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Differential reflectance spectra and band structure of V_2O_3

P. Shuker and Y. Yacoby
Microwave Division, The Racah Institute of Physics, The Hebrew University, Jerusalem, Israel

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Polarized measurements of the reflectance and temperature-modulated reflectance spectra of V_2O_3 in the range of 0.5–5.8 eV are reported. The experimental results strongly support the level scheme of Goodenough and are in good agreement with the theoretical model of Ashkenazi and Chuchem, provided the energy gaps between valence and conduction electrons are increased uniformly by about 0.8 eV. The over-all width of the $3d$ T_{2g} band is found to be ~ 2.5 eV and the gap between the $2p$ valence level and the Fermi level is about 3.75 eV.

INTRODUCTION

In this work we report the results of differential optical measurements on metallic V_2O_3 and analyze them in terms of the complicated band structure of this material. The interest in this material emerges from its phase transitions. V_2O_3 is an unsaturated transition-metal oxide. There are two $3d$ electrons in the conduction band; thus, according to the simple band theory, this material should be a metal. Experiments show that V_2O_3 is a paramagnetic metal at room temperature, but at 150 K it undergoes a first-order phase transition to an antiferromagnetic semiconductor with a change of about seven orders of magnitudes in electrical conductivity.[1] There is also a change in the lattice structure at the phase transition, from a hexagonal lattice in the metallic state to a monoclinic lattice in the insulating state.[2] At a temperature of about 550 K, V_2O_3 undergoes another second-order phase transition.[3]

Several models have been proposed to explain the first-order phase transition. Some models are based on electron correlation as a reason for the phase transition. A phenomenological theory of this phase transition was first proposed by N. F. Mott.[4] M. Weger applied the exitonic model to V_2O_3.[5] Other models explain the phase transition as due to lattice distortion. Adler and Brooks[6] calculated a thermodynamic model for such a transition. Another proposal based on lattice distortion was given by Goodenough.[7,8] The second-order phase transition was explained by McWhan *et al*. as a Mott transition.[9] Lately Zeiger[10] has proposed a unified model of the insulator-metal transition in V_2O_3, based on the crossing of band edges.

The theories proposed so far do not provide a satisfactory microscopic explanation of the features of these phase transitions. To obtain a quantitative microscopic model, a good knowledge of the band structure is needed.

Goodenough suggested an energy-level scheme for the conduction band of V_2O_3 based on physical considerations.[8] Although this model is qualitative, it appears to represent the main results found in this study quite well. The first tight-binding calculation of the $3d$ T_{2g} conduction band has been performed by I. Nebenzhal and M. Weger.[11] They took into consideration only the V^{3+} cations. and ignored the e_σ band. An improved band-structure calculation, taking into account overlap integrals between the V^{3+} ions and the O^{2-} ion, and also the e_σ band, has been performed lately by J. Ashkenasi and T. Chuchem.[12] We shall relate to this band structure in the interpretation of our experimental results.

Experimental investigation of the band structure can be of great help in obtaining a detailed and reliable band-structure scheme. However, only few optical measurements have so far been done of V_2O_3. Fischer measured the absorption and emission spectra of soft x rays.[13] From the absorption band it seems that the overall width of the $3d$ band is about 4 eV. Four peaks appear on the absorption band which can be interpreted as peaks in the density of states. J. M. Honig *et al.* measured the x-ray photoelectron spectrum.[14] According to their results the overall width of the full part of the d band is about 2 eV and the gap between the valence and the conduction bands is about 1 eV.

Both transmittance[3] and reflectance[15] spectra of V_2O_3 have been taken. These measurements show large differences between the spectrum of the metallic and insulating phases of V_2O_3, especially below 1 eV. Unfortunately they fail to provide any information about the band structure because of their structureless character above 1 eV. Electroreflectance[16] and thermoreflectance[17] spectra of V_2O_3 also have been published. These spectra exhibit much more structure than the ordinary spectra, yet negligible efforts have been made to relate these spectra to band structure. The electroreflectance spectra[16] are very sensitive to the dc electric field, and the authors explained this fact as a phase transition induced by the electric field. However, it seems that the electric field is too complicated a parameter to use, since one has to know the penetration depth of the electric field into the metal and its effect on the phase transition. We have chosen to use the thermoreflectance technique[17] because of its simplicity. In the following section we describe briefly the experimental setup. Following that we present the polarized thermoreflectance spectra (TR) and compare them with the derivative of the reflectance spectra with respect to photon energy (PR). Finally, we discuss the experimental spectra in terms of the theoretical band structure.

EXPERIMENTS

Differential reflectance measurements on pure V_2O_3 crystal obtained from W. Paul from Harvard University have been carried out at room temperature in two polarizations parallel and perpendicular to the c axis. The crystal was cut, polished mechanically, and etched, so that the c axis lies in the reflecting plane. In the TR measurements, the heating was indirect because of the small resistance of the samples. The 100-μm-thick crystal was cemented by Boron-Nitride Pasta to a heating element made of Ge crystal. The thickness of the Ge crystal was about 200 μm, so that its heat capacity would be larger than the sample's heat capacity, but not too large to create difficulties in the modulation of its temperature. The dimensions were chosen so that the time constant of heat flow to the ends of the Ge crystal would be comparable to the period of temperature changes, namely, 0.7 sec. The ends of the Ge crystal were mounted on heat sinks made of copper. Since the sample was small compared to the heater its temperature could be considered uniform. The Ge crystal was heated by $\frac{1}{2}$ W pulses at a frequency of 1.4 Hz and unity duty cycle. In this way we got temperature amplitudes of about 10 °K.

Typical values of the ratio between the reflectivity change (due to temperature change) ΔR and the reflectivity R were about 10^{-2}. To achieve sufficient sensitivity for such measurements, we used phase-sensitive detection. The ratio $\Delta R/R$ was measured directly using an automatic gain control unit. In this unit the dc output was equal to RA (where A is the amplifier's gain), and was kept at constant value of 1 V by automatically adjusting the gain A. The ac component of the output, which was proportional to $\Delta R_0 A$, is then proportional directly to $\Delta R/R$. The scanning of wavelength was digital. To avoid errors caused by drifts in external parameters, we chose an integration time of 1 min at the most for each wavelength. A computer for averaging transients was used to store and average the results over many repetitive measurements. The signal-to-noise ratio in the visible and infrared regions was better than 50:1 but in the ultraviolet beyond 3000 Å it was down to 5:1.

The PR spectra were obtained numerically from accurate measurements of the reflectance spectra themselves. The reflectivity was measured by the same phase-sensitive detection system, using light mechanically chopped at 440 Hz. The incident and reflected intensities were measured separately by rotating the light source in a goniometric arrangement, with the sample at the center. To obtain accurate absolute reflectivity results, we were careful to measure the incident and reflected intensities with the same mask with and without the sample, and the same area on the photomultiplier. The polarization measurements were performed by using polarized light in one direction and rotating the crystal by 90°. All the measurements in the energy range from 0.5 to 5.8 eV were performed using a Perkin-Elmer E_1 monochromator. Further details on the electronic and optical setups are given in Ref. 18.

RESULTS

The thermoreflectance spectra of V_2O_3 in two polarizations are shown in Fig. 1. The unpolarized TR spectrum[17] is shown for comparison in

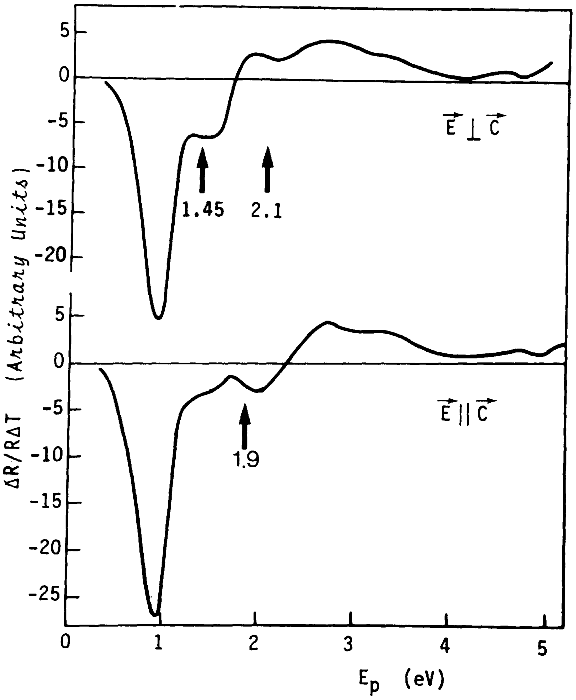

FIG. 1. Polarized thermoreflectance spectrum of V_2O_3 as a function of photon energy at room temperature.

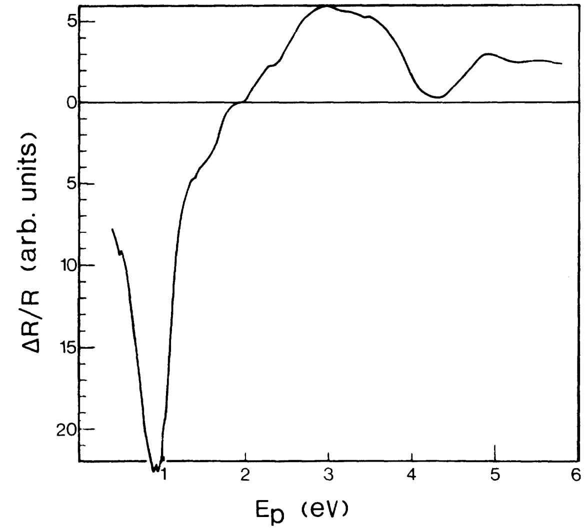

FIG. 2. Unpolarized thermoreflectance spectrum of V_2O_3.

Fig. 2. The shoulders in the neighborhood of 2 eV in the unpolarized spectrum are resolved in the polarized light measurements and appear as two differently polarized peaks in the spectra. The peak at 1.75 eV appears only in the parallel polarization, whereas the peak at 2.00 eV appears only in the perpendicular polarization. Two other peaks are partially polarized: the peak at 1.4 eV is stronger in the perpendicular polarization, whereas the peak at 3.4 eV is stronger in the parallel polarization. The peaks above 4 eV are more intense in the unpolarized spectrum. This is attributed to experimental inaccuracy in the measurements of the polarized spectra. Below 2800 Å the polarizer itself begins to absorb significantly, consequently the stray light intensity becomes about as strong as the reflected light. Thus the magnitude of $\Delta R/R$ in this region of the spectrum is distorted.

The calculated derivative of the reflectance spectra of V_2O_3 with respect to photon energy in two polarizations is shown in Fig. 3. The only difference between the TR and the PR spectra is in the region of 3 eV. The unpolarized broad negative peak appears only in the PR spectra at 2.5 eV, while an unpolarized broad positive peak appears only in the TR spectra at 2.75 eV. There is a tiny partially polarized shoulder at 3.4 eV in the TR spectra, which does not appear in the PR spectra. On the other hand, the intense unpolarized peak in the PR spectra at 3.75 eV does not appear at all in the TR spectra.

DISCUSSION

The spectrum above 1.2 eV is attributed to one-electron transitions. Thus the imaginary part of the dielectric constant ϵ_2 gives a fairly good idea of the joint density of states of the crystal. In general, particularly sharp changes in ϵ_2 appear at Van Hove critical energies, for which $\vec{\nabla}_{\vec{k}}[\omega_0(\vec{k})-\omega_v(\vec{k})]=0$. [$\omega_c(\vec{k})$ and $\omega_v(\vec{k})$ are the energies of conduction and valence electrons, respectively.] Peaks in ϵ_2 correspond approximately to saddle or fluted points in $\omega_c(\vec{k})-\omega_v(\vec{k})$. ϵ_1 is related to ϵ_2 through the Kramers-Kronig relations. Thus ϵ_1 also undergoes sharp changes at the Van Hove critical energies and so does the reflectivity. Differential measurements have generally sharp peaks at Van Hove critical points. Thus they allow, in general, an accurate determination of energy gaps at these points.

The electronic energy bands in V_2O_3, which originate in d orbitals are generally rather flat. Because of the large number of atoms per unit cell most of the bands, especially the T_{2g} bands, greatly overlap each other. This gives rise to a very smooth reflectivity spectrum and also shows up in the theoretically calculated joint density of states. Differential measurements are therefore unable to reveal energy gaps at Van Hove singularities and they were used here only as a tool to enhance our ability to see the structure in the spectra.

The temperature dependence of the dielectric constant is due either to the shift of energy bands with temperature, or to changes of the broadening parameter. If the main contribution of temperature changes is shifting the energy bands, then

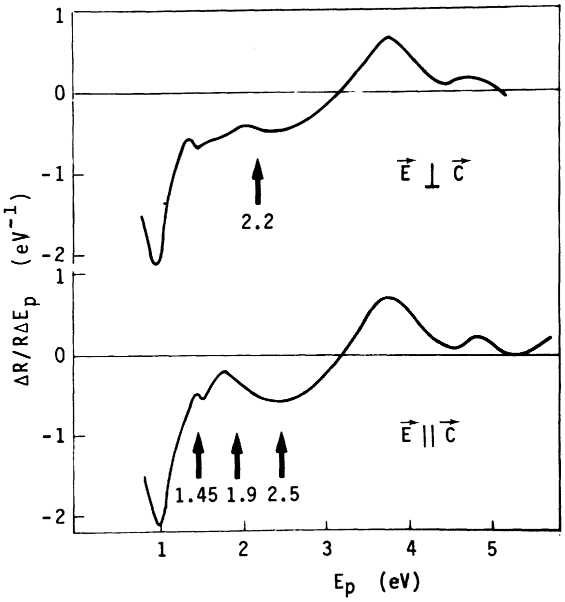

FIG. 3. Derivative of the reflectance spectrum with respect to photon energy as a function of photon energy.

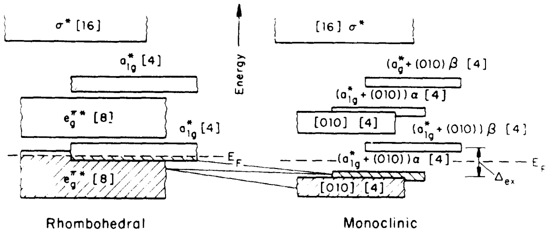

FIG 4. Schematic band diagram of V_2O_3 according to Goodenough (Ref. 8).

$$\frac{\Delta\epsilon_2}{\Delta T} = \frac{\Delta\epsilon_2}{\Delta E_0}\,\frac{\partial E_0}{\partial T} = \frac{\partial E_0}{\partial T}\,\frac{\Delta\epsilon_2}{\Delta(\hbar\omega_p)}\,, \qquad (1)$$

where E_0 is the energy difference between the bands which are involved in the transition, and $\hbar\omega_p$ is the photon energy. Therefore the TR spectrum and the PR spectrum should be similar. There is a great similarity between the measured TR spectrum and the PR spectrum as can be seen from Figs. 1 and 3. Thus we can conclude that temperature changes affected mainly the energy gaps.

The most intense umpolarized peak at 0.95 eV which appears in all the spectra was attributed to plasma oscillations.[19] The main reason for this interpretation was as follows: The contribution to conductivity from *interband transition* must show an increase with increasing photon energy in both metals and semiconductors before showing a decrease in the conductivity resulting from a decrease in the joint density of states. Barker's conductivity measurements[15] of V_2O_3 at room temperature show no increase before 1 eV, where there is a strong decrease in conductivity, on the other hand such an increase clearly shows up in the semiconducting state at 80 °K. We can therefore conclude in agreement with Barker that the negative peak at 0.95 eV is not a result of a decrease in *interband transition* probability, but a *plasma edge.* The line shape of the peak at 0.95 eV is consistent with the theory. The best fit of the theoretical line shape with the PR spectrum is obtained for the following values:

$$\omega_p = 1.08_{\text{eV}}, \quad \omega_T = 0.53_{\text{eV}}, \quad \epsilon_0 = 24\,,$$

where ω_p is the plasma frequency, ω_T is the collision frequency, and ϵ_0 is the high-frequency dielectric constant. We used these values to calculate the theoretical line shape of the TR spectrum of the plasma peak, and got a good agreement between the theoretical and experimental line shapes.

The other structures which appear in the spectra are attributed to interband transitions. The valence and the conduction bands of V_2O_3 consist of oxygen $2p$ orbitals and V^{3+} $3d$ orbitals, respectively. The conduction band is partly filled. According to x-ray photoelectron measurements made by J. M. Honig *et al.*[14] on V_2O_3, the energy difference between the top of the valence band and the Fermi level is about 3 eV. Therefore, it is expected that the transition between the valence and the conduction bands will occur at energies above 3 eV. All peaks below 3 eV must be attributed to a transition within the $3d$ level. Since there are four V^{3+} ions per unit cell, the band structure is very complicated. The $3d$ conduction band splits in a cubic symmetry to a lower triply degenerate T_{2g} band and to higher doubly degenerate E_σ band. In the hexagonal symmetry the T_{2g} band splits further to the a_1 subband which contains functions directed along the a axis. Therefore the V^{3+} ions are arranged in pairs along the c axis; a_1 and e_π bands split into bonding and antibonding levels. Since the overlap of the a_1 orbitals is larger than that of e_π, the separation between bonding and antibonding levels is larger in the a_1 band than in the e_π band. The energy of these subbands cannot be predicted from symmetry considerations alone.

According to Goodenough's model, which is reproduced for convenience, in Fig. 4 the e_π bonding

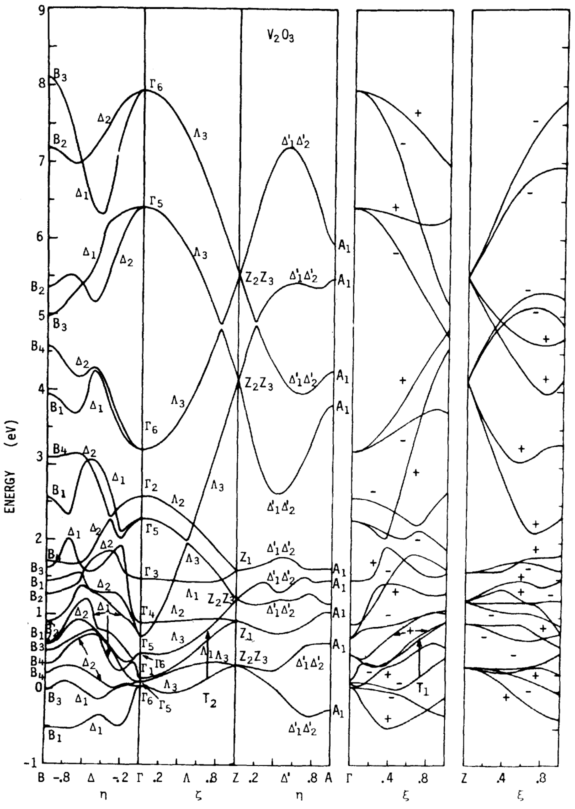

FIG. 5. Structure of the $3d$ band of V_2O_3 calculated by Ashkenazi and Chuchem (Ref. 12).

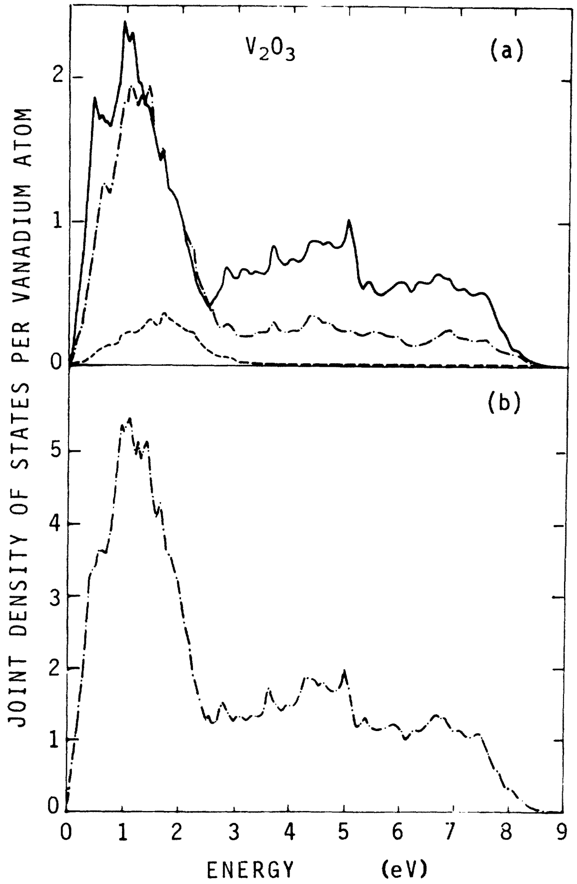

FIG. 6. Joint density of states within the $3d$ band of V_2O_3: (a) separated to a_1-a_1 transitions (dashed line), e-e transitions (full line), and e-a_1 transition (dotted-dashed line). (b) Total taken from Ref. 12.

level is the lowest level in the conduction band, whereas in Ti_2O_3 the lowest level is the a_1 bonding level. The reason for this level ordering is the anomalously large ratio between the length of the c axis and the length of the a axis (c/a ratio) in V_2O_3.

The structure of the $3d$ band according to the Ashkenazi–Chuchem calculations is given in Fig. 5. In the following we shall analyze our results for energies less than 3 eV in terms of this band-structure model. There is a sharp decrease in the theoretical joint density of states (JDS) shown in Fig. 6 at approximately 1.8 eV caused by the end of the transitions within the $3d$ T_{2g} band. It is, therefore, tempting to assign the negative wide unpolarized peak at 2.5 eV in the PR spectrum to the decrease in the theoretical JDS, namely, to transitions from the bottom to the top of the $3d$ T_{2g} band. The sign of this peak is consistent with this interpretation as can be seen from the following argument.

The relation between changes in the reflectance $\Delta R/R$ and changes in the dielectric constant is given by[20]

$$\Delta R/R = B_1\Delta\epsilon_1 + B_2\Delta\epsilon_2\,,$$

where B_1 and B_2 are functions of the dielectric constant. We calculated B_1 and B_2 from the values of the refractive index given by V. P. Zhuze *et al.* [21] According to these values $B_2 \gg B_1$ at energies greater than 1.5 eV and B_2 is positive at this energy range. Thus $\Delta\epsilon_2$ has also a negative peak at 2.5 eV which is consistent with the decrease in the JDS.

The positive wide unpolarized peak at 2.8 eV in the TR spectra is attributed to the same transition which causes the 2.5-eV peak in the PR spectrum. So according to Eq. (1), $dE_0/dT > 0$ for this transition. This fact is in agreement with low-temperature TR measurements, where this peak shifts slightly towards lower energy. Ordinarily, temperature gives rise to the broadening of bands, thus the fact that $dE_0/dT > 0$ for this transition sustains the assumption that the transition is from the bottom to the top of a band.

The theoretical band structure (Fig. 5) shows that the bands are quite narrow in the ξ and η directions, in the neighborhood of point z in the Brillouin zone. Thus the volume around this surface is expected to contribute strongly to the JDS. There are three possible transitions at the z point: from the e_π subband to the a_1, e_π, and a_1 subbands. These transitions give rise to the peaks at 0.6, 1.0, and 1.4 eV, respectively, in the theoretical JDS (Fig. 6). It can be seen, from the point-symmetry group at z, that the transition from e_π to a_1 is forbidden in the parallel polarization. Thus a plausible interpretation of the structures that appear in the experimental data can be made in the following way: The inflection point at 1.45 eV which is partially polarized in the perpendicular direction is attributed to transition around z from e_π bonding to a_1 bonding. However, in the same energy range (0.6 eV in the theoretical model), there are two additional transitions denoted by T_1 and T_2 in Fig. 5. These transitions are allowed in both polarizations and are expected to be rather strong because the bands involved are almost parallel over a large portion of the Brillouin-zone dimension. This may explain the depolarization of the experimental peak.

The parallel polarized structure at 1.9 eV is attributed to a transition from e_π to e_π at point z. The perpendicularly polarized structure at 2.25 eV is attributed to transitions from e_π to a_1 at point z. A comparison between peaks in the theoretical JDS and experimental results is given in Table I. As can be seen from Table I, the experimental values are shifted by about 0.8 eV to-

TABLE I. Comparison between the inflection point energies in the experimental differential reflectance spectra and the peaks in the theoretical joint density of states.

Transition	Theoretical value (eV)	Experimental value (eV)	Difference (eV)
T_1, T_2 $e_\pi \rightarrow a_1$	0.5–0.6	1.45	0.87–0.87
$e_\pi \rightarrow e_\pi$	1.0	1.90	0.89
$e_\pi \rightarrow a_1$	1.4	2.20	0.84
$3d\ T_{2g}$ width	1.8	2.5–2.8	0.7–1.0

wards higher energy in comparison with the theoretically predicted values. In their analysis of the theoretical results, Ashkenazi and Chuchem claim that electron correlation effects, not taken into account in their present calculation, would give rise to a more or less uniform increase of the gap between valence-and conduction-electron energies. This is in qualitative agreement with our results.

As mentioned before, transitions from the $2p$ band to the $3d$ band are expected to occur at energies greater than 3 eV. The start of interband transitions is caused by an increase in the JDS. Therefore a positive peak is expected in the differential spectrum of ϵ_2 with respect to photon energy. It is reasonable then to assign the unpolarized positive peak at 3.75 eV in the PR spectra to the onset of transitions from the $2p$ band to the $3d\ T_{2g}$ band. The partial polarized peak at 3.4 eV in the TR spectra can be attributed to the same transition. The unpolarized peaks at 4.9 and 5.5 eV can then be explained as transitions from the $2p$ band to the two a_1 subbands. The energy difference of 0.6 eV is close to the value of 0.77 eV found in the transition within the $3d\ T_{2g}$ bands. The energy-band scheme suggested here[22] is quite different from that proposed by I. Balberg. In his scheme the overall width of the $3d\ T_{2g}$ band is 1.6 eV, and is much narrower than the value found here. On the other hand, the energy difference between the $2p$ band and the Fermi level in Balberg's scheme is 3.5 eV and is in good agreement with our results. Fischer's data from absorption of soft x-rays[13] can be fitted to the suggested band structure. The shoulders on the absorption band at energies at 1.1, 1.9, and 2.9 eV can be interpreted as transitions from the Fermi level to two a_1 subbands and to an e_σ subband, respectively.

The experimental results presented here strongly support the qualitative band model of Goodenough.[8] The order of all levels at the z point which, because of the large amount of states around it can be taken as representative of the bands, is indeed e_π bonding, a_1 bonding, e_π antibonding, and a_1 antibonding. The change of the order in Ti_2O_3 indicated by Goodenough is also experimentally supported as can be seen from the following argument. The highest energy peak which is still attributed to transition within the $3d\ T_{2g}$ band (2.2 eV) is perpendicularly polarized. Thus it was attributed to an e_π bonding a_1 antibonding transition. On the other hand, the highest energy structure in Shin's data[23] in Ti_2O_3 (2.9 eV) is parallel polarized, and is therefore attributed to an a_1 bonding a_1 antibonding transition which is in agreement with Goodenough's band scheme.

SUMMARY

We have reported here experimental differential optical spectra of V_2O_3. We have measured both the temperature-modulated and wavelength-modulated reflectance spectra using polarized light. Light was polarized parallel and perpendicular to the c axis over a range from 0.5 to 5.8 eV. The experimental findings were compared to the results of x-ray fluorescence and photoemission and analyzed in view of several band-structure models suggested in the literature. We find that the width of the $3d\ T_{2g}$ bands is approximately 2.5-eV wide. The onset of transitions from the $2p$ to the $3d$ bands appears to take place above 3.75 eV. The order of bands proposed by Goodenough appears to fit the experimental results very well. According to Goodenough, bands in increasing energy order are: e_π bonding (below the Fermi level), a_1 bonding, e_π antibonding, and a_1 antibonding. The polarization of the reflectance arising from transitions from e_π bonding to the conduction bands would be: e_π bonding$\rightarrow a_1$ bonding, perpendicular polarization; e_π bonding$\rightarrow e_\pi$ antibonding, unpolarized; and e_π to a_1 antibonding, perpendicular polarization. The order of the polarized structures is indeed as predicted by Goodenough except that the first peak is somewhat depolarized. This is attributed to two unpolarized transitions denoted by T_1 and T_2 in the electron dispersion relations calculated by Ashkenazi and Chuchem.

Comparison of our results to the calculations of Ashkenazi and Chuchem shows that all structures corresponding to transitions within the $3d\ T_{2g}$ band may be understood in terms of a transition in the vicinity of point z in the Brillouin zone provided all the gaps between the valence and conduction bands are increased by about 0.8 eV. Point z is also the only point where polarization effects are expected to be strong. As pointed out, transitions T_1 and T_2 apparently also contribute to the first peak at 1.45 eV.

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