an electron is U_1-W_{FM}, where the effective bandwidth is given by $W_{\mathrm{FM}} = 2t$. If on the other hand, the ions of the pair are antiferromagnetically aligned due to a different orbital occupation, then the band gap is given by the larger U_1-W_{AF}, because the effective bandwidth is reduced to $W_{\mathrm{AF}} \approx \sqrt{t^2 + \frac{1}{4}J_H^2} - \frac{1}{2}J_H + t^2/(U_0\text{-}U_1)$ due to the extra energies J_H and $(U_0$-$U_1)$ that are now involved for the hopping of the extra hole and electron, respectively. We stress here that $J_H \approx 0.65$ eV and $(U_0$-$U_1) \approx 2.0$–2.5 eV (Ref. 27,29,30,35) are not at all small compared to $t \approx 0.5$–0.8 eV.[36] Taking for example $t \approx J_H$, we obtain $W_{\mathrm{AF}} \approx 0.9t$. This example therefore shows, that a change in orbital occupation can cause a considerable change in the band gap and effective band width, by as much as several tenths of an eV. Thus the band gap will not any longer determine directly the metal-insulator transition temperature, very much unlike in the one-band Hubbard model where thermal excitations across the band gap are required for the transition to take place. In other words, the single-particle contribution to the total energy need not change by as much as the band gap, if across the transition the orbital occupation changes causing a drastic redistribution of the states as is observed by photoemission.[17,18]

The dramatic change in the exchange interactions across the AFI-PM transition as observed in neutron experiments[21] coincides well with the large changes in the orbital occupation reported here, since these two phenomena are intimately linked together. Based on our analysis, we actually expect that some degree of ferromagnetic exchange interactions should be present in the PM phase, but so far there is no report available. For the PI phase, neutron data reveal that the exchange interactions are even more short ranged than for the PM. Together with the observed differences in the orbital occupation, this may suggest that in the PI phase there are not enough ferromagnetic exchange interactions left to help stabilize the metallic state. A more subtle issue is the AFI-PI transition at high Cr doping, for which the change in the band gap seems to be almost of the same energy scale as the transition temperature. The fact that the transition is first order indicates that it cannot be attributed solely to the loss of the spin ordering. The simultaneous occurrence of the monoclinic-to-rhombohedral lattice transition and measured changes in the orbital occupation, may point towards the involvement of some form of orbital ordering, but probably different from the one so far proposed.[12]

In summary, we have observed that the V $3d^2$ ion is always in the high-spin state, and that the orbital occupation is different for the different phases. We conclude that the a_{1g} orbital cannot be projected out by means of a molecular orbital formation, and that V_2O_3 cannot be treated as a $S=\frac{1}{2}$ system. The spin and orbital dependence of the on-site $3d$-$3d$ Coulomb energy is found to play a crucial role in the metal-insulator transitions. It is therefore worthwhile now to reconsider certain so far discarded scenarios of Castellani *et al.*;[12] namely those for the highest values of the Hund's rule exchange. These were discarded on the (wrong) assumption that such an on-site exchange will be strongly screened in a solid.

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*Present address: Department of Physics, POSTECH, Pohang 790-784, Korea.

†Present address: Synchrotron Radiation Research Center, Hsinchu Science-Based Industrial Park, Hsinchu 30077, Taiwan.

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