Raman Spectrum of Semiconducting and Metallic VO_2†

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The Raman scattering spectrum of VO_2 is reported between 4.2 and 600°K. In the semiconducting monoclinic phase only sharp phonon structure is observed. The metallic rutile phase exhibits a pronounced softening and damping in the observed phonon spectrum. This evidence supports a recently proposed phenomenological mechanism for the semiconductor-to-metal transition.

Vanadium dioxide has been studied extensively in recent years because of its phase transition from semiconductor to metal at 68°C which is accompanied by a slight lattice distortion from a monoclinic structure in the semiconducting phase to the tetragonal rutile structure in the metallic phase. Most of the available information on the electronic and vibrational properties of VO_2 has been derived from the studies of electrical transport and other bulk measurements[1] which have not as yet allowed a determination either of the cause of the phase transition or of the electronic properties of both the phases. Because of the probable importance of electron-phonon interactions to these properties, the study reported here helps to fill an urgent need for observations of the lattice vibrational properties of both phases. The importance of Raman-scattering measurements is augmented by the difficulty in performing inelastic neutron-scattering measurements on VO_2 due to the large incoherent cross section of vanadium; also, the infrared measurements of the vibrational properties of the metallic phase have not been successful because of free-carrier absorption.[2]

In the high-temperature metallic phase of VO_2, the V^{4+} ions are equally spaced along the rutile c axis and the unit cell consists of two VO_2 molecules with each V^{4+} ion occupying a nearly octahedral position between six oxygen ions. The unit cell doubles in size in the low-temperature monoclinic phase and the V^{4+} ions pair such that they are no longer collinear and the alternate distance between them is 2.65 and 3.12 Å.

The phonon symmetries and their polarizations are given in Table I. The metallic rutile phase has space group $D_{4h}{}^{14}$ and four Raman-active phonons.[3] The monoclinic phase has space group $P2_1/c$ and eighteen Raman-active phonons. Our notation is such that the monoclinic screw diad axis is the rutile Y axis. The monoclinic phase has a domain structure[4] such that X and Y axes are interchanged in different parts of the crystal and XX and YY or XZ and YZ polarizations cannot be observed separately.

Since the samples are opaque at all visible wavelengths, the experiments were done in a back-scattering geometry. The light from an argon- or krypton-ion laser was focused by a cylindrical lens onto a slit-shaped region on the sample surface to minimize the heating of the sample. The crystals were x-ray oriented to obtain accurate polarization data. The detection system consisted of a double-grating spectrometer, a FW-130 photomultiplier tube, pulse-counting electronics, and digital averaging. The single crystals of VO_2 studied included samples grown by vapor transport[5] in this laboratory, flux-grown crystals obtained commercially, and some excellent quality samples grown by Guggenheim.[6] The samples were polished mechanically, in most cases, with 0.1-μm Al_2O_3. Some data obtained with natural growth faces of vapor-grown crystals and cleaved surfaces of flux-grown samples show that the polishing treatment causes no noticeable changes in the Raman data. The incident laser light was in the energy range from 2.0 to 2.5 eV which is well above the 1.0-eV plasma frequency in the metallic state and in a spectral region where the optical properties of both phases are nearly identical.[2] Therefore it is not likely that the qualitative differences

TABLE I. Raman polarizations of rutile and monoclinic phonons.

Rutile ($D_{4h}{}^{14}$)	
$1A_{1g}$	$ZZ, XX=YY$
$1B_1$	$XX=-YY$
$1B_{2g}$	XY
$1E_g$	$XZ=YZ$
Monoclinic ($P2_1/c$)	
$9A_g$	ZZ, XX, YY, ZX
$9B_g$	XY, XZ

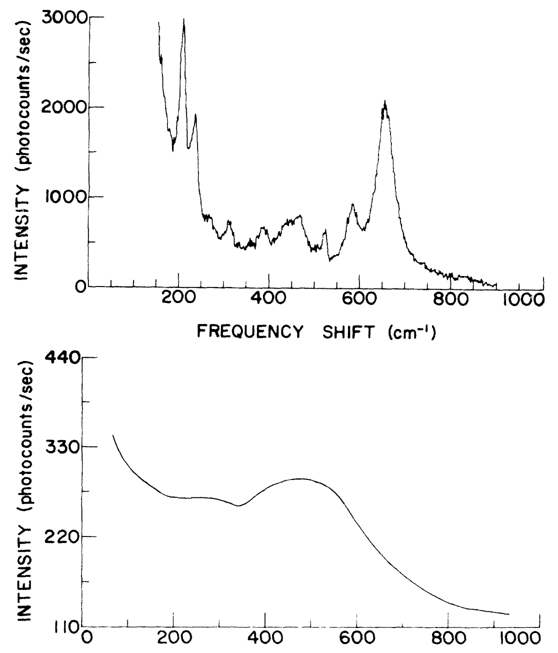

FIG. 1. Unpolarized Raman spectra of VO_2 at 300°K (upper trace) and 375°K (lower trace).

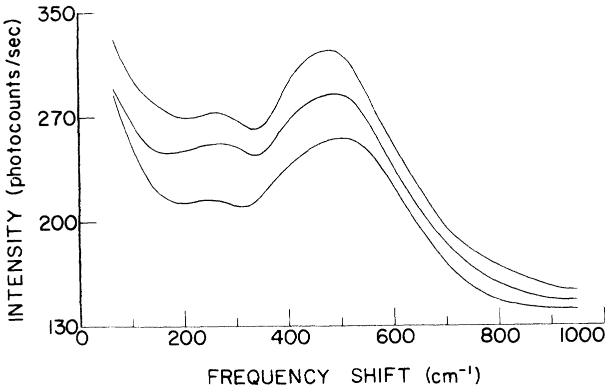

FIG. 2. Unpolarized Raman spectra of metallic VO_2 at 400°K (lower curve), 500°K (middle curve), and 600°K (upper curve). The traces have been displaced vertically with respect to each other for clarity.

in the spectra in the two phases result from their optical properties. The penetration depth of the incident laser light in VO_2, of the order of 1000 Å, is much greater than the thickness of any carrier depletion layer that may be present at the surface. Evidence for this has been found in photoemission measurements[7] and in the absence of rectifying behavior at metal-VO_2 junctions using various metals at temperatures from 150°K to the transition temperature.[1]

Figure 1 summarizes the spectra observed at 300 and 375°K. These traces are for mixed polarizations. Two general features of the spectra for $T < 340$°K are (a) the lack of any unusual temperature dependence of the positions, intensities, and widths of the lines, and (b) the absence of the strong, broad, multiphonon bands similar to those observed in TiO_2.[3] The peaks at 208, 450, 655, and 850 cm^{-1} are assigned respectively to phonons derived from B_{1g}, E_g, A_{1g}, and B_{2g} modes of the rutile structure. The corresponding modes in TiO_2[3] are at 143, 447, 612, and 826 cm^{-1} with polarizations XX, XZ, $(XX+ZZ)$, and XY, respectively. The details of the polarization measurements as a function of temperature will be published elsewhere.

The Raman spectrum of the metallic state consists of a strong, broad band near 550 cm^{-1} which is observable only in XX polarization, a small, broad peak near 300 cm^{-1}, and possibly some inelastic scattering at lower frequencies from other heavily damped excitations. In addition, there is a strong fluorescence background extending up to energy shifts of about 1 eV which possibly arises from radiative recombination of photoexcited carriers and is an order of magnitude lower in intensity in the semiconducting state. We have studied the metallic spectrum down to frequency shifts of 40 cm^{-1} as a function of temperature with the use of a molecular iodine filter[8] to eliminate the elastic scattering. Figure 2 shows the results at 400, 500, and 600°K. The temperature dependence of the intensity of the 550-cm^{-1} band is consistent with that of a single, heavily damped excitation rather than a multiphonon peak. We have fitted this mode at $T = 400$°K with a Lorentzian oscillator function

$$I(\omega)=\frac{\omega\gamma\omega_0^2[n(\omega,T)+1]}{(\omega_0^2-\omega^2)^2+4\gamma^2\omega^2},$$

where $\omega_0 = 545\ cm^{-1}$, $\gamma = 140\ cm^{-1}$, and $n(\omega, T)$ is the Bose factor. The fit is fairly good in the high-energy side of the peak but at lower energies there is considerable uncertainty due to subtraction of the low-energy scattering tail and the small peak near 300 cm^{-1}. Considering the dominance of the A_{1g} mode in XX polarization in the Raman spectrum of monoclinic VO_2 and that of TiO_2,[3] it seems likely that this broad band is the A_{1g} mode in the metallic state. The frequency of this band decreases from about 545 cm^{-1} at 400°K to about 520 cm^{-1} at 600°K. We have not been able to observe any temperature dependence in the position and intensity of the peak near 300

cm^{-1} and, because of lack of good polarization data, we cannot assign it to any particular Raman-active mode of the rutile structure. The large width and heavily damped character of the peak near 550 cm^{-1} suggest that the weaker lines expected for the metallic spectrum may be similarly broadened, but we have not been able to observe them. The featureless scattering tail at lower frequencies may, therefore, arise from one or more heavily damped modes, particularly the rutile B_{1g} mode which is intense in the monoclinic spectrum.

The most important characteristics of the VO_2 spectra are the apparently heavily damped character of the phonon spectrum in the metallic phase and its softening with increasing temperature. The infrared reflectivity spectrum[2] of the metallic state of VO_2 also shows no sharp structure, although the sensitivity of that experiment is reduced by the reflectivity of the carriers. The characteristics of the Raman spectra of VO_2 are unlike those in the few other polar metals which have been examined by Raman scattering,[9,10] in particular the metallic phases of Ti_2O_3 and V_2O_3[10] which also exhibit semiconductor-to-metal transitions. The qualitative difference between the sharp phonon structure in Ti_2O_3 and V_2O_3 and the broad phonon features in VO_2 suggests a stronger electron-phonon coupling in metallic VO_2. The low value of the electronic mean free path in VO_2,[1,11] of the order of the interatomic distance, is also a manifestation of this coupling.

These results appear to lend support to a phenomenological mechanism for the phase transition proposed by Paul.[11] In this scheme, the free energy of the metallic phase decreases with increasing temperature faster than that of the semiconducting phase because of the softening of the metallic phonons by the electron-phonon interactions, and the phase transition results when the metallic-state free energy becomes less than that of the semiconducting phase. It has been argued that the electronic contribution to the entropy change at the phase transition can be neglected for reasonable estimates of the widths of the 3*d* bands.[11] If this is correct, the measured latent heat of 1020 cal/mole can be accounted for by the additional lattice entropy associated with an average decrease of vibrational frequency, over the entire lattice spectrum, of about 18%. This estimate has been obtained by assuming a constant density of vibrational states extending from the zone-boundary acoustic region near 75 cm^{-1} to 750 cm^{-1}, which is slightly below the highest optic-mode frequency. This is a reasonable approximation to the recently published[12] density of states for TiO_2 calculated from a shell-model fit to inelastic neutron-scattering data.

If our assignment of the band near 550 cm^{-1} to the metallic-phase A_{1g} mode is correct, then its energy has decreased by about 15% above the transition. At higher temperatures, this peak continues to decrease in energy at a rate of about 0.1 $\text{cm}^{-1}/°\text{K}$. However, this progressive softening of the metallic phonon spectrum with increasing temperature may not be required to bring about the phase transition by way of the mechanism outlined above since the lattice free energy of both phases decreases with temperature, but at a faster rate for the metallic phase because of its lower average phonon energy. The significant result is that the softening of the observed Raman-active phonon spectrum is consistent with the average softening expected for this model.

Since the A_{1g} mode in the rutile structure involves only motions of the oxygen ions, its frequency is determined mainly by the radial vanadium-oxygen force constants. Our interpretation of the metallic spectra would therefore require an average decrease of about 30% in this force constant due to the delocalization of the single 3*d* electron per vanadium ion. A conclusive identification of the metallic E_g mode would have allowed a comparison of the decrease in the V^{4+}-O^{2-} force constants for the bonds perpendicular and oblique to the *c* axis. Unfortunately, we have not been successful in this identification.

The effects of the electron-phonon coupling in metallic VO_2 are very strong and include too large a portion of the Raman spectrum to allow us to draw any conclusions about the details of the coupling. To examine these effects further, we are now extending our work to metallic CO_2 and semiconducting MoO_2 and MnO_2 which have a different number of *d* electrons in the same band structure and crystal lattice as VO_2.

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Statistical Properties of Disordered Semiconductors*

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Basic statistical considerations are shown to imply pronounced effects on many properties of materials having energy-band tails. For extrinsic cases a metallike temperture dependence of the Fermi energy occurs; in consequence, a method is proposed for directly measuring the density of states in the tail. For intrinsic amorphous semiconductors, severe limitations are found for the inference of a sharp mobility edge from temperature-dependent conductivity data.

It is generally accepted that many of the interesting and potentially useful electronic properties of disordered semiconductors are associated with energy-band tails. These tails on the energy distribution of density of states create systems which are not conventional semiconductors, insulators, or metals. Therefore, the equilibrium statistical behavior cannot be obtained from any of the standard forms. This paper shows from calculations of this behavior for a simple model density of states that the statistical effects lead to new insights for both extrinsic and intrinsic cases. The essential conclusions appear to be independent of the details of the model.

The model used for the density of states was chosen as a simple, but fairly good, approximation to the several theoretical results appropriate to compensated semiconductors.[1-3] Each band edge is taken to be a normal parabolic band joined to a Gaussian tail as seen in Fig. 1(a). For a conduction band then

$$N(E)=\begin{cases} A(E-E_c)^{1/2}, & E>E_{jc}>E_c \\ N_j\exp\{-[(E-E_{jc})/E_0]^2\}, & E<E_{jc}, \end{cases}$$

where E_{jc} is the energy at which the pieces join, $N_j=A(E_{jc}-E_c)^{1/2}$ for continuity, and E_0 is the (adjustable) tail-width parameter.

We treat first the extrinsic case, i.e., one in which only one band plays a significant role because of an excess of one type of carrier (electrons for definiteness). The initial need, before any of the physical properties can be computed, is to evaluate the temperature dependence of the Fermi energy. This has been done numerically by the usual method of particle conservation. The results shown in Fig. 2 are representative of heavily doped, closely compensated semiconductors. A primary result is that the Fermi en-

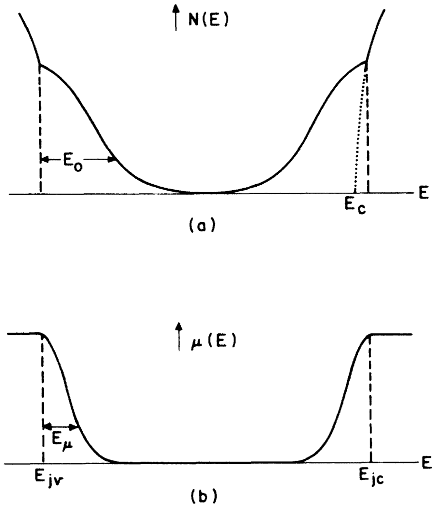

FIG. 1. The model functions used in these calculations. (a) Density of states and (b) mobility on the same energy scale. E_0 and E_μ are the respective width parameters. $E_\mu=0$ corresponds to an ideal mobility edge.