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SAWATZKY, GA; POST, D

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X-ray photoelectron and Auger spectroscopy study of some vanadium oxides

G. A. Sawatzky and D. Post

Physical Chemistry Laboratory, Material Science Center,

University of Groningen, The Netherlands

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A detailed investigation of V_2O_5 , VO_2 , V_2O_3 , and V metal is presented. The vanadium core lines in the x-ray photoelectron spectra are anomalously wide for V_2O_3 and VO_2 . It is shown that this is a consequence of the narrow $3d$ band in these materials and the relatively strong core-hole $3d$ Coulomb interaction. The influence of electron correlation effects in the $3d$ band on the core linewidths is discussed. The valence bands are compared to band-structure calculations and the difference in the band structure above and below the semiconductor-metal transition is discussed. The Auger results are discussed in terms of the $3d$ partial density of states. It is found that there is a large amount of d character in the O- $2p$ region of the valence band. Also the average "on-site" Coulomb interaction of $3d$ electrons is obtained from the Auger spectra and is discussed in terms of electron correlation effects.

I. INTRODUCTION

The vanadium oxides, especially VO_2 and V_2O_3 , have been intensively studied with many experimental and theoretical tools in an attempt to understand the interesting physical properties of these solids. One of the most important controversies which still remains is to what extent the electron-electron interaction and electron correlation effects are important in these materials for an understanding of the physical properties. It is for example difficult to determine whether the electron-phonon or electron-electron interaction is the driving force for the semiconductor-metal phase transitions. Also the role played by the electron-electron interaction in determining the magnetic properties is not understood. This together with the fact that there is so much known about these compounds has prompted this detailed x-ray photoelectron (XPS) and x-ray excited Auger (AES) study of V_2O_5 , VO_2 , V_2O_3 , and V metal. In addition to learning more about their electronic structures these materials can also serve as examples for a study of core line shapes in narrow-band conductors.

II. MATERIALS

V_2O_5 is a diamagnetic insulator used in this study as a reference material. It has a distorted tetragonal pyramidal crystal structure and the V ions are in an octahedral coordination of oxygen. Formally V is $5+$ and the d band is empty, although as will be shown the V- $3d$ -O- $2p$ covalent mixing results in a partial occupation of the d orbitals. The material used was 99.8% V_2O_5 powder obtained commercially.

In VO_2 the vanadium is formally $4+$, containing

on the average one $3d$ electron per V atom. VO_2 displays a semiconductor-metal transition¹ at 340°K and undergoes a crystallographic phase transition from monoclinic in the low-temperature phase to distorted rutile in the high-temperature phase. In both phases V is approximately octahedrally coordinated by oxygen. The details of the transition have been described by numerous authors,^{2,3} although the nature of the ground-state semiconducting phase is still rather uncertain. In the low-temperature phase the V atoms are paired, which has led to the suggestion that the electron-phonon interaction is responsible for the splitting⁴ of the $d-t_{1g}$ band resulting in a full lower bonding band. Recent first-principles band-structure calculations tend to support this idea⁵ showing that the crystallographic transition would be explained by the formation of a charge-density wave accompanied by a lattice distortion and a subsequent condensation of phonons. Other calculations⁶ however indicate that a crystallographic distortion is not sufficient to open up a gap and that electron correlation effects probably also play an important role in the transition.^{7,8} Experimental investigation^{3,9} of chromium-doped VO_2 as well as theoretical investigations suggest that the ground state of VO_2 consists of singlet V-V pairs with strong electron correlation. In the metallic phase the spin susceptibility^{3,10} suggests either a strong enhancement¹¹ or a very narrow band with a very high density of states at the Fermi level.⁸ The materials used in this investigation are single crystals of pure VO_2 with a typical conductivity jump of five orders of magnitude at the transition temperature of 340°K .¹²

V_2O_3 crystallizes in the corundum phase above 170°K . A semiconductor-metal transition occurs at 170°K with a very large conductivity jump.¹ The low-temperature phase is antiferromagnetic, as shown

by neutron diffraction, with localized magnetic moments of $1.2\mu_B$ per V atom.¹³ Since V in V_2O_3 is formally $3+$ with two $3d$ electrons per V atom, the observed magnetic moment suggests that the semiconducting phase consists of close to two exchange-coupled d electrons localized on each V ion. The magnetic spin susceptibility of V_2O_3 in the metallic phase is, as in VO_2 , either strongly exchange enhanced or due to a very narrow band with a high density of states at the Fermi level.

There is another phase transition in V_2O_3 at about $520^\circ K$ above which temperature the conductivity is again lower than in the metallic phase. Several suggestions^{14,15} have been made for the nature of this transition but it is still quite controversial. In this study we will concentrate on the metallic and low-temperature insulating phases. The materials used are single crystals obtained from J. M. Honig at Purdue.

V metal was as V_2O_5 used as a reference material. It contains about three $3d$ electrons per V atom. The spin susceptibility is consistent with weak exchange enhancement indicating that electron correlation effects are not very important. For this study V foils (99%) obtained commercially were used.

III. EXPERIMENTAL

The spectra were obtained with an AEI ES200 spectrometer controlled by a PDP-8 computer. The spectrometer is pumped with diffusion pumps and a Ti sublimation pump. In all cases the vacuum was better than 5×10^{-10} Torr. Usually the Al and Mg $K\alpha$ x-ray sources without monochromatization were used. Since in most samples the intrinsic linewidth was very large the monochromatized Al $K\alpha$ source was not required. Only in a few cases did we use the monochromatized source, to study the valence and conduction bands. The switching from one source to another could be done without breaking the vacuum. The samples were brought into a N_2 -filled glove box attached to the sample inlet system of the spectrometer. The glove box contains a copper coil through which liquid N_2 can be passed. This was done prior to and during the sample handling in the glove box. In this way any water in the glove box is condensed on the Cu coil resulting in a very dry atmosphere. The powder samples were then repowdered and the single crystals crushed to expose new, clean surfaces. The samples were pressed into indium mounted on the sample holder and introduced into the spectrometer. No further treatment of V_2O_5 , VO_2 , or V_2O_3 was required. The indium assured good electrical contact between the sample particles and the spectrometer virtually eliminating charging effects, as can be seen for example in the V_2O_5 spectra. An improper treatment of the vanadium oxides could be detected quite

easily from the O-1s and V-2p lines. In Fig. 1(a) an O-1s line of unclean VO_2 is shown. It is obvious that the sample is strongly contaminated probably with adsorbed oxygen and water. The above mentioned treatment resulted in an O-1s spectrum shown in Fig. 1(b) which displays only a slight asymmetry towards the high-binding energy side. A doublet in the O-1s spectrum of dirty VO_2 as well as V_2O_3 was usually accompanied by a V-2p spectrum corresponding to a large amount of V_2O_5 .

FIG. 1. XPS spectrum of the O-1s region of VO_2 . (a) is "dirty" VO_2 displaying a strong peak at a position corresponding to water. (b) a "clean" sample showing only a small asymmetry.

The V foil was polished in the glove box and argon ion etched *in situ* in the spectrometer. A succession of etching and heating to 600 °C was found to reduce the oxygen content to a tolerable level. The oxygen remaining in the sample amounted to about an equivalent of 0.7 monolayers of VO as could be determined from the relative intensity of the O-1s and V-2p peaks.

In addition to monitoring the O-1s line the carbon contamination was checked and for the measurements reported here the C-1s line was in all cases less than 15% of the V-2p intensity.

To further check the composition of the samples we determined the area of the O-1s and V-2p^{3/2} peaks for all samples. Because of the large differences in the linewidths for the various samples the areas under the peaks, obtained by fitting the x-ray satellite and background corrected peaks¹⁶ to partial Gaussian and Lorentzian line shapes, were used. The results of the O-1s to V-2p area ratios are 0.98, 0.80, and 0.61 for V₂O₅, VO₂, and V₂O₃, respectively. These ratios are consistent with the chemical composition and result in a O-1s to V-2p photoelectron cross section of 0.40 in good agreement with the value of 0.45 from Scofield's¹⁷ calculations.

IV. RESULTS AND DISCUSSION

The results and discussion will be split up into three corresponding regions of the spectra; core lines, valence bands, and Auger spectra. All of the spectra shown have been corrected for scattered electrons and where applicable, x-ray source satellites. The procedure for this is described in a previous paper.¹⁶ All binding energies are given relative to the Fermi level without any correction for charging.

A. Core lines

In Fig. 2 are shown the V-2p and O-1s core lines for V₂O₅, VO₂, V₂O₃, and V metal. These lines have been fitted with partial Lorentzian and Gaussian line shapes. The peak positions and widths at half maximum of some of the core lines are given in Table I.

FIG. 2. XPS spectra of the V-2p and O-1s region. (a) indicates the 2p^{3/2} peaks and (b) indicates the 2p^{1/2} peaks.

TABLE I. Binding energies and widths of core lines and the valence bands of the materials studied. All values are in electron volts and referenced to the Fermi level.

Material	Temperature (K)	O-1s		O-2s	O-2p	V-2p ^{3/2}		V-2p ^{1/2}		V-3p	V-3d
		Binding Energy	Width	Binding Energy	Binding Energy	Binding Energy	Width	Binding Energy	Width	Binding Energy	Binding Energy
V ₂ O ₅	273	529.8	1.7	21.5	5.6	516.9	1.6	524.3	3.7	42.1	
VO ₂	273	529.9	1.8	22.0	6.4	516.2	3.2	523.5	4.5	40.4	1.7
VO ₂	373	529.7	2.0	21.9	6.4	515.9	4.1	523.3	5.0	40.2	1.2
V ₂ O ₃	273	530.1	1.6	22.2	6.3	515.7	4.2	523.3	4.9	40.3	1.1
V ₂ O ₃	90	530.3	1.7	22.4	6.4	515.9	3.8	523.6	5.1	40.6	1.4
V	273					512.4	2.0	519.9	2.4	37.8	1.0

For VO_2 and V_2O_3 the results for both above and below the semiconductor-metal transition temperature are given. These results have several interesting features. First of all considering the $\text{V-}2p$ binding energies, we see a systematic decrease on going from V_2O_5 to V metal as expected from the increase in the number of $3d$ and $4s$ electrons. It can be seen however that the changes are not proportional to the number of $3d$ electrons. The largest jump occurs between the metal and V_2O_3 whereas the additional removal of two $3d$ electrons in going from V_2O_3 to V_2O_5 produces a much smaller change. Although part of this could be due to the larger relaxation effects in the metal the dominant contribution is probably the Madelung energy shift in the compounds.

Another interesting feature evident from Table I is the large variation in linewidth, especially of the $\text{V-}2p^{3/2}$ and $\text{V-}3p$ lines, whereas the $\text{O-}1s$ linewidth remains almost constant. The $\text{V-}2p^{3/2}$ line is reasonably narrow for V_2O_5 and V metal, while it is very wide for VO_2 and V_2O_3 . Also, we note a distinct increase in the $2p^{3/2}$ linewidth in VO_2 and V_2O_3 upon going through the semiconductor-metal transition. This has been reported in a previous paper¹² for VO_2 in which we suggest that the broad lines are characteristic of narrow-band metals. This suggestion is consistent with the model calculations done by Hush¹⁸ in which he shows that if the Coulomb interaction between the core hole and the valence electrons is large compared to the valence bandwidth the core-level spectrum will look like that of a mixed-valence compound. If on the other hand the interaction is small compared to the bandwidth the core spectra will exhibit only one line corresponding to the average valence. In other words, we can consider the core-hole valence-electron interaction to determine the characteristic frequency Q which should be compared to the "valence fluctuation" frequency W , which in our case is the one-electron bandwidth. In the limit of large interactions ($Q \gg W$) the relative intensities of the core lines corresponding to the various "valences" will be determined by the valences occurring in an instantaneous picture of the valence-band charge distribution. As noted by Herring¹⁹ and Hubbard²⁰ the instantaneous charge distribution in a metal with negligible electron correlation effects is given by the binomial distribution

$$P(n) = \frac{m!}{(m-n)!} \frac{(1-c)^{m-n} c^n}{n!},$$

where P is the probability that an atom has n electrons, m is the maximum number of allowed electrons per atom, and the concentration of electrons is given by $m \times c$. If the electron correlation effects are important the distribution will peak more about some preferred value. For example in the Hubbard²⁰ model, in the limit of strong valence-electron—valence-electron interactions VO_2 would prefer to have

one $3d$ electron on every site and V_2O_3 would prefer to have two. We note that in the Hubbard model the peaking will occur around the average value. To illustrate this we have given in Table II the expected number of peaks in the core-level spectrum for the various limiting values of the three different interactions [the core-hole—valence-electron interaction (Q), the valence-electron bandwidth (W), and the valence-electron—valence-electron interaction (U) as in the Hubbard model]. The table has been set up assuming a $\frac{1}{2}$ filled s -like tight-binding band for the valence electrons. We see that only for $U \ll W$ will we get strong line broadening from this mechanism.

Other broadening mechanisms could also be present, like broadening due to multiplet splitting or phonons.²¹ If, however, phonons were the dominant mechanism we would have also expected the $\text{O-}1s$ lines to be like that of the $\text{V-}2p$ lines and it would be difficult to explain the narrow lines in V_2O_5 and V metal. Also the multiplet splitting expected to be present in VO_2 and V_2O_3 cannot explain the magnitude of the observed broadening. To get an idea of the size of this effect on the $\text{V-}2p^{3/2}$ linewidth we note that in the organometallic compounds $(\text{C}_2\text{H}_5)_2\text{VCl}$ with two unpaired electrons, $(\text{C}_5\text{H}_5)_2\text{V}(\text{C}_7\text{H}_7)$ with one unpaired electron, and $(\text{C}_5\text{H}_5)_2\text{V}$ with three unpaired electrons the $\text{V-}2p^{3/2}$ widths are 2.1, 1.8, and 2.3 eV, respectively.²² These widths are much less than those observed in VO_2 and V_2O_3 .

In our explanation we would expect V_2O_5 as well as V metal to exhibit narrow lines since in V_2O_5 the d band is empty and in V metal the $3d$ band is very wide so that $Q \ll W$ which results in a narrow line as seen from Table II.

The V_2O_3 $\text{V-}2p^{3/2}$ line in the metallic phase even suggests that there is some structure on the low-binding energy side. Such structure is even more evident in the $\text{V-}3p$ line shown in Fig. 3. This spectrum was obtained with monochromatical $\text{Al K}\alpha$ radiation with a width of about 0.4 eV. It is tempting to fit this line to three components as shown by the dashed curves in Fig. 3 and to interpret these in the

TABLE II. Core lines expected for various limiting values of the relevant interactions, the one-electron bandwidth (W), the core-hole—conduction-electron interaction (Q), and the on-site conduction-electron—conduction-electron interaction (U).

	$Q \gg W$	$Q \ll W$
$U \ll W$	3 lines	1 line
$U \gg W$	1 line	1 line

FIG. 3. V-3 p region of the XPS spectrum of V_2O_3 taken using an x-ray monochromator. The solid line is the computer fit to the spectrum and the dashed lines are the three components of the spectrum as discussed in the text.

same way as the 2 p lines. It has, however, been shown by Yamauchi and Miwa²³ that a large amount of multiplet splitting is expected in the 3 p lines. Detailed experiments on the 3 p lines of well characterized V^{3+} and V^{4+} compounds have not, to our knowledge, been reported. Such studies are being carried out on some organometallic compounds and we will have to wait for these results before the consequences of the multiplet splitting on the 3 p line shape are known.

From the broadening of the 2 p lines in VO_2 and V_2O_3 we conclude that the electron-electron interaction in the 3 d band is not sufficiently large to cause a Mott-Hubbard insulating ground state in which the instantaneous charge on the V ions would be equal to the average one.

Up to now we have concentrated mainly on the V-2 $p^{3/2}$ lines. We note from Table I that the V-2 $p^{1/2}$ linewidths do not show the same behavior. Although, as discussed recently²⁴ the 2 $p^{1/2}$ line is expected to be wider than the 2 $p^{3/2}$ line because of Coster-Kronig transitions, we cannot explain the large variation in the differences in these two linewidths for the materials studied. Also as can be seen in Fig. 2 the V-metal 2 p lines are quite asymmetric. This is most likely a result of many-body effects as discussed by Mahan²³ and Nozieres and Dominici.²⁵

B. Valence bands

In Fig. 4 we show the valence-band region of the materials studied. We note the appearance of a low-binding energy peak for VO_2 and V_2O_3 as expected because of the occupation of the d band. The occu-

FIG. 4. Valence-band region of the XPS spectra. The spectra of VO_2 and V_2O_3 are of the metallic phase.

ried d -band width corrected for the x-ray source amounts to about 1.2 eV for VO_2 and 1.4 eV for V_2O_3 in the semiconducting phases.

There has been some question as to what one is really measuring in the valence-band spectra of the transition-metal oxides. According to Wertheim²⁶ and Eastman and Freeouf²⁷ the x-ray photoelectric cross section for 3 d electrons is much larger than that for O-2 p electrons and in their papers they argued that a large part of the valence-band region is actually due to the d band. In the vanadium oxides the situation is also not clear although there are only one or two V-3 d electrons as compared to six O-2 p electrons.

According to cross-section calculations of Scofield¹⁷ we would expect the V-3 d to O-2 p intensity ratio to be about 1:2 for V_2O_3 (after correcting Scofield's O-2 p cross section for an extra two O-2 p electrons in O^{2-}). This would indicate that the broad peak centered at about 6 eV is also largely of V-3 d character. These calculations were, however, done for free O and V. Especially for oxygen we expect the O^{2-}

outer $2p$ wave functions in a compound like VO_2 to be considerably different from the free atom because of the large $\text{O-}2p$ – $\text{O-}2p$ overlap in these compounds. The core orbitals and $\text{V-}3d$ orbitals are expected to change little so that the conclusions reached from $\text{O-}1s$ and $\text{V-}2p$ intensities mentioned above are still valid. To obtain an experimental determination of the $\text{O-}2p$ cross section we studied Al_2O_3 . This is expected to be a quite ionic compound and even if there is some $\text{Al-}3p$ character in the $\text{O-}2p$ region the cross sections are expected to be comparable. From the Al_2O_3 results we found the $\text{O-}2p$ to $\text{O-}2s$ area ratio to be 0.57 ± 0.05 . This is considerably larger than the value found by Scofield (0.24 for O^{2-}), and is in our opinion a more suitable value to use in analyzing the vanadium oxide results.

The valence band of the vanadium oxides has been split into two regions. The broad portion centered around 6 eV ($\text{O-}2p$) and the narrow low-intensity region centered around 1 eV ($\text{V-}3d$). In Table III the intensity ratios $\text{O-}2p$ to $\text{O-}2s$ and $\text{V-}3d$ to $\text{O-}2s$ for V_2O_3 are listed together with the values determined from Scofield's¹⁷ calculations and those obtained from the Al_2O_3 results. We see that using the Al_2O_3 $\text{O-}2p$ to $\text{O-}2s$ ratio the broad region of the spectrum must indeed be of mainly $\text{O-}2p$ character. The narrow part centered around 1 eV must then be of mainly $\text{V-}3d$ character. For the $3d$ electrons we expect Scofield's¹⁷ calculations to be applicable even in the vanadium oxides since the $3d$ wave functions will not be very much different from those of the free ion. From Table III we see that taking the Al_2O_3 result and the calculated $3d$ cross section we obtain close to two $3d$ electrons in the $\text{V-}3d$ region of the spectrum as expected for V_2O_3 . For VO_2 the relative intensity in the $3d$ region of the valence-band spectrum is very close to $\frac{1}{2}$ of that for V_2O_3 corresponding, therefore, to one $3d$ electron in VO_2 as expected. Since we find the relative cross section per $\text{O-}2p$ electron ($\text{O-}2p$ to $\text{O-}2s \approx 0.08$) to be the same as that for $\text{V-}3d$ electrons ($\text{V-}3d$ to $\text{O-}2s \approx 0.08$) we cannot from these results obtain the amount of $\text{V-}3d$ character in the $\text{O-}2p$ region of the spectrum. Important to note, however, is that the broad region of the spectrum is mainly of $\text{O-}2p$ character.

TABLE III. Comparison of the measured and calculated relative photoelectron cross sections.

	Measured V_2O_3	Calculated ^a	Measured Al_2O_3
$\text{O-}2p/\text{O-}2s$	0.60	0.21	0.57
$\text{V-}3d/\text{O-}2s$	0.12	0.10	

^aTaken from the calculations in Ref. 17.

In Fig. 5 we show the valence-band region for VO_2 and V_2O_3 above and below the semiconductor-metal transition. As reported previously for VO_2 ¹² we find a gap in the semiconductor phase of about 0.4 eV. These spectra agree well with those found by Wertheim *et al.*²⁸

We also find a band gap for V_2O_3 in the semiconducting phase of ≈ 0.35 eV. Honig *et al.*²⁹ did not observe any change in the core line spectra on going through the semiconductor-metal transition. They did not, however, observe the $\text{V-}3d$ band below the transition because of a large background. The positions and widths of the core lines indicate that their sample was strongly contaminated with V_2O_5 on the surface. In addition to the opening of a gap at E_F we also note a decrease in the d -band width on going to the semiconducting phase. The gap in V_2O_3 is considerably larger than that determined by optical measurements.³⁰ This may be due to the nature of the measurements made since in XPS the sudden removal of an electron from the d band need not leave the system in the $(N-1)$ -electron ground state especially if electron correlation effects are important.

One can compare the d -band part of the V_2O_3 spectrum in the metallic phase to band-structure calculations of Ashkenzai and Chuchem.³¹ We find good agreement as far as the width of the band is concerned as well as some structure appearing at about 1.5 eV below the Fermi level.

FIG. 5. Valence-band region of VO_2 and V_2O_3 . The solid line is in the metallic phase and the dashed line in the semiconducting phase.

C. Auger spectra

As we pointed out recently³² one can directly obtain the on-site electron-electron interaction from a combination of Auger and photoelectron spectroscopy. However, for vanadium oxides we also mentioned that the $L_{23}M_{45}M_{45}$ Auger spectrum, corresponding to a final state with two holes in the $3d$ band, would be largely masked out by the very intense $KL_{23}L_{23}$ oxygen Auger spectrum.³¹ A more careful study of this region and a comparison with the Auger spectrum of V metal showed that it is quite impossible to separate the $KL_{23}L_{23}$ oxygen Auger spectrum from the $L_{23}M_{45}M_{45}$ spectrum of vanadium in the oxides. The Auger spectra have nonetheless proven to be quite interesting. In Fig. 6 we show the Auger spectra of oxygen $KL_{23}L_{23}$, KL_1L_{23} , KL_1L_1 , and vanadium $L_{23}M_{23}M_{45}$, $L_{23}M_{45}M_{45}$ for V, V_2O_3 , VO_2 , and V_2O_5 . We see that the $KL_{23}L_{23}$ transition is very strong, masking out the $L_{23}M_{45}M_{45}$ V Auger transition which in the oxides will be even less intense than in V metal.

In Table IV the kinetic energies of the Auger electrons corresponding to the transitions marked in Fig. 6 are listed. Of special interest is the $L_{23}M_{23}M_{45}$ Auger transition. A magnified view of this part of the spectrum is shown in Fig. 7(a) for the materials studied. The average Auger energy (E_k) depends on the binding energies of the $2p$ (E_{2p}), $3p$ (E_{3p}), and $3d$ (E_{3d}) electrons according to

$$E_k = E_{2p} - E_{3p} - E_{3d} - U(3p, 3d) ,$$

where $U(3p, 3d)$ is the average $3p-3d$ on-site Coulomb interaction as it occurs in the material (i.e., all relaxation effects are included). In Fig. 7(a) the energy scale is shifted according to the photoelectron binding energies, so that the peaks will be centered around $U(3p, 3d)$ (plotted is the intensity versus $E_{2p} - E_{3p} - E_k$).

There are three components in this spectrum. The low-intensity peak on the low U_{eff} side in Fig. 7(a) is probably due to an oxygen KL_1L_1 transition as indicated in Fig. 6. Its intensity decreases in going from

FIG. 6. Most prominent O and V Auger lines obtained using x-ray excitations.

V_2O_5 to VO_2 to V_2O_3 as expected from the oxygen content.

In what follows we will consider all the structure to result from the L_3 core hole. Although Auger lines originating from the L_2 hole could also be present these will be at least a factor of 2 lower in intensity and probably strongly suppressed because of Coster-Kronig transitions. The absence of any structure corresponding to an L_2 originating transition in V metal suggests that it is reasonable to neglect these in the interpretation of the oxides.

TABLE IV. Auger kinetic energies for some of the peaks marked in Fig. 7.

Material	O $KL_{23}L_{23}$	O KL_1L_{23}	O KL_1L_1	V $L_{23}M_{23}M_{45}$		V $L_{23}M_{45}M_{45}$
				A	B	
V_2O_5	513.4	493.3	479.7	...	467.6	
VO_2	513.0	493.0	477.6	473.3	468.5	
V_2O_3	513.0	493.1	...	473.0	467.0	
V	...	...	...	472.5	...	510.2

FIG. 7. V- $L_{23}M_{23}M_{45}$ region of the Auger spectra expanded to show the two regions marked *A* and *B*. For comparison also the valence-band regions of the XPS spectra are shown in (b).

Aside from the KL_1L_1 peak in the oxides we see considerable changes in the shape of the Auger spectrum upon going from V to V_2O_5 . In general we can split this spectrum (aside from the KL_1L_1 transition) into two regions, one centered at about 1 eV (*A*) and the other at about 6 eV (*B*). We see that in the metal only *A* is present and in V_2O_5 *B* is dominant while VO_2 and V_2O_3 exhibit spectra in between these extremes. In Fig. 7(b) we have shown the valence-band region of the photoelectron spectra. Upon comparing these the interpretation of the Auger spectra becomes quite clear. The peak marked *A* originates from the *d* band close to the Fermi level which is not occupied in V_2O_5 and the peak marked *B* originates from the O-2*p* position of the valence band which is not present in V metal.

The reason for the two peaks can be understood as follows. The Auger transition matrix elements result

from Coulomb interactions and are of the form

$$\int \psi_{2p}(r_1)\psi_k(r_2) \frac{1}{|r_1-r_2|} \psi_{3p}(r_1)\psi_x(r_2) d\tau,$$

where ψ_k is the Auger-electron wave function and ψ_x is in our case a valence-band wave function which will be of partial V-3*d* and O-2*p* character. For O-2*p* character one speaks of an interatomic Auger transition,³³ whose matrix elements squared are estimated to be a factor of 10^3 lower³⁴ than the intra-atomic Auger transitions and are therefore probably negligible in our spectra. It is, however, also expected that the O-2*p* region of the valence band contains considerable V-3*d* character because of covalent bonding. We then in general write $\psi_x = a\psi_{2p} + b\psi_{3d}$ where for the 2*p* region of the spectrum $a \gg b$ and for the 3*d* region $b \gg a$. The Auger intensity will be proportional to $b(E)^2$ with b taken to be energy dependent. This shows that the Auger spectrum ($L_3M_{23}M_{45}$) samples the V-3*d* partial density of states if we can neglect interatomic Auger transitions.

In principle we could from the areas under the regions *A* and *B* determine the amount of *d* character in the O-2*p* region of the valence band. Since, however, the two peaks are very broad and because of the difficulties associated with area determinations the uncertainties are very large. To obtain a value for $|b(E)|^2$, which corresponds to the amount of *d* character in the band, the following procedure was used. The area under the O- $KL_{23}L_{23}$ Auger line was used as an internal standard for the areas of the V- $L_3M_{23}M_{45}$ Auger lines. The $L_3M_{23}M_{45}$ region was fit to the sum of two lines corresponding to the regions *A* and *B* in Fig. 7. Since *A* corresponds to the V-3*d* band the area under it will correspond to one 3*d* electron in VO_2 and two in V_2O_3 . In this way we can obtain the relationship between the area and the number of *d* electrons. Doing this we obtain 2.5, 1.6, and 1.1, 3*d* electrons per V ion in the O-2*p* region of the valence band in V_2O_5 , VO_2 , and V_2O_3 , respectively. Although there may be a large error in the absolute values the trend in going from V_2O_5 to V_2O_3 is as expected in that it shows an increasing covalency with oxidation state. It is interesting to note that the total *d* occupancy is nearly constant for these compounds; 2.5, 2.6, and 3.1 for V_2O_5 , VO_2 , and V_2O_3 , respectively, and is close to the V-metal value of 3.

The region marked *C* in Fig. 6 in the oxygen KL_1L_{23} region is probably from the oxygen 2*p* character in the vanadium 3*d* band. The intensity of this part of the spectrum is however too low compared to the background to carry out an analysis as described for the vanadium $L_{23}M_{23}M_{45}$ region of the spectrum. The observation that there is little O-2*p* character in the occupied part of the 3*d* band is consistent with

TABLE V. Measured and calculated values of the average Coulomb interactions obtained as described in the text. All values are in electron volts.

Material	Temperature (K)	Measured U		Free-ion calculation $V\ 3d - V\ 3p$	$O\ 2p - O\ 2p$	$O\ 2p - O\ 2s$	$V\ 3p - V\ 3d$
		$O\ 2p - O\ 2p$	$O\ 2p - O\ 2s$				
V_2O_5	273	5.2	9.4		15.2	15.9	23.15
VO_2	373	3.7	8.1	1.2	15.2	15.9	22.66
V_2O_3	273	4.3	8.5	1.3	15.2	15.9	21.56 (3F)
V metal	273			1.1	15.2		20.35 (3F)

band-structure calculations on VO_2 and with the idea that the covalent bonding is most important for the higher-lying unoccupied " e_g " states.^{8,35}

As mentioned above we can also determine the on-site Coulomb interactions from the Auger and XPS spectra. These are listed in Table V, together with the ionic Coulomb integrals from Clementi³⁶ and Watson³⁷ for various configurations for vanadium and O^{2-} . As in the transition metals¹⁶ we see that these Coulomb interactions are strongly reduced from the free-ion values. This strong reduction is partly due to atomic relaxations (about 6 eV for vanadium) and to a large extent due to polarization of the outer valence electrons of the material. For the vanadium oxides we cannot determine the $V\ 3d-3d$ Coulomb interaction directly because of the interference of the $O\ KL_{23}L_{23}$ transition. However from a study of the $3d$ transition metals¹⁶ it is found that the average $3p-3d$ Coulomb interaction is always larger than the $3d-3d$ Coulomb interaction. We can therefore place an upper limit on $U(3d,3d)$ of 1.3 eV which is very close to the upper limit found by Smothers and Doniach³⁸ using optical measurements and semi-empirical calculations. We can do a little better than just obtain an upper limit if we assume that $U(3p,3d) - U(3d,3d)$ is the same for the oxides as for metal. In the metal the $L_{23}M_{45}M_{45}$ transition can be measured as seen in Fig. 6. The Auger kinetic energy is also given in Table IV. Using the $2p$, $3p$, and $3d$ binding energies in Table I we find $U(3p,3d) = 1.1$ eV and $U(3d,3d) = 0.4$ eV, a difference of 0.7 eV. Using this difference for VO_2 and V_2O_3 we find a $3d-3d$ Coulomb interaction of 0.5 and 0.6 eV, respectively. Although the uncertainties in these values are quite large, $\approx \pm 0.5$ eV, the Coulomb interaction is less than the one-electron bandwidth but perhaps comparable to it. These materials should therefore not be treated in either the one-electron band limit or in the strongly correlated limit. Even if the Coulomb interaction is only 0.5 eV it is still comparable to structure in the $3d$ band density of states, which as pointed out by Ashkenazi and Weger,³⁹ will lead to strong correlations in those regions where peaks occur in the density of states.

In addition to the average Coulomb interaction as just discussed we also need information concerning the exchange interactions to describe the properties of these materials, especially since we concluded that the Coulomb interactions were not dominant as compared to the one-electron bandwidth. Knowledge of the exchange interactions is especially important for V_2O_3 since it exhibits localized magnetic moments below the transition temperature and in fact orders antiferromagnetically. Castellani *et al.*⁴⁰ have described this behavior by suggesting a strong Hund's rule exchange coupling of the electrons in the lower e_g band. Although we cannot obtain this exchange interaction from these measurements there is strong evidence from other materials that the exchange interaction is not strongly reduced from the free-ion values. From our study of Cu, Zn, Ga, and Ge (Ref. 16) we determined the Slater-type integrals F^0 , F^2 , and F^4 . We found that although F^0 was strongly reduced from the free-ion value as mentioned above, F^2 is reduced by only about 7% and F^4 by about 15%. If we consider one electron in a $d_{3z^2-r^2}$ and one in the $d_{x^2-y^2}$ orbitals the Coulomb interaction would be given by $F^0 - \frac{4}{49}F^2 + \frac{6}{441}F^4$ and the exchange interaction by $\frac{4}{49}F^2 + \frac{15}{441}F^4$. Reducing F^2 by 7% and F^4 by 15% from the free-ion value we obtain an exchange interaction of 1.0 eV for the d^2 and 0.9 eV for the d^3 configuration. This indicates that the atomic exchange interactions are indeed very important in VO_2 and V_2O_3 especially since the bandwidths are of the same order of magnitude. Usually one has, in model calculations using a Hubbard²⁰ Hamiltonian, assumed that both the Coulomb and exchange interactions are reduced by about the same factor (about 10) from the free-ion values. From our work on the transition metals, however, the exchange interaction should be taken as close to the free-ion value and only the average Coulomb interaction should be strongly reduced. Using the above mentioned exchange interaction it is quite reasonable to expect a large local moment on the vanadium ions in V_2O_3 since the exchange is of the same order of magnitude as the bandwidth.

V. CONCLUSIONS

We have shown that both VO_2 and V_2O_3 display very wide core lines in the XPS spectra relative to those of V_2O_5 and V metal. We show that this can be explained if the core-hole-conduction-electron interaction is large or at least comparable to the one-electron bandwidth and that electron correlation effects in the $3d$ band are not too large. The valence bands in both the metal and semiconductor phases of VO_2 and V_2O_3 are quite narrow exhibiting a gap of several tenths of a volt in the semiconductor phase. The Auger spectra show considerable structure which is attributed to the $3d$ character in the O- $2p$ region of the valence band and which is the largest for V_2O_5 as expected. From these results it is shown that the partial $3d$ density of states can be obtained from a detailed Auger spectroscopy study. We also obtain the $3p$ - $3d$ and $3d$ - $3d$ average Coulomb repulsion and show that the $3d$ - $3d$ average Coulomb repulsion is

less than the one-electron bandwidth which is consistent with the broadening observed in the $2p$ linewidths. Although we find that the Coulomb interaction is less than the one-electron bandwidth this does not mean that it can be neglected. In fact both the average Coulomb interaction and the exchange are of the same order as the bandwidth indicating that both VO_2 and V_2O_3 are examples of intermediate correlation for which there is no satisfactory theory available.

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