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Electronic Properties of VO_2 near the Semiconductor-Metal Transition

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Optical, thermal, magnetic, and transport properties of VO_2 in the vicinity of the semiconductor-metal transition temperature of 68°C are discussed in terms of a simple one-electron band picture. Particular emphasis is placed on the variation in these properties from sample to sample. It is shown that all of the available experimental data can be qualitatively explained in terms of such a model. In the metallic state, there are at least two overlapping and partially occupied bands, resulting in a complex Fermi surface characterized by a conductivity effective mass near unity and carrier mobilities in the range between 1 and 10 cm^2/V sec. There is no consistent evidence of a very narrow high-mass band near the Fermi level. In the semiconductor state, it is probable that the band overlap described above is removed by the lattice distortion, resulting in an energy gap of approximately 0.6 to 0.7 eV. This energy gap is filled to a density of typically 10^{19} to 10^{20} cm^{-3} with donorlike and acceptorlike states, the energy distribution and density depending on the sample, so that it is impossible to obtain an accurate measure of the energy gap. The charge density associated with these donorlike and acceptorlike states is normally larger than that associated with the carriers in the band, resulting in electronic properties characteristic of heavily compensated semiconductors. The conduction-band effective mass and the electron mobility are both near unity in the semiconducting phase of VO_2. Some implications of these experimental results with respect to the application to VO_2 of several of the published theories on semiconductor-metal transitions in solids are pointed out.

I. INTRODUCTION

SINCE the early work of Morin,[1] a relatively large number of solids have been found which exhibit a sudden transition at some temperature from high-temperature metallic behavior to low-temperature semiconductor behavior with a discontinuous change in conductivity of several orders of magnitude.[2] Although some theoretical models have been proposed to explain such transitions,[2–7] the detailed mechanism does not appear to be well understood, and it is possible that several different explanations may be valid depending on the material.

One of the best known solids which exhibit a semiconductor-metal transition is vanadium dioxide.[1,8] Its electronic transition occurs at 68°C and is accompanied by a first-order displacive phase transition from a tetragonal (rutile) high-temperature to a monoclinic low-temperature crystal structure.[9] The discontinuity in conductivity at the transition varies from sample to sample from a factor of less than one hundred to as high as 10^5,[10] typically being approximately a factor of 10^4. Recent interest in VO_2 has resulted in a great deal of experimental work, but the experimental data and their interpretations have often been contradictory. One of the most likely explanations for contradictory experimental results is that the impurity content, stoichiometry, and quality of the VO_2 crystals studied by different workers varies considerably. For this reason, it is most desirable that a wide variety of measurements be made on each of several different crystals in order to obtain a consistent interpretation. In this paper, some optical, thermal, transport, and magnetic properties of VO_2 and their variation from sample to sample will be discussed.

In Sec. II some general features to be expected of the one-electron band structure of VO_2 in both the metal and semiconductor phases are described; in Sec. III, the presently available experimental data on VO_2 are discussed in terms of a one-electron band model with relatively large electron-phonon interactions, and agreement of this model with theories of the semiconductor-metal transition are briefly considered.[2–7,11]

II. GENERAL BAND FEATURES OF VO_2

A. Metallic State

In discussing the general band features of transition metal oxides, Goodenough[7,12] has suggested that when direct cation-cation interactions are possible, the cation-anion-cation interactions can often be neglected. With this assumption, he has explained many of the properties of transition metal oxides. However, VO_2 has around each vanadium ion an octahedra of oxygen ions similar to that which exists around the titanium ions in TiO_2, $SrTiO_3$, or $BaTiO_3$, and the interatomic spacings are very similar. Band calculations on $SrTiO_3$ where only the interactions between the oxygen $2p$ and titanium $3d$ orbitals have been included show that the bands derived primarily from the $3d$ orbitals have bandwidths of 1 eV and wider, and conductivity effective masses near

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[1] F. J. Morin, Phys. Rev. Letters **3**, 34 (1959).

[2] See, for instance, David Adler, Rev. Mod. Phys. **40**, 714 (1969).

[3] David Adler and Harvey Brooks, Phys. Rev. **155**, 826 (1967).

[4] N. F. Mott, Proc. Phys. Soc. (London) **A62**, 416 (1949).

[5] G. J. Hyland, J. Phys. **C1**, 189 (1968).

[6] B. I. Halperin and T. M. Rice, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1968), Vol. 21, p. 115.

[7] J. B. Goodenough, Phys. Rev. **120**, 67 (1960).

[8] See, for instance, K. Kosuge, J. Phys. Soc. Japan **22**, 551 (1967) and references therein.

[9] George Anderson, Octa. Chem. Scand. **10**, 623 (1956).

[10] H. J. Guggenheim and J. B. MacChesney (unpublished).

[11] J. Hubbard, Proc. Roy. Soc. (London) **A276**, 238 (1963); **A272**, 237 (1964); **A281**, 401 (1964).

[12] J. B. Goodenough, Phys. Rev. **117**, 1442 (1960).

unity.[13] This indicates that the cation-anion-cation interactions cannot be neglected in VO_2, a fact which has been suggested by Bongers[14] on the basis of his experimental results. It also implies that when the direct cation-cation interactions are included in a band calculation of VO_2, wider $3d$ bands and lower effective masses (before dressing by polaron and other effects) than those resulting from a calculation which considers only cation-anion-cation interactions should be found. Thus, VO_2 might be expected to have $3d$ bands wider than 1 eV and effective masses near unity.

A band calculation for tetragonal VO_2 is not presently available, nor has one been made for the closely related and better known material TiO_2. However, it has been pointed out by Verleur *et al.* that many of the major features of the bands can be qualitatively explained by an extrapolation of the $SrTiO_3$ band calculation,[15] and they were able to interpret their optical data satisfactorily using such a model. From their work and the photoemission measurements of Powell *et al.*,[16] the density of states of VO_2 in its metallic state is approximately as shown in Fig. 1. There is a set of bands derived primarily from the oxygen $2p$ orbitals which are completely occupied. They cover an energy range of approximately 3 eV beginning approximately 2.5 eV below the Fermi level. There is probably fine structure in this density of states but it was not derivable from the optical data and is not shown. The Fermi level lies within the bands derived primarily from the vanadium $3d$ orbitals. The band gap between the oxygen $2p$ bands and the vanadium $3d$ bands, if one exists, could not be determined from the experimental data.

In the metallic state there are 10 spin-degenerate d bands derived from the five $3d$ orbitals of the two vanadium ions in each unit cell. These bands are occupied by the extra valence electron contributed by each vanadium ion. Thus, if one of the d bands were completely below in energy the other nine, it would be completely filled. Since metallic behavior is observed, the lowest d band in VO_2 must partially overlap one or more of the higher-lying bands. Although the nature and degree of overlap cannot be easily predicted, it can be stated that at any general point in the Brillouin zone it is likely that all bands will be nondegenerate. Thus, the concept that the two lowest d bands are degenerate throughout the Brillouin zone and do not significantly overlap higher-lying bands, resulting in an exactly half-filled band, is not very probable. A more likely possibility is that the lowest band is nearly filled and overlaps slightly one or more higher-lying bands. This latter band model was proposed by Verleur *et al.*[15] on the basis of their optical work, and it will be shown here that it is consistent with other experimental data also.

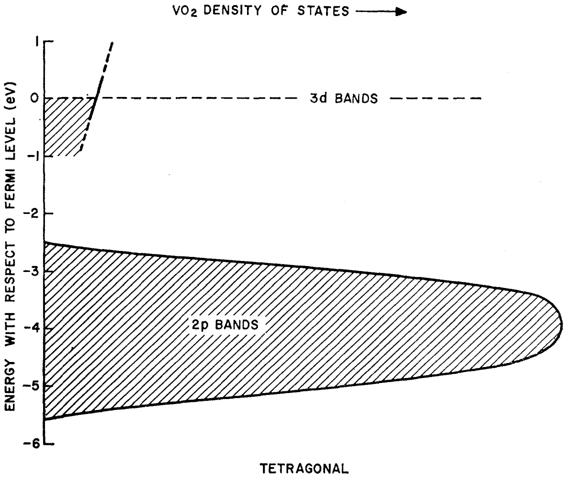

FIG. 1. Simplified representation of the density of states in metallic (tetragonal) VO_2.

B. Semiconductor State

When VO_2 is cooled below 68°C, it changes from a tetragonal to a monoclinic structure.[9] The ionic distortion is similar to that which occurs at an antiferroelectric transition, the unit cell doubling in size and the maximum ionic movement being in the range of 0.1 Å. Goodenough has pointed out that the major feature of the distortion is the formation of vanadium ion pairs along the rutile c axis,[7] and he refers to this as the formation of homopolar bands. However, in view of the large degree of hybridization expected between oxygen $2p$ and vanadium $3d$ orbitals, this pairing of vanadium ions may be only one of several important characteristics of the distortion rather than the dominant one.

The doubling in size of the unit cell results in a reduction by one-half of the size of the Brillouin zone and a doubling of the number of bands. There will be twenty $3d$ bands, and since semiconductor behavior is observed two of these will be completely filled and separated by an energy gap from the other eighteen. The oxygen $2p$ bands will also double in number; but their total bandwidth and their energy location with respect to the Fermi level is not expected to be significantly different from those in the tetragonal rutile phase. The density of states, again ignoring possible fine structure, derived from the optical measurements is shown in Fig. 2. As in the tetragonal state, the energy gap between the oxygen $2p$ bands and the vanadium $3d$ bands is not apparent from the experimental data. However, the energy gap which forms within the $3d$ bands is roughly estimated from the optical measurements to be 0.6–0.7 eV, a number in reasonable agreement with the conclusion of other authors.[17]

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[13] A. H. Kahn and A. J. Leyendecker, Phys. Rev. **135**, A1321 (1964).

[14] P. F. Bongers, Solid State Commun. **3**, 275 (1965).

[15] Hans W. Verleur, A. S. Barker, Jr., and C. N. Berglund, Phys. Rev. **172**, 788 (1968).

[16] R. J. Powell, C. N. Berglund, and W. E. Spicer, Phys. Rev. **178**, 1410 (1969).

[17] L. Ladd and W. Paul (unpublished).

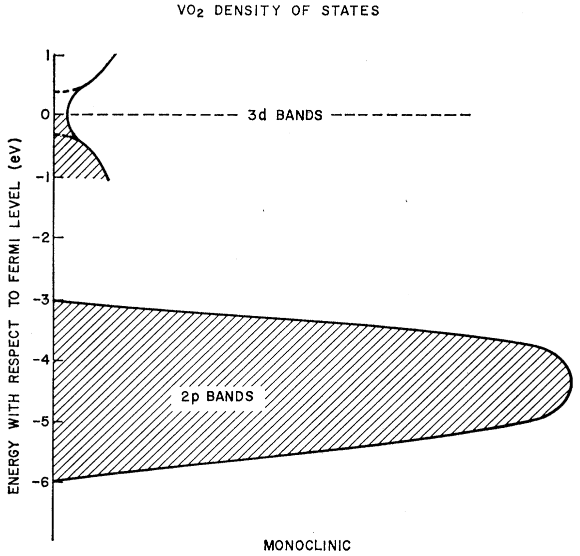

FIG. 2. Simplified representation of the density of states in semiconducting (monoclinic) VO_2.

A significant feature of the VO_2 density of states shown in Fig. 2 is the continuum of states within the *3d* band energy gap. The nature and density of these states will be discussed in more detail later. However, some of their general features are evident from the optical measurements and will be described here. Verleur *et al.*[15] found that there was no abrupt optical absorption threshold at the energy gap photon energy in semiconducting VO_2, and that a significant and nearly temperature-independent absorption tail extended from approximately 0.8 eV down to less than 0.2 eV. This absorption was generally structureless although some samples showed small peaks near 0.4 eV, and it varied somewhat from sample to sample. Several possible mechanisms were proposed to explain the absorption, one of which was absorption from donor and acceptor states within the energy gap. These donor and acceptor states may be partially due to impurities, but are more likely to arise from crystalline imperfections such as oxygen vacancies, interstitial vanadium ions, dislocations, domain boundaries, or cracks. Although other mechanisms may be responsible for part of the absorption below the band edge in semiconducting VO_2, an explanation of most of the absorption in terms of such localized states is consistent with the transport and optical data to be described.

The variation in the optical absorption measured on several samples indicates that the density and energy distribution of these states within the energy gap varies somewhat from sample to sample, but some general conclusions are possible. Since the optical absorption coefficient is typically in the range from 10^3 to 10^4 cm^{-1}, and since impurity photoionization cross sections are usually near 10^{-16} cm^2 for a rather wide range of photon energies above the impurity binding energy, the integrated density of these states is probably in the range from 10^{19} to 10^{20} cm^{-3}. There is no simple way of determining the energy distribution of these states from the optical absorption alone, and even if there were, it is evident that the distribution will vary from sample to sample. Fortunately, for the purposes of discussion in this paper, it is the existence of such states within the gap which is most important; so that as a first approximation, and in the absence of more detailed information, it is reasonable to represent them as a relatively structureless continuum of states, as shown in Fig. 2.[18] Since their density is so low compared to the density of vanadium ions, and since it is variable from sample to sample, they probably arise from departures from crystalline perfection or impurities similar to those which result in donor and acceptor states in more conventional semiconductors. It is important to point out, however, that their density is sufficiently high to completely mask the optical absorption threshold at the band gap energy. For this reason, the energy gap in our VO_2 samples cannot be measured accurately by optical means and the 0.6 to 0.7 eV energy gap value mentioned previously must be recognized as only an estimate.

III. ELECTRONIC PROPERTIES OF VO_2

A. Resistivity and Hall Effect

The temperature dependence of the conductivity of VO_2 has been reported by many authors.[1,8,14] Some typical curves for our samples which are in substantial agreement with the published results are shown in Fig. 3. In the metallic phase the resistivity is relatively temperature-independent varying slightly from sample to sample over the range between 2×10^{-4} and 5×10^{-4} Ω cm. In the semiconductor state, the resistivity may be between 10^{-3} and 10 Ω cm at the transition depending on the sample, but is usually reported to be in the range of 1 Ω cm. It nearly always exhibits an approximately exponential dependence on the reciprocal of the absolute temperature over rather wide temperature ranges below the transition with the activation energy varying from less than 0.1 to as high as 0.65 eV. The highest activation energies are usually associated with the highest resistivities at the transition temperature as illustrated in Fig. 3. Similar results have been observed on sputtered VO_2 films approximately 700 Å thick.[19,20]

The results shown in Fig. 3 and those to be described in the remainder of this paper were taken from single crystals grown from a supersaturated solution of V_2O_5. The growth technique has been described elsewhere.[10] Different conductivities and conductivity activation energies in the semiconducting state of the various crystals studied were obtained by varying the growth rate.

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[18] This representation is similar to that proposed recently by Morrel H. Cohen for amorphous semiconductors.

[19] D. H. Hensler, J. Appl. Phys. **39**, 2354 (1968); E. N. Fuls, D. H. Hensler, and A. R. Ross, Appl. Phys. Letters **10**, 199 (1967).

[20] E. N. Fuls, D. H. Hensler, and A. R. Ross, Appl. Phys. Letters **10**, 199 (1967).

Although not shown in Fig. 3 because of the scale used, thermal hysteresis is always observed in measurements of conductivity versus temperature. Like most other properties of VO_2, the hysteresis varies from sample to sample, being as low as 0.5 deg on samples exhibiting the highest conductivity discontinuity at the transition but being typically in the range from 1 to 2 degs. While the origin of this hysteresis is not known, it is likely that at least some is due to internal stresses induced by domain boundaries in the semiconductor state.[21] There is no conclusive evidence that measureable hysteresis is inherent in the phase transition of VO_2.

Figure 3 also illustrates that the transition temperature T_t is essentially independent of the conductivity, and the activation energy for the conductivity, in the semiconductor phase within the experimental uncertainty resulting from the hysteresis.

One important experimental fact associated with VO_2 and many other materials that exhibit metal-semiconductor transition is that on passing through the transition they tend to crack. In VO_2 the tendency toward cracking varies from sample to sample and the cracks which do form are usually aligned along the rutile *c* axis. Careful conductivity measurements on several samples made before and after cycling them through the transition several times indicate that in both the metal and the semiconductor state these cracks usually have a nearly negligible effect on conductivity measurements, but if effects do occur the largest ones occur in the metallic state. However, they appear to affect Hall measurements, especially in the metallic phase.[22] For this reason there is very little reliable Hall effect data on VO_2. Nevertheless, from the available Hall data, it can be stated that in the semiconductor state the current carriers have always been found to be electrons and the exponential dependence of the resistivity on reciprocal temperature has always been found to be due primarily to a temperature dependence of the carrier concentration (Hall coefficient) rather than that of the mobility.[19,23] The mobility is in the range from 0.1 to 1 cm^2/V sec near room temperature and is anisotropic, the mobility parallel to the rutile *c* axis being approximately a factor of 2 larger than that perpendicular to the rutile *c* axis. Given these electron mobilities and the measured conductivities in the semiconductor state, the carrier concentration just below the transition is typically in the range from 10^{18} to 10^{19} cm^{-3}.

Since Hall measurements indicate that only electrons contribute significantly to the conductivity of VO_2 in its semiconductor state, the conductivity σ is

$$\sigma = q\mu_n N_c e^{-E_F/kT}, \qquad (1)$$

where μ_n is the electron mobility, N_c is the effective conduction band density of states, k is Boltzmann's constant, T is the absolute temperature, and E_F is the energy separation of the Fermi level from the conduction band edge. Since the conductivity varies nearly exponentially with reciprocal temperature and since the mobility can not account for such a strong temperature dependence, E_F must contain a temperature-independent term. One possibility is that in the semiconductor state VO_2 is intrinsic with E_F equal to one-half the band gap. However, in this case all samples should have the same activation energy. A more likely explanation is that the position of the Fermi level is influenced by donorlike and acceptorlike states within the energy gap, the distribution and density of these states varying from sample to sample to account for the observed variations in conductivity and activation energy. This requires that there be a density of such states in excess of the density of electrons, namely, more than 10^{18} to 10^{19} cm^{-3}. Note that this conclusion, based only on the variation from sample to sample of the conductivity and its temperature dependence, is consistent with the explanation of the optical absorption in terms of donorlike and acceptorlike states.

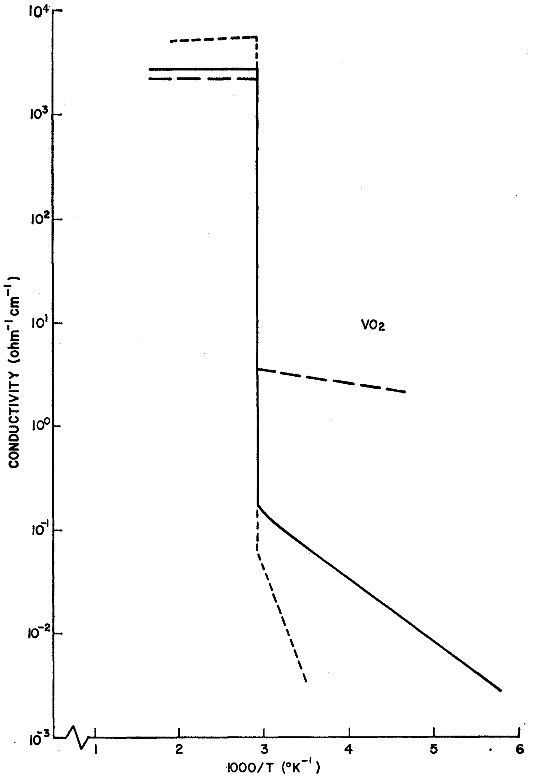

FIG. 3. Temperature dependence of the conductivity of three typical samples of VO_2.

It should be pointed out that the existence of a large density of donor and acceptor states within the energy gap of semiconducting VO_2 explains two other properties. It has been found that polycrystalline thin films of thicknesses of approximately 700 Å have reproducibly

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[21] P. J. Fillingham, J. Appl. Phys. 38, 4823 (1967).

[22] A. S. Barker, Jr., H. W. Verleur, and H. J. Guggenheim, Phys. Rev. Letters 17, 1286 (1966).

[23] See, for instance, J. L. Moll, *Physics of Semiconductors* (McGraw-Hill Book Co., New York, 1964), p. 85.

exhibited conductivity similar to that of single crystals both in the magnitude of the conductivity and in the values of conductivity activation energies in the semiconductor state.[19,20] Such behavior is unexpected unless the space-charge regions associated with the surface and grain boundaries are considerably thinner than 700 Å. Also, attempts to obtain rectifying behavior at a metal-semiconducting VO_2 contact were unsuccessful with gold, platinum, aluminum, copper, and indium-gallium at temperatures from 150°K to the transition temperature. Both of these observations can be explained if there is a density of donor and acceptor states in excess of approximately 10^{19} cm^{-3} within the energy gap which will result in very narrow space-charge regions nearly transparent for electron transport by tunneling.

Referring to Eq. (1), if E_F is essentially temperature-independent even over a limited temperature range where μ_n is temperature-independent, an extrapolation of a plot of $\log\sigma$ versus $1/T$ back to $1/T$ equal zero will provide a direct measure of $q\mu_n N_c$. In the range from approximately 0°C up to the transition temperature, all the samples measured exhibited a unique conductivity activation energy, and six of seven samples measured gave an extrapolated value of conductivity of 8 Ω^{-1} cm^{-1} within approximately a factor of 2. The one exception had an anomalously high conductivity activation energy of 0.65 eV and is shown in Fig. 3. Thus, it is reasonable to conclude that in all but one of our samples in the temperature range from approximately 0°C up to the transition temperature the Fermi level is pinned by the donor and acceptor states at a fixed temperature-independent value and that $q\mu_n N_c$ is approximately 8 Ω^{-1} cm^{-1}. Using the limits on the mobility between 0.1 and 1 cm^2/V sec, and the conventional expression relating density-of-states effective mass m_D to N_c,[23]

$$N_c = (\tfrac{1}{2}\pi)^{1/2}/\pi^2\hbar^3 m_D{}^{3/2}(kT)^{3/2} \tag{2}$$

the density-of-states effective mass for the conduction band of VO_2 is between 1.6 and 7 times the free-electron mass. These values are similar to those measured on $SrTiO_3$,[24] and $BaTiO_3$.[25]

In the metallic state, there are conflicting Hall results in the literature. If one type of carrier is assumed, the measurements of Barker *et al.*[22] indicate that the carriers are electrons, and from the conductivity they must have a mobility of between 1 and 10 cm^2/V sec. The spread in mobility values comes from uncertainty in the density of carriers. The value of 10 arises from the density of 3×10^{21} cm^{-3} used by Barker *et al.*, and the value of one arises from the assumption of one carrier per vanadium ion. In either case, however, it is interesting to note that the mobility is higher than that for electrons in the semiconductor state. Hensler's Hall data[19] indicate that the carriers making the dominant contribution to the conductivity are electrons, and that if a single type of carrier is assumed its mobility must be approximately 0.1 cm^2/V sec. However, the effective concentration of carriers estimated from his Hall coefficient is over 10^{23} cm^{-3}. Since the density of vanadium ions is approximately 3×10^{22} cm^{-3} in VO_2 and each vanadium ion contributes only one extra electron, these results indicate that more than one type of carrier exists in the metallic state and that the mobility obtained may be considerably lower than the actual mobility. Hence the Fermi surface of metallic VO_2 must be complex and must include at least two bands. Attempts to measure the details of the Fermi surface have not been successful because conventional low-temperature measurements on the metallic phase of VO_2 are not possible, and measurements at higher temperature lack the required sensitivity.

B. Infrared Optical Properties

The ir optical properties of one of our crystals of VO_2 have been measured by Barker *et al.*[22] They found that in the semiconducting phase, the ir free-carrier absorption combined with Hall measurements resulted in a conductivity effective mass for conduction-band electrons at optical frequencies between one and four times the free-electron mass. Given that the low-frequency mass may be somewhat larger, it can still be concluded that these values for the conductivity effective mass are consistent with the previously described estimates of the density-of-states effective mass.

One important parameter that can be deduced from the infrared measurements of Barker *et al.* is the electron-phonon coupling coefficient α. This parameter, commonly employed in polaron theories, was originally defined by Froehlich *et al.*,[26] as

$$\alpha = \frac{e^2}{2\hbar\omega_l}\left(\frac{2m^*\omega_l}{\hbar}\right)^{1/2}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right), \tag{3}$$

where ω_l is the longitudinal optical phonon frequency, m^* is the effective mass, ϵ_∞ is the high-frequency dielectric constant, and ϵ_0 is the low-frequency dielectric constant. Using an effective mass of four times the free-electron mass and the measured dielectric constants, α in VO_2 is approximately two. Since the conductivity effective mass may be as small as the free-electron mass α may be as small as one. In either case its value is approximately the same as that of $BaTiO_3$,[27] $SrTiO_3$,[27] and TiO_2.[28] While it is sufficiently large that a simple band theory treating electron-phonon interactions as a small perturbation is not a very good approximation, it seems too small (and the effective mass seems too small) to justify the application of present small polaron

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[24] H. P. R. Frederikse and G. A. Candela, Phys. Rev. **147**, 583 (1966).

[25] C. N. Berglund and W. S. Baer, Phys. Rev. **157**, 358 (1967).

[26] H. Frohlich, H. Pelzer, and S. Zienau, Phil. Mag. **41**, 221 (1950).

[27] A. S. Barker, Jr., Phys. Rev. **145**, 391 (1966).

[28] D. M. Eagles, J. Phys. Chem. Solids **25**, 1243 (1964).

theories[29] as suggested by Mott.[30] A large polaron intermediate-coupling treatment is probably more applicable to VO$_2$.[31]

In the metallic state, the free-carrier part of the ir optical properties combined with Hall data can be used to deduce the optical effective mass and the mobility of the carriers if only one type of carrier is present. Making such an assumption Barker *et al.*[22] estimate from their data an optical effective mass of one-half the free-electron mass and an optical mobility of 2 cm^2/V sec. Since more than one type of carrier is probably present and since dressing effects may occur at lower frequencies, this effective mass must be considered as a lower limit for the conductivity effective mass of metallic VO$_2$.

Photoconductivity measurements of VO$_2$ in its semiconducting phase have been attempted over the photon energy range from 0.1 to 5.5 eV and over the temperature range from 77°K to 68°C. Single crystals, epitaxial thin films, and sputtered thin films were used. In all cases there was no observable photoconductivity. While there are several possible explanations for this result, an extremely high density of trap states existing within the energy gap seems to be the most straightforward.

C. Seebeck Effect

Some typical results of Seebeck coefficient measurements on VO$_2$ are shown in Fig. 4. In the semiconductor state, there is no measurable anisotropy, whereas, in the metallic state at 75°C the Seebeck coefficient is -23.1 ± 0.2 μV/°C perpendicular to the rutile c axis and -21.1 ± 0.2 μV/°C parallel to the rutile c axis. Essentially identical results for the metallic state were obtained from all samples measured while the Seebeck coefficient for the semiconductor state varied from approximately -30 to -400 μV/°C, the most negative values being measured on samples with the largest activation energy and resistivity in the semiconductor state. Some authors have measured Seebeck coefficients as large as -1000 μV/°C.[14] The temperature dependence of the Seebeck coefficient is weak, but in the metallic state it always increases slightly with temperature. In the semiconducting phase small and variable decreases with temperature in the range from 25 to 68°C are observed.

In principle, the Seebeck coefficient and data from other transport measurements can be used to interpret unambiguously conduction mechanisms and band properties. However, most models predict similar behavior for the Seebeck coefficient, the differences generally being smaller than the variation from sample to sample which has been observed. For this reason only a qualitative interpretation will be given here using as a first approximation a simple band model.

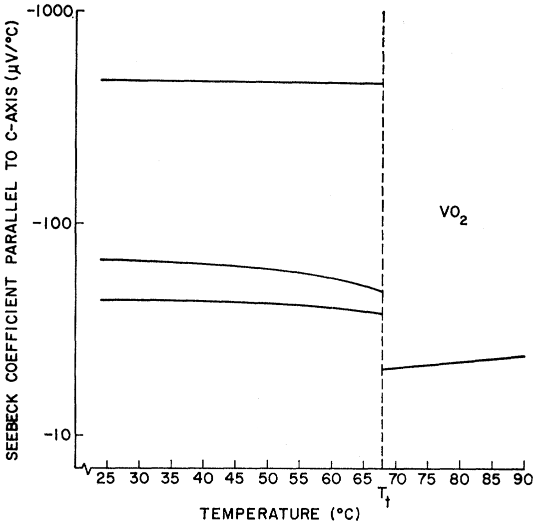

FIG. 4. Temperature dependence of the Seebeck coefficient measured parallel to the rutile c axis for three samples of VO$_2$.

For a nondegenerate semiconductor with one type of carrier (electrons), the Seebeck coefficient is usually written as

$$S = (k/q)[(-E_F/kT) + \beta], \tag{4}$$

where E_F is the Fermi energy relative to the conduction band minimum, and β is a constant which depends on the energy dependence of the electron-scattering mechanism (usually between two and three for lattice scattering). For lattice scattering, S for a given carrier is isotropic,[32] but the measured Seebeck coefficient can be anisotropic if more than one type of carrier contributes since the Seebeck coefficients add in the following way:

$$S = \frac{\sigma_1}{\sigma} S_1 + \frac{\sigma_2}{\sigma} S_2 + \cdots, \tag{5}$$

where S is the measured Seebeck coefficient, σ is the total conductivity, and σ_i and S_i are the conductivity and Seebeck coefficient, respectively, of the ith carrier. Thus, even if the S_i's are isotropic, any anisotropy in the σ_i's would result in an anisotropic S.

The fact that the Seebeck coefficient is always negative in VO$_2$ shows that the dominant current carriers are electrons. In the semiconductor state, its lack of anisotropy and its variation from sample to sample are qualitatively consistent through Eq. (4) with the variation in conductivity activation energy and are in agreement with simple theories where only one current carrier is present. In the metallic state, the anisotropy in the Seebeck coefficient can be explained using Eq. (5) if more than one type of current carrier with different (and anisotropic) mobilities are present.

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[29] See, for instance, T. Holstein, Ann. Phys. (N. Y.) 8, 325 (1959).

[30] N. F. Mott, Rev. Mod. Phys. **40**, 677 (1969).

[31] R. P. Feynman, R. W. Hellworth, C. K. Iddings, and P. M. Platzman, Phys. Rev. **127**, 1004 (1962).

[32] See, for instance, A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, England, 1953), p. 205.

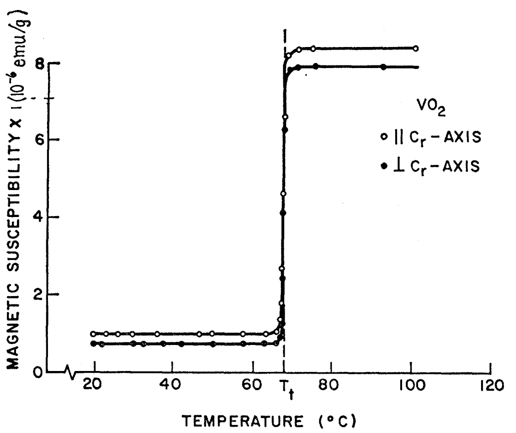

FIG. 5. Magnetic susceptibility (10^{-6} emu/g) of a typical sample of VO_2 near the transition temperature measured parallel and perpendicular to the rutile *c* axis.

D. Magnetic Susceptibility

The magnetic susceptibility of one of our samples of VO_2 is shown in Fig. 5 for a relatively restricted temperature range near the transition. These results are in general agreement with previously reported susceptibilities,[33] showing that VO_2 is paramagnetic both above and below the transition. In addition the relatively small but measurable anisotropy is shown.

At temperatures below 68°C, the susceptibility is small and temperature-independent, and is probably due to a combination of the negative diamagnetic susceptibility of the atomic cores and the positive Van Vleck paramagnetism. At the transition, the susceptibility increases discontinuously by a relatively large value of approximately 7×10^{-6} emu/g. Part of this discontinuity is due to changes in the core and Van Vleck contributions, but some part must be due to the appearance in the metallic state of a relatively high density of free carriers. Although negligible temperature dependence of χ above 68°C is shown in Fig. 5, several authors have observed that χ decreases slightly with temperature.[33,34]

If the entire discontinuity in χ at the transition is attributed to the change in the density of free carriers, and if a simple one-band free-electron model is applied, it is found that the Fermi surface density of states in VO_2 in its metallic state must be approximately 10^{23} cm^{-3} eV^{-1}. Such a density would require bandwidths of approximately 0.1 eV, and, in view of the previous discussion and experimental results appears to be inconsistent. However, if it is assumed that there are two partially occupied bands overlapping in energy, one very narrow and of very high mass making the major contribution to χ and the other relatively wide and of mass near unity responsible for the transport properties, the data can be explained. A similar model explains the high paramagnetic susceptibility of palladium[35] and V_3Si.[36] This model is rather unlikely in VO_2 since there is at present no evidence of such a narrow band in the optical[15] and photoemission[16] data. Even with the limited resolution of the photoemission experiment, such a narrow band would give rise to striking and unambiguous behavior if it did exist. Note also that such a model would have to explain the anisotropy which is shown in Fig. 5.

It is also possible that all or part of the discontinuity in χ at the semiconductor-metal transition is caused by other effects. The separate magnitudes, anisotropies, and changes at the transition in the Van Vleck and core diamagnetism contributions are not presently known. Since these two contributions are of opposite sign, small changes in one or both may make a much larger relative change in χ. Another possibility is that the magnetic susceptibility of the carriers has been affected by large polaron or electron correlation and exchange effects resulting in a considerable enhancement.[37] In this case, even though the density of states at the Fermi surface is relatively small, the free carriers could make a major contribution to the susceptibility. Since some or all of these possibilities contribute, the discontinuity in χ at the transition in VO_2 cannot be considered as evidence for a high Fermi surface density of states or for very narrow bands.

E. Heat Capacity and Latent Heat

The heat capacity of VO_2 is of importance not only because it should provide information on the type and nature of the transition but because the latent heat and heat capacity at the transition can be interpreted using models of the semiconductor metal transition such as that by Adler and Brooks[3] in terms of the width of bands near the Fermi level. A plot of the specific heat at constant pressure for VO_2 is shown in Fig. 6 from the data of Cook[38] and Ryder *et al.*,[39] and clearly shows that the transition in VO_2 is first order. The latent heat at the transition as measured by Ryder *et al.* is 1020±5 cal/mole of VO_2, and the Debye temperature extrapolated from the low-temperature specific heat is approximately 750°K. The data at temperatures above the transition temperature T_t are not sufficiently good to extract a Debye temperature at high temperatures. Ryder *et al.*'s data were taken from the same samples used in the other measurements described here, and the sharpness of the transition provides an indication of the high quality of the VO_2.

The rather large latent heat at the transition of 1020 cal/mole corresponding to an entropy change ΔS of about 3 cal/mole°C is made up of two contributions, one

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[37] See, for example, D. Pines, Phys. Rev. **95**, 1090 (1964).

[38] O. A. Cook, J. Am. Chem. Soc. **69**, 331 (1947).

[39] E. J. Ryder, F. S. L. Hsu, H. J. Guggenheim, and J. E. Kunzler (unpublished).

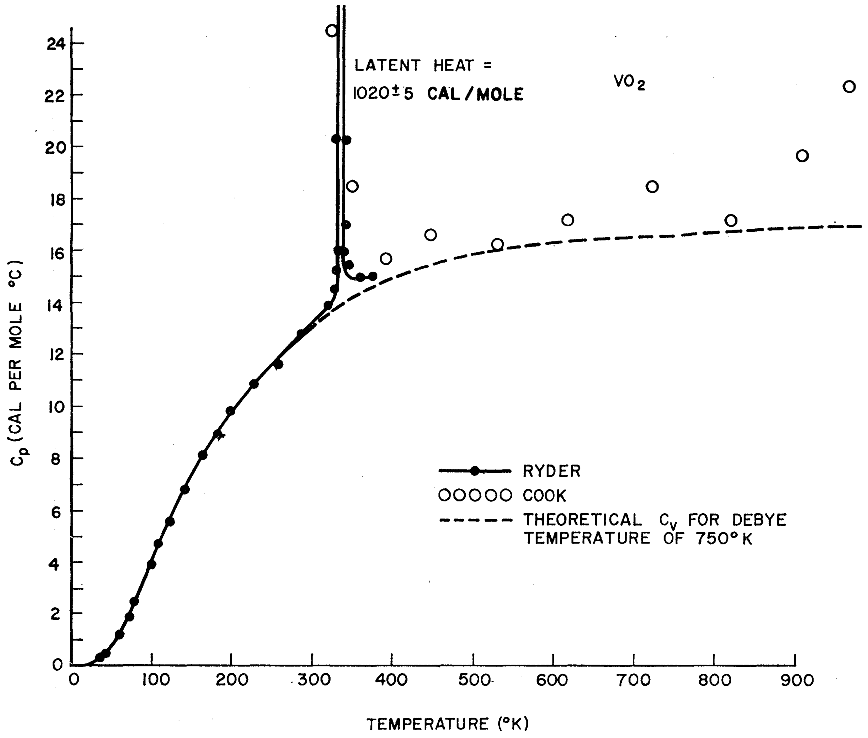

FIG. 6. Heat capacity of VO_2.

from the lattice which results from the crystalline distortion, and the other from the conduction electrons which results because of the discontinuity in the carrier density. These two contributions could possibly be separated if very exact specific heat data on high quality material were available over a wide temperature range above the transition. Since such data is not presently available, it is of interest to examine whether all or most of the latent heat can be explained on the basis of either contribution, and what effect each contribution would have on the specific heat measured above and below the transition.

Regardless of which mechanism is primarily responsible for the observed latent heat, the free carriers which appear in the metallic phase will make a contribution to the measured specific heat above the transition temperature. However, if in addition the free carriers were entirely responsible for the observed latent heat in VO_2, the effective Debye temperature above and below the transition would not be expected to be significantly different and the specific heat would be larger in magnitude just above T_t than just below T_t by an amount which would be approximately equal to the electronic contribution to the specific heat in the metallic phase. Referring to Fig. 6, it can be seen that even though accurate data to temperatures well above the transition are not available, the discontinuity appears to be less than 0.5 cal/mole °C. Using the free-electron model which relates electronic specific heat to the Fermi surface density of states, this experimental fact implies that the Fermi surface density of states is less than 1.5×10^{22} states/cm^3 eV. While this conclusion is not expected to be extremely accurate in view of the likely complexity of the Fermi surface, it is in qualitative agreement with the conclusions from the optical, photoemission, and transport measurements in indicating that the Fermi surface effective mass for metallic VO_2 is near unity.

If the observed latent heat is primarily due to the appearance of the free carriers in the metallic state as assumed above; then the latent heat must be equal to the entropy of these free carriers just above the transition temperature, multiplied by the transition temperature T_t. However, the entropy of free carriers and their contribution to the specific heat are normally approximately equal. From Fig. 6 the entropy change associated with the transition is approximately 3 cal/mole °C, whereas, from the previous discussion the electronic contribution to the specific heat must be less than 0.5 cal/mole °C. This observation indicates that either there is some correction to the simple free-electron theory which allows the entropy of free carriers to be more than a factor of 6 higher than their contribution to the specific heat, or there must be a significant lattice contribution to the latent heat.

If the lattice contribution were primarily responsible for the latent heat, it would be expected that the effective Debye temperature above the transition would be different than that below the transition. The magnitude of the entropy change would depend to a first approximation on the change in Debye temperature. Since the Debye temperatures have not been evaluated

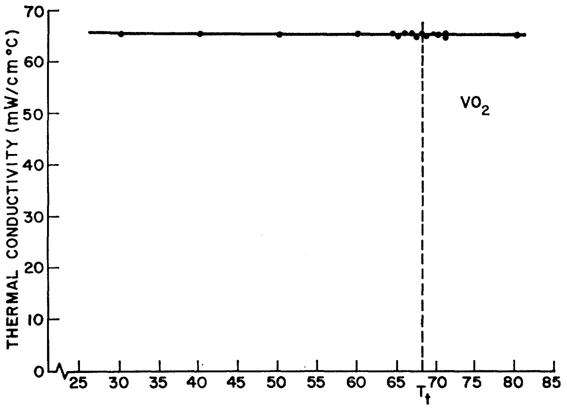

FIG. 7. Thermal conductivity of a typical sample of VO_2.

with sufficient accuracy, it is not possible to state that all or even most of the observed latent heat can be accounted for by a lattice contribution in VO_2, but it is interesting to note that many first-order ferroelectric, antiferroelectric, and other transitions [for example, those in $PbZrO_3$ [40] and $(NH_4)_2SO_4$ [41]] in which there is no significant change in conductivity have latent heats and entropy changes similar in magnitude to those observed in VO_2. Thus it is possible that much of the latent heat in VO_2 comes from the lattice.

F. Thermal Conductivity

The thermal conductivity of a typical sample of VO_2 is shown in Fig. 7. There is a negligible temperature dependence in the thermal conductivity over the temperature range from −25°C through the metal-semiconductor transition to 80°C, and no observable discontinuity at the transition. These two results were found on all samples which were measured although the magnitude of the thermal conductivity varied depending on the sample from about 40 mW/cm °C to about 70 mW/cm °C.

Thermal conductivity in solids has two components, a lattice thermal conductivity κ_l and an electronic thermal conductivity κ_e. Based on several simplifying assumptions, the electronic thermal conductivity can be related to the electronic conductivity by the well-known Wiedemann-Franz law[42]

$$\kappa_e = \tfrac{1}{3}\pi^2(k/e)^2\sigma T\,, \qquad (6)$$

where k is Boltzmann's constant, e is the electronic charge, and T is the absolute temperature. Using Eq. (6), the measured electronic conductivity of VO_2 indicates that a discontinuity of 20 to 50 mW/cm °C, depending on the sample, should occur in κ_e at the semiconductor-metal transition. Experimentally it is found that the discontinuity is less than the experimental error (about 2 mW/cm °C) as seen in Fig. 7.

There are two reasons why the Wiedemann-Franz law may fail in a solid; the electron scattering mechanism may not be adequately represented by a simple scattering time, and the scattering process may not be elastic.[43] Both probably apply to VO_2. Using a scattering time model, the low mobility of carriers corresponds to a mean free path of the order of 5 Å, a distance comparable to the lattice constant. It is not clear that a relaxation time representation for scattering is a good approximation when the mean free path is so short. In addition, the scattering is not well approximated as being elastic not only because the Debye temperature for VO_2 is well above the transition temperature T_t at approximately 750°K but also because the dominant scattering is probably with one of the longitudinal optical phonons whose energy is well above kT_t. It is not likely that the dominant scattering of carriers in the metallic phase is with impurities or defects because such scattering is elastic and would tend to validate the Wiedemann-Franz law.

Since it has been shown that the electronic thermal conductivity is negligible in VO_2 up to 80°C, all of the measured thermal conductivity must be due to the lattice. However, lattice thermal conductivity in most pure crystals free of imperfections is found theoretically and experimentally to vary reciprocally with the absolute temperature at high temperatures and even more rapidly at temperatures well below the Debye temperature.[44] In VO_2, no significant temperature dependence was noted in κ over the measured range, so it must be concluded that our crystals contained a very high density of crystalline imperfections.

G. Pressure Dependence

The pressure dependences of several properties of VO_2 have been measured by Neuman, Lawson, and Brown,[45] and by Kawakubo and Nagasaki,[46] but the results do not agree and are not definitive. More complete measurements over a wide pressure range on some of the same crystals used here have recently been reported by Berglund and Jayaraman,[47] the results of which are shown in Fig. 8. They found that the transition temperature increased linearly with hydrostatic pressure at a rate of approximately 0.08 deg/kbar in good agreement

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[41] S. Hoshino, K. Vedam, Y. Okaya, and R. Pepinsky, Phys. Rev. **112**, 405 (1958).

[42] J. R. Drabble and H. J. Goldsmid, *Thermal Conduction in Solids* (Pergamon Press, Inc., New York, 1961), p. 8.

[43] See, for instance, J. M. Ziman, *Theory of Solids* (Cambridge University Press, Cambridge, England, 1964), p. 196.

[44] See, for instance, J. R. Drabble and H. J. Goldsmid, *Thermal Conduction in Solids* (Pergamon Press, Inc., New York, 1961), p. 140.

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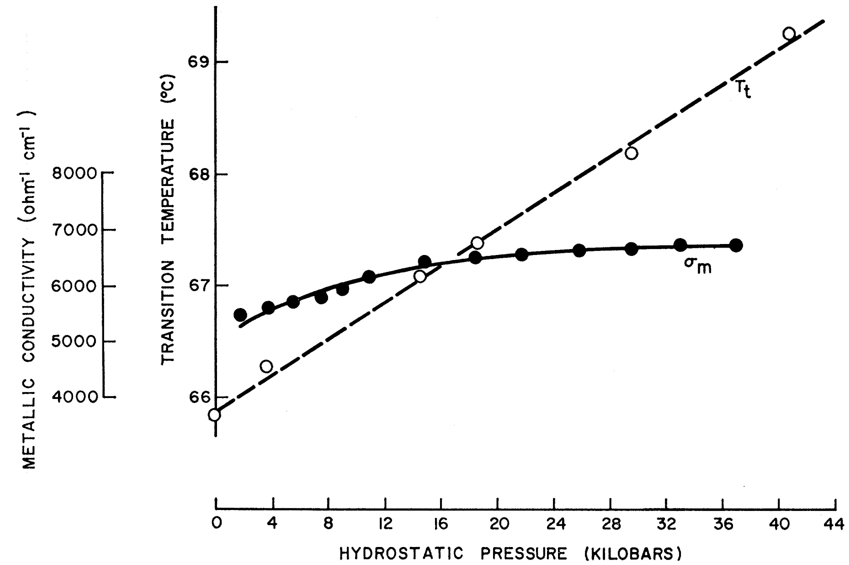

FIG. 8. Hydrostatic pressure dependence of the transition temperature and metallic conductivity in VO_2.

with the Clausius-Clapeyron equation using previously measured values of volume change at the transition[48] and the latent heat. They also found that in the metallic state, the conductivity increased with pressure relatively rapidly at low pressures, then tended to saturate at pressures above 15 to 20 kbar. They pointed out that the nonlinearity in the pressure dependence was more likely to be caused by a pressure dependence of the effective carrier concentration rather than of the carrier mobility. This result implies that the Fermi surface of VO_2 in its metallic state consists of two or more overlapping bands in which the degree of overlap is pressure-dependent.

IV. DISCUSSION AND CONCLUSIONS

A. Metallic State

The experimental data which have been described for tetragonal metallic VO_2 are generally similar to those which would be expected from a simple extrapolation from TiO_2 and are qualitatively consistent with a conventional one-electron picture. There is a set of energy bands, derived primarily from oxygen $2p$ orbitals, lying between 2.5 and 5.5 eV below the Fermi level. The Fermi level lies within a set of ten bands derived primarily from the vanadium $3d$ orbitals. These $3d$ bands are probably wide (1 eV or more) because of both strong cation-cation interactions and significant hybridization with the oxygen $2p$ orbitals. The Fermi surface is complex, the lowest-lying $3d$ band probably being nearly fully occupied and overlapping slightly in energy one or more higher-lying bands.

The relatively poor conductivity of VO_2 has been shown by electron transport and infrared absorption data to be caused by a combination of the small density of carriers, perhaps up to an order of magnitude less than the density of vanadium ions which results from the above described Fermi surface, and a relatively small mobility between 1 and 10 cm^2/V sec. The dominant current carriers are electrons, and their low mobility is caused by strong scattering due to a large electron optical phonon interaction rather than by a large conductivity effective mass. The thermal conductivity tends to rule out the possibility of significant impurity or defect scattering, since the Wiedemann-Franz law is not obeyed, and optical and transport data indicate that the conductivity effective mass is in the range from 0.5 to 4 times the free-electron mass.

In discussing the optical, transport, hydrostatic pressure, magnetic, and thermal measurements on VO_2, it was not necessary nor consistent to invoke unusual correlation effects or a small polaron picture. However, the discontinuity in the magnetic susceptibility and the latent heat at the transition, if attributed entirely to electronic effects, are both sufficiently large that unusual electron correlation and exchange effects may be important. The magnetic susceptibility is quite large, positive, and nearly temperature-independent, and if a large fraction of this susceptibility is attributed to the conduction electrons, direct application of the free-electron theory of metals requires that the Fermi surface density of states be extremely large. A similar requirement arises if a large fraction of the latent heat is attributed to the conduction electrons. Such a density of states would require a band at the Fermi level approximately 0.1 eV wide in addition to the previously described low-mass band, but there is no evidence in the optical data, particularly the photoemission data, for such a narrow band or a high density of states near the Fermi level. In addition, there are other indications in the heat capacity data which tend to rule out the possibility that the latent heat should be explained

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entirely on the basis of an electronic contribution. Given these facts and recognizing that the free-electron theory of spin paramagnetism is rarely expected to provide a good estimate of the electronic contribution to measured susceptibilities without significant corrections for electron correlation, exchange, and other effects, the large discontinuity in magnetic susceptibility and the large latent heat at the transition in VO_2 cannot be considered as strong evidence for very narrow bands at the Fermi surface.

B. Semiconductor State

In the semiconductor state of VO_2, the monoclinic lattice distortion and ionic movements do not seem to significantly alter the energy location with respect to the Fermi level or the total width of the bands derived primarily from the oxygen $2p$ orbitals. However, the optical and photoemission data show that they do produce an energy gap of approximately 0.6 to 0.7 eV within the vanadium $3d$ bands at the Fermi level. The most likely explanation for the existence of this energy gap is that the monoclinic distortion removes the overlap which is present within the $3d$ bands at the Fermi level in the tetragonal state.

The optical, transport, and thermal properties of semiconducting VO_2 are also consistent with a simple band model provided that the energy gap in semiconducting VO_2 has within it donor and acceptor states with an integrated density typically between 10^{19} cm^{-3} and 10^{20} cm^{-3}. The thermal conductivity indicates that such a density of lattice defects or impurities exists in VO_2. These states are probably not intrinsic since their density varies from sample to sample and is well below the density of vanadium ions. Their energy distribution as well as their density varies from sample to sample and is unknown in detail, but for convenience to a first approximation they have been considered to be a relatively structureless continuum of nonmobile states within the energy gap. The actual distribution could not be determined from the experimental data.

The existence of such a large and variable density of states within the gap, without making specific assumptions concerning their energy distribution, explains many of the electronic properties of VO_2 which are difficult to explain using any other single model. The activated conductivity nearly always observed below 68°C arises because the position of the Fermi level within the gap is strongly affected by these states. The charge associated with the density of carriers is nearly negligible in comparison to the charge associated with the donor and acceptor states. The strong optical absorption at photon energies below that corresponding to the energy gap which makes it impossible to obtain optically an accurate measure of the energy gap is due to optical excitation into and out of these levels. The fact that all metallic contacts to VO_2 are Ohmic and thin films both epitaxial and polycrystalline exhibit essentially bulk properties arises because space-charge regions are narrow and essentially transparent for tunneling with such high donor and acceptor densities. Finally, the variations in conductivity, thermal properties, optical properties, and activation energy from sample to sample are easily and consistently accounted for without invoking any other mechanisms if it is assumed that the density and energy distribution of these states varies slightly from sample to sample.

The conduction band effective masses can be estimated in two ways. The density-of-states effective mass is available from the conductivity, Seebeck coefficient and Hall measurements, and is found to be between 1.6 and 7 times the free-electron mass. The uncertainty is primarily because of uncertainty in the electron mobility, which lies between 0.1 and 1 cm^2/V sec, but within this uncertainty the effective mass is in good agreement with that of similar materials such as $BaTiO_3$ and $SrTiO_3$. The conductivity effective mass must always be equal to or less than the density-of-states effective mass. Since it is found from infrared absorption data to lie between one and four times the free-electron mass, this result also is consistent.

The carriers in semiconducting VO_2 are electrons in all samples measured and their mobility is 0.1 to 1 cm^2/V sec, smaller than that in the metallic state. Since the effective masses are similar in magnitude in both the metallic and semiconducting states, it appears that the electron scattering in semiconducting VO_2 may be stronger than in metallic VO_2. The reason for this is not clear.

The infrared absorption data and the measured effective mass result in a maximum electron-optical phonon (polaron) coupling coefficient α of 2. This number is similar to that of TiO_2, $BaTiO_3$, and $SrTiO_3$ and means that VO_2 is in an intermediate (large polaron) coupling regime. Application of present small polaron theories to VO_2 is probably not a good approximation not only because α is not sufficiently large, but because the effective masses are so small.

C. Semiconductor-Metal Transition

Although not of primary interest in this paper, the nature of the semiconductor-metal transition in VO_2 has been of considerable general interest for many years, and since many of the results and conclusions here are important to the understanding of the transition a short discussion is included.

The heat-capacity data clearly show that the transition in VO_2 is first order with a latent heat of 1020 cal/mole of VO_2, and the pressure dependence of the transition temperature is in agreement with the Clausius-Clapeyron equation for first-order transitions. There is a thermal hysteresis at the transition usually in the range from 1 to 2°C which varies from sample to sample, the smallest hysteresis occurring in those samples exhibiting the largest conductivity discontinuity.

While there is no evidence that this hysteresis is physically fundamental to the transition, experimentally all samples measured exhibited some hysteresis and a slight dependence of their properties on thermal history. The transition temperature, within the uncertainty imposed by the hysteresis, is a constant independent of the conductivity or conductivity activation energy of the semiconductor state. This conclusion is valid over a conductivity variation of nearly three orders of magnitude and an activation energy variation from less than 0.1 to over 0.6 eV.

Many of the existing theories of semiconductor-metal transition in solids require or assume that the conduction and/or valence bands in the semiconductor state are of high mass and narrow width.[3–5,7] The data presented here indicate that this is not the case at least in the conduction band of the semiconductor phase and that the effective masses are near unity in the vicinity of the Fermi level in the metallic phase. Some theories require or assume strong electron correlation effects or small polaron effects.[4–6] Experimentally it is found that a small polaron approach of the sort treated in the literature may not be a very good approximation. While there is no evidence against the possibility of unusually large electron correlation effects, it is possible to explain at least qualitatively nearly all of the data without them. In general many of the theories picture the transition from semiconductor to metal as being electronic and triggered by the thermal excitation of electrons across an energy gap. The gap is assumed to be dependent on the density of electrons which have been excited across it. The experimental results here show that the density of electrons thermally excited across the gap is much smaller at all temperatures below the transition than the density of donor and acceptor states which are present. The existence of such states is usually ignored in most theories. In addition, a variation of the density of electrons of over three orders of magnitude by varying the growth conditions of the VO$_2$ (thus varying the density and distribution of the donor and acceptor states) makes no measurable change in the transition temperature. These facts, the fact that repopulation among bands on going through the transition apparently affects only a small fraction of the total number of valence electrons, and the recent pressure data of Berglund and Jayaraman suggest that the transition in VO$_2$ may not be electronic in origin. Given these observations, it should be pointed out that there is no *a priori* reason to eliminate the possibility that the transition in VO$_2$ is primarily a lattice-dominated transition similar to those common in many insulators and metals but which are not accompanied by drastic changes in electronic properties (e.g., antiferroelectrics). This seems to be a most likely explanation since in VO$_2$ the change in electronic properties from those of a semiconductor to those of a metal represent a repopulation of only a small fraction of the total number of valence electrons in VO$_2$, namely, only a fraction of the one electron per vanadium ion which resides within the 3*d* bands. Hence, the changes in electronic properties might be looked upon to a better approximation as a consequence of the lattice transition rather than as a cause of it. Such a model for the transition is consistent with all the described experimental data.

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