Spin and orbital occupation and phase transitions in V$_2$O$_3$

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(Received 6 January 2000)

Polarization dependent x-ray-absorption spectroscopy (XAS) measurements were performed on pure and Cr-doped V$_2$O$_3$ single crystals in the antiferromagnetic insulating, paramagnetic insulating, and metallic phases. The orbital occupation of the V$^{3+}$d$_{2}$ ion is found to depend appreciably on the phase, but always with the S$_{51}$ 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$_2$O$_3$ system displays a very rich phase diagram which involves antiferromagnetic insulating (AFI), paramagnetic metallic (PM), and paramagnetic insulating (PI) regimes. The crystal structure in the PM and PI phases is rhombohedral (corundum), while in the AFI phase it becomes monoclinic with an unusual magnetic structure. The metal-insulator transitions, from PM to AFI at low temperatures and from PM to PI at high temperatures, are considered to be classical examples of Mott transitions, in which changes in the interplay between band formation and electron correlation causes a crossover between the metallic and insulating regimes. Many models have been proposed to explain these metal-insulator transitions and the AFI magnetic structure, mostly using the Mott-Hubbard picture, with some of them also involving orbital ordering or band crossing phenomena.

Despite the large body of work on the V$_2$O$_3$ 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. 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$_2$O$_3$ single crystals at the V L$_{2,3}$ edges. XAS is a well-established technique to determine the orbital and spin 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$_2$O$_3$ 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\textsubscript{2,3} x-ray-absorption spectra. The top panels show the experimental spectra of (V\textsubscript{0.998}Cr\textsubscript{0.012})\textsubscript{2}O\textsubscript{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\textsubscript{g} and e\textsubscript{g}\textsubscript{1}g initial states, respectively. The spectra are given for the polarization vector E of the light parallel and perpendicular to the hexagonal e\textsubscript{H} basis vector. The difference spectra are also included. The bottom-left panel shows the experimental geometry, where the surface normal n is 58.5° off from e\textsubscript{H}.

The measurements were performed at the Dragon beamline at the National Synchrotron Light Source,\textsuperscript{22} using the total electron yield mode. The light has a degree of linear polarization of \(\approx 98\%\) and an energy resolution of \(\approx 0.16\) eV. Well annealed (V\textsubscript{1-x}Cr\textsubscript{x})\textsubscript{2}O\textsubscript{3} single-crystal samples with \(x = 0.0\%, 0.4\%, 1.2\%, \text{ and } 1.8\%\) were cleaved to expose a hexagonal (101\textsubscript{2}) cleavage plane\textsuperscript{23} in a vacuum better than \(2 \times 10^{-10}\) Torr. The surface normal n is 58.5° off from e\textsubscript{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 E and e\textsubscript{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 E||e\textsubscript{H} and E⊥e\textsubscript{H} alignments.

XAS results at the V L\textsubscript{2,3} edge are shown in the top panels of Fig. 1 for the (V\textsubscript{1-x}Cr\textsubscript{x})\textsubscript{2}O\textsubscript{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\textsubscript{3} (\(h\nu \approx 512–518\) eV) and L\textsubscript{2}(518–528 eV) regions, and are strongly influenced by the multiplet structure given by the 2p-3d Coulomb interactions and crystal fields. The E||e\textsubscript{H} spectra are clearly different from the E⊥e\textsubscript{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.\textsuperscript{24}

The bottom panels of Fig. 1 show the results of a VO\textsubscript{6} cluster multiplet calculations\textsuperscript{25–28} in which the V 3d\textsuperscript{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.\textsuperscript{29,30} In addition to the octahedral crystal field of 10 D\textsubscript{q} = 1.0 eV, the calculations include a small trigonal crystal field (0.05 eV), positive to get a pure e\textsubscript{g} initial state and negative for a pure e\textsubscript{g} initial state. The figure includes not only the individual E||e\textsubscript{H} and E⊥e\textsubscript{H} spectra, but also their differences. An important result is that the difference spectrum for the e\textsubscript{g}\textsubscript{1}g initial state has a shape which is inverse to that for the e\textsubscript{g}\textsubscript{1}g. Apart from this and a factor of close to 2, the difference spectra have a similar line shape.\textsuperscript{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\textsuperscript{2} ions are indeed in the high spin (S = 1) state, since the spectrum for a low spin (S = 0) 3d\textsuperscript{2} is completely different.\textsuperscript{20} A more careful inspec-
tion of the experimental $E\|c_H$ minus $E\perp c_H$ difference spectra, shows that the initial state in all the phases considered cannot be $e_x^\pi a_{1g}$, 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 $e_x^\pi e_g^\sigma$ 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 $E\|c_H$ and $E\perp c_H$ 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 $e_x^\pi e_g^\sigma$ initial state and $-41\%$ for a pure $e_x^\pi a_{1g}$. We then deduce that the $e_x^\pi e_g^\sigma$ to $e_x^\pi a_{1g}$ 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 experimental $c_H$ and $c_{1g}$ 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.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$V_2O_3$</th>
<th>$(V_{0.996}Cr_{0.004})_2O_3$</th>
<th>$(V_{0.988}Cr_{0.012})_2O_3$</th>
<th>$(V_{0.992}Cr_{0.018})_2O_3$</th>
<th>Average $e_x^\pi e_g^\sigma : e_x^\pi a_{1g}$ occupation</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFI</td>
<td>34% (140 K)</td>
<td>30% (145 K)</td>
<td>32% (140 K)</td>
<td>35% (150 K)</td>
<td>2:1</td>
</tr>
<tr>
<td>PM</td>
<td>18% (170 K)</td>
<td>19% (180 K)</td>
<td>18% (190 K)</td>
<td>18% (190 K)</td>
<td>1:1</td>
</tr>
<tr>
<td>PI</td>
<td>27% (290 K)</td>
<td>27% (190 K)</td>
<td>27% (190 K)</td>
<td>27% (190 K)</td>
<td>3:2</td>
</tr>
</tbody>
</table>

Note: 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 interaction,12,15 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 $(e_x^\pi e_y^\sigma)_A + (e_x^\pi e_y^\sigma)_B \rightarrow (e_x^\pi)_A + (e_x^\pi e_y^\sigma)_B$. Changing now the orbital occupation of B to $(ae_y)$, causes the exchange interaction between the two ions to become ferromagnetic: with the $(e_x)_B$ completely empty, the process $(e_x^\pi e_y^\sigma)_A + (a^\pi e_y^\sigma)_B \rightarrow (e_x^\pi)_A + (a^\pi e_y^\sigma)_B$ 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 interaction. 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.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 $W_{FM} = 2t$. 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 $W_{AF} \approx \sqrt{t^2 + J_H^2} - \frac{1}{2}J_H + t^2/(U_0 - U_1)$ 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 $t = J_H$, we obtain $W_{AF} \approx 0.9$. 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.31
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.

In summary, we have observed that the $V^{3+}d^{2}$ 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.,

We acknowledge K. Schönhammer and D.I. Khomskii for helpful discussions. This work was supported by the U.S. Department of Energy under Contract Nos. DE-FG02-90ER45416 (UoM), DE-FG02-90ER45427 (PU), and DE-AC02-76CH00016 (NSLS), by the U.S. National Science Foundation under Contract Nos. DMR-91-08015 (UoM) and DMR-96-12130 (PU), and by the Netherlands Foundation for Fundamental Research on Matter (FOM) with financial support from the Netherlands Organization for Scientific Research (NWO). The research of LHT and FMFdG has been financially supported by the Royal Netherlands Academy of Arts and Sciences.

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