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Optical Spectra of the Intermediate Oxides of Titanium, Vanadium, Molybdenum, and Tungsten

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Optical absorption spectra have been measured for 25 transition metal oxides in systems Ti–O, V–O, Mo–O, and W–O by a diffuse reflectance technique. Each spectrum shows one or more maxima above an intense background absorption. The transition energies of the maxima vary logarithmically with the carrier concentration in accordance with Meyer's rule.

Introduction

The intermediate oxides of the transition metals titanium, vanadium, niobium, molybdenum, technetium, tungsten, and rhenium are interesting because of their electrical characteristics. Most of these oxides are semiconductors, and some show a metallic conductivity which has been associated with mobile electrons moving in narrow bands formed by either the direct overlap of $3d$-orbitals or by mixing of metal $3d$-orbitals with oxygen p-orbitals to form π^* bands. The theory of transition metal oxide conductivity has been the subject of much discussion with the most easily applied model being provided by Goodenough (*1–3*).

The optical absorption spectra of these compounds would be of value in interpreting the energy level scheme and for this reason we have examined the spectra of some 25 intermediate oxides in the systems Ti–O, V–O, Mo–O, and W–O. A few diffuse reflectance spectra of these oxides have been published. These include Ti_2O_3 by Companion and Wyatt (*4*), VO_2 by Rüdorff et al. (*5*), and some titanium and vanadium oxides (*6*, *7*).

Experimental

The oxides used in this study were prepared by reacting the appropriate metals with the highest valency oxide in correct proportion or by reacting two oxides. Reactions were carried out in evacuated sealed silica tubes at temperatures in the range of 600–900°C according to the results of previous synthesis studies. The preparation of the Magneli phases in the Ti–O system was originally described by Andersson et al. (*8*), and more recently the complete phase diagram for the system has been established (*9*, *10*). Because of the large number of titanium oxide phases, great care had to be taken to insure phase purity, and usually mixtures of Ti_2O_3 and TiO_2 were used as starting materials. The vanadium oxides were prepared by S. Kachi as part of his study of the phase diagram of the V–O system and were kindly made available by him. The molybdenum and tungsten oxides were prepared as described by Phillips and Chang (*11*, *12*). Phase purity on all specimens was checked by X-ray powder diffraction.

Spectra were obtained on a Beckman DK-2A spectrophotometer utilizing a diffuse reflectance technique. All spectra were measured relative to MgO. The absorbance axis on the spectra is defined as

$$A = \log[R(\text{MgO})/R(\text{Sample})].$$

The baseline has been translated in the figures for the sake of clarity.

Although diffuse reflectance techniques give good results for weakly absorbing materials ($\alpha \sim 1$–100) there is some question about the meaning of diffuse reflectance spectra of highly absorbing powders ($\alpha \sim 10^3$–10^5). Fochs (*13*) showed that a good measure of the absorption edge of a semiconductor

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powder could be obtained by diffuse reflectance measurements. However, Dickens et al. (*14*) found that both specular and diffuse components were present. By measuring the reflectance from pure powders diluted with MgO, they were able to separate the specular reflectance spectra of some tungsten bronzes from the diffuse reflectance spectra. Taylor (*15*), however, was unable to reproduce the dilution effect and found that the spectra of tungsten bronzes diluted with MgO differed only in intensity from the undiluted specimens.

Spectra

Spectra for the 25 pure (undiluted) oxides are shown in Figs. 1–4. The titanium system Magneli phases exhibit a single broad intense band in the visible which gradually shifts in frequency as the composition varies. Reduced rutile exhibits a band in the near ir which has been observed by a number of previous investigators. The band of Ti_2O_3 is split into two components.

The vanadium oxide spectra are rather similar, each having a single broad intense peak which shifts gradually in frequency with changing composition. The V_2O_3 has a definite second maximum on the low-frequency side of the main absorption feature.

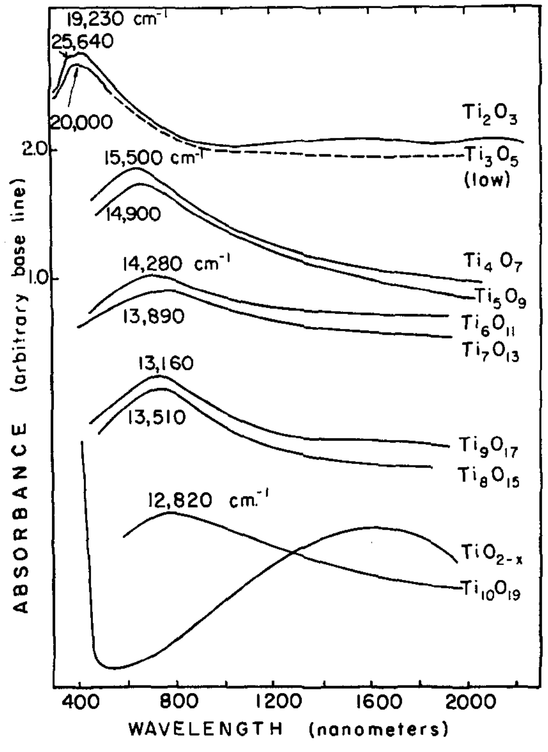

FIG. 1. Reflectance spectra of the intermediate oxides of titanium.

The molybdenum and tungsten oxide spectra have considerably sharper bands than those of the vanadium and titanium oxides, a feature which seems to distinguish the 4*d* and 5*d* electronic transitions from those in the 3*d* systems. The WO_2 has a second broad maximum in the near ir and the peak for Mo_4O_{11} is split. Beyond this the spectra are very similar to the 3*d* oxides: one main absorption band which shifts with changing composition.

Some comparison can be made with the literature. Dickens et al. (*14*) measured the reflectance spectra of $W_{20}O_{58}$ and $W_{18}O_{49}$. Their frequencies for undiluted powder specimens are in good agreement with ours. The maximum at 1600 nm for reduced rutile (Fig. 1) is in good agreement with the single

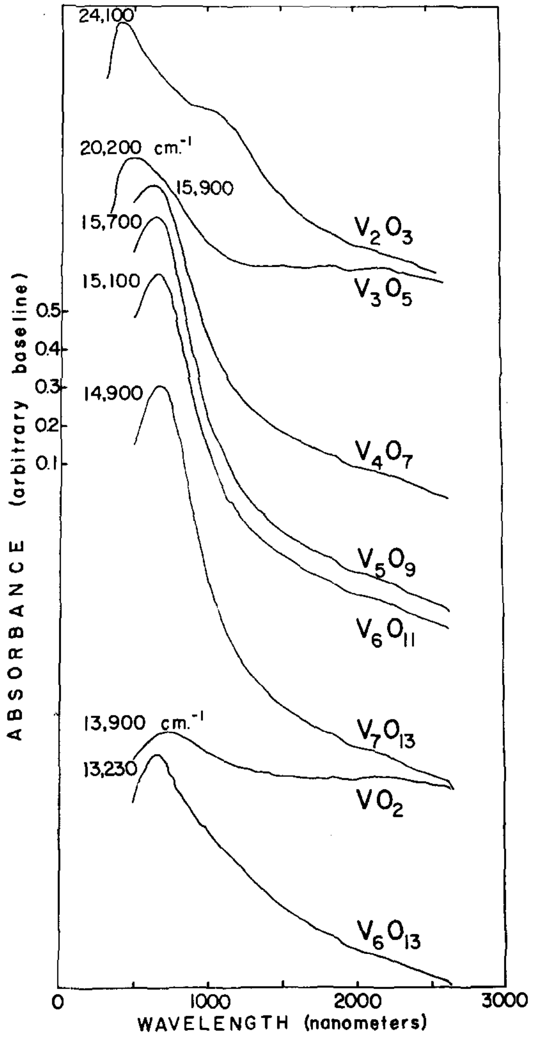

FIG. 2. Reflectance spectra of the intermediate oxides of vanadium.

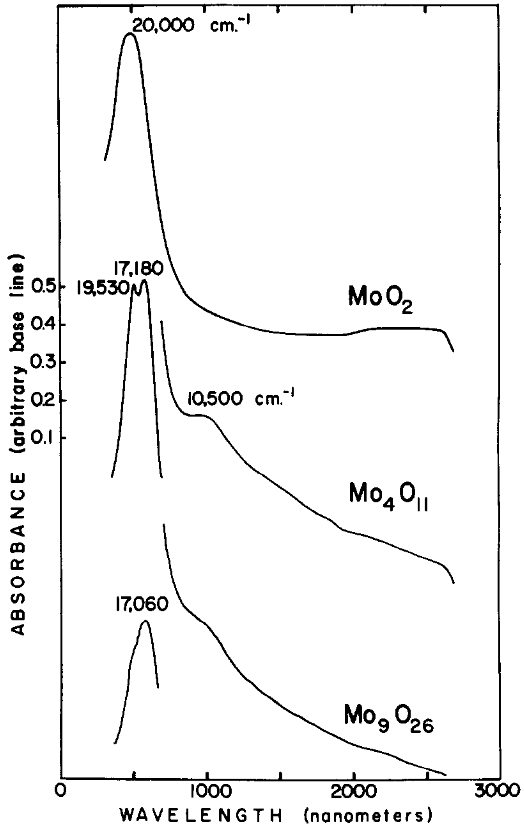

FIG. 3. Reflectance spectra of the intermediate oxides of molybdenum.

crystal transmission measurements of Cronemeyer (*16*) and Johnson et al. (*17*). However, our spectrum of VO_2, which shows a broad maximum at 13,900 cm^{-1} is not in agreement with the thin film transmission measurement of Verleur et al. (*18*), and likewise, the powder spectrum of VO_2 does not match the single crystal specular reflectance spectrum which exhibits two maxima near 10,000 and 20,000 cm^{-1}. The diffuse reflectance band does correspond in a rough way to the reflectivity minimum of the single crystal. The powder spectra of high TiO and low TiO (not shown) were found to have broad featureless maxima at 28,300 and 29,400 cm^{-1}, respectively. The band in high TiO, 3.5 eV is in rough agreement with the reflectance minima in single crystals measured by Rao et al. (*19*) and assigned to plasma resonance.

Discussion

The most obvious feature about the spectra is the systematic shift in band position with changing metal–oxygen ratio. In many oxide semiconductors, there is a relation between the conductivity and the activation energy of the form

$$\log \sigma = A + \Delta E, \qquad (1)$$

commonly known as Meyer's rule (*20*). If the band structure and the mobility of carriers do not change, then the conductivity should be directly proportional to the number of carriers. In the homologous series Ti_nO_{2n-1}, the oxygen/titanium ratio can be represented by $(2n-1)/n = 2-(1/n)$ and, if the carriers are electrons from Ti^{3+} moving in narrow d bands, the number of carriers should be proportional to $1/n$. Figure 5 shows a plot of the absorption maximum versus n for the Magneli phase series of titanium oxides with points shown for compounds between Ti_4O_7 and $Ti_{10}O_{19}$. An excellent straight line fit is obtained suggesting that the same conduction mechanism holds for this series of oxides.

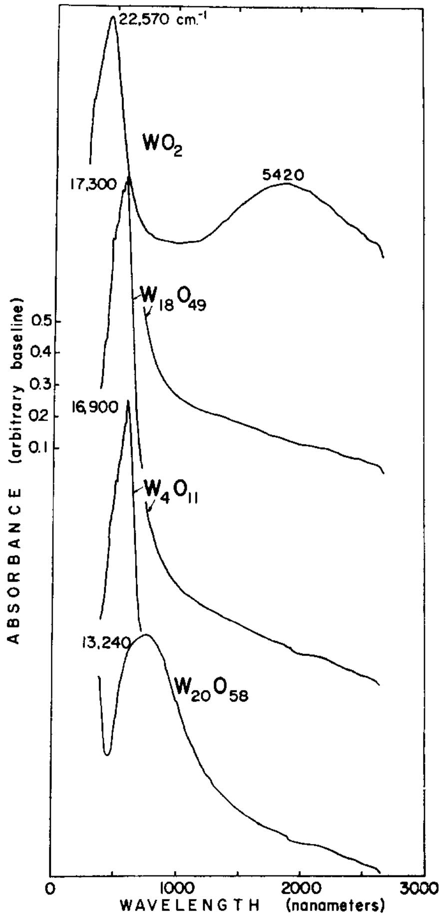

FIG. 4. Reflectance spectra of the intermediate oxides of tungsten.

More interesting is the position of the near-ir peak of reduced rutile. Porter (*9*) has shown that the

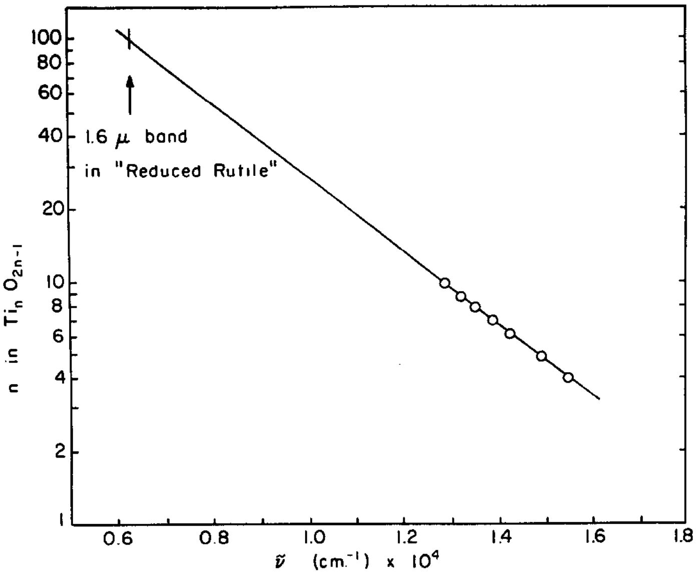

FIG. 5. Relation of the absorption maxima in the Magneli phases to that of reduced rutile.

limit of stoichiometry for reduced rutile is near $TiO_{1.99}$. If this is written as the limiting value of the Magneli phase, $Ti_{100}O_{199}$, the 6200 cm^{-1} near-ir band fits exactly on the extrapolation of the straight line in Fig. 5. A relation between the Magneli phases and reduced rutile is thus established.

Cronemeyer (*15*) found a second absorption maximum at 1.18 eV (9520 cm^{-1}), which he interpreted as the second ionization of a helium-like pair of electrons trapped in an oxygen vacancy. Cronemeyer obtained his specimens by a non-equilibrium reduction of TiO_2 in hydrogen at 600–800°C for short times. That he may have carried the reduction of his rutile below the limits of the rutile stability field and formed a high Magneli phase seems an equally likely explanation for the 1.18 eV absorption feature. This would correspond to a Magneli phase with composition $Ti_{32}O_{63}$. Bartholomew in this laboratory has prepared materials by the long-time equilibrium reduction of single crystal rutile in CO/CO_2 mixtures, which have the characteristic X-ray powder patterns of high ratio Magneli phases. A diffuse reflectance spectrum obtained on one of these materials gave a broad absorption maximum at 9700 cm^{-1}, corresponding to the composition $Ti_{36}O_{71}$. The broadness of the maxima prohibits exact analysis by this method, but it does seem clear that high ratio ordered phases may exist in the composition gap between $Ti_{10}O_{19}$ and the composition limit of reduced rutile. Anderson and Khan (*21*) by a thermodynamic argument arrive at much the same conclusion, although they place the upper limit for ordered shear structures at $Ti_{40}O_{79}(TiO_{1.975})$.

Figure 6 presents the observed band maxima as a function of the number of *d* electrons per cation. The higher members of the titanium series, the molybdenum series, and the tungsten series all plot as straight lines to within the limits of error of the

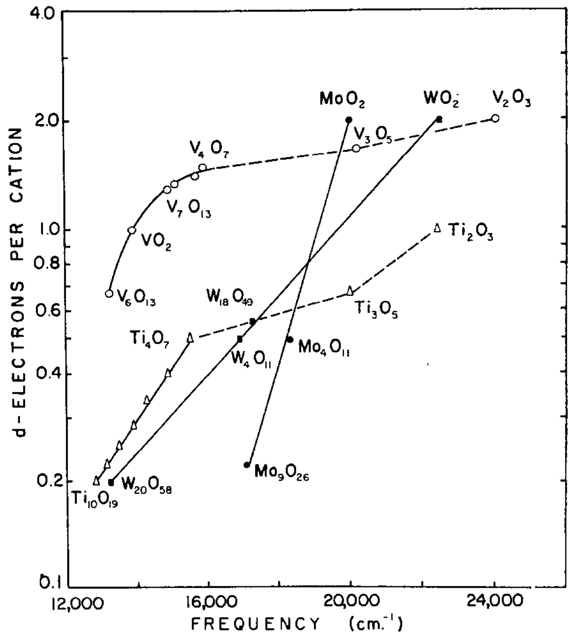

FIG. 6. Relation of number of *d* electrons to absorption band maxima.

data. Again a relationship of the Meyer's rule form is indicated if

$$n_d \sim n_c = Ae^{K\nu}, \qquad (2)$$

where n_d = number of d electrons, n_c = number of carriers, and A and K are proportionality constants.

The higher vanadium oxides do not exhibit a linear relationship for reasons unknown.

In both the titanium series and the vanadium series, there is a sharp break between the end of the Magneli phase compounds and the Ti_3O_5 and Ti_2O_3 frequencies. Goodenough (*2*) makes a distinction between his type I narrow d-band models and type II narrow d-band models. The type I model contains a narrow band formed by the direct overlap of the t_{2g} nonbonding orbitals. In type II compounds the overlap is through the oxygen ions with the formation of π^* antibonding bands. The close relationships of the titanium Magneli phases, the vanadium Magneli phases, and the molybdenum and tungsten oxides suggests a common electronic structure and all are predicted to be type II. The V_2O_3 and Ti_2O_3 should be type I, and it appears that V_3O_5 and Ti_3O_5, which have a crystal structure different from the Magneli shear structures, also belong to type I.

The explanation for the observed spectra and the frequency shift remains uncertain, in the absence of more single crystal transmission data. Dickens et al. (*14*) related the absorption maximum to a plasma frequency which they defined as

$$\nu_p' = [n_c e^2/m^* \pi(1 + \epsilon_c)]^{\frac{1}{2}}, \qquad (3)$$

where m^* is the optical electron mass, and ϵ_c is the contribution to the dielectric constant from interband transitions and lattice vibrations, and Rao et al. (*19*) used a similar expression. If the observed spectra are to be interpreted as plasma resonances the increase in frequency with increasing number of d electrons is easily understood. However, the functional dependence for the Ti, Mo, and W oxides is exponential rather than the form of Eq. (3). The agreement with known plasma frequencies is good in the case of TiO and VO_2, both known to be metallic conductors. The other alternative is that the peaks represent interband transitions. In favor of this view is the exponential dependence of frequency on carrier concentration, the relation between the Magneli phase reflection peaks and the band in reduced rutile, which was measured by transmission through a single crystal, and the increase in band sharpness in the $4d$ and $5d$ oxides. A decision between the two does not seem possible on the basis of presently available data.

Acknowledgment

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