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Hydrostatic-Pressure Dependence of the Electronic Properties of VO_2 Near the Semiconductor-Metal Transition Temperature

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The hydrostatic-pressure dependence of the electronic properties of VO_2 near the semiconductor-metal transition to a pressure of 40 kbar is described. The temperature dependence of the VO_2 resistivity from 0°C through the semiconductor-metal transition temperature near 68°C to approximately 80°C at several pressures, and the pressure dependence of the resistivity at 26 and 74°C, are presented and discussed. It is shown that the transition temperature *increases* linearly with hydrostatic pressure at a rate of 0.082 $\pm$0.005°C/kbar, in agreement with the measured volume change and latent heat at the transition, as determined from the Clausius-Clapeyron equation. This value is sample-independent within experimental error. Also, the conductivity activation energy in the semiconductor phase decreases linearly with hydrostatic pressure typically at a rate of between 1 and 2 mV/kbar, but varying significantly, depending on the sample. If the activated conductivity is due to an activated density of carriers, it is shown that, at a fixed temperature in the semiconductor phase, the carrier concentration must increase with pressure and the mobility must decrease with pressure. The results are compared with those expected on the basis of some of the published theories on semiconductor-metal transitions in solids.

1. INTRODUCTION

THE semiconductor-metal transition exhibited by some of the transition metal oxides and sulphides has been of considerable interest for several years.[1] However, there has been insufficient experimental data in the past to allow detailed and unambiguous conclusions to be reached not only on the nature of the transition but also on the electronic properties of the materials. Recently a great deal of work has been done on VO_2,[2–7] an oxide which exhibits a semiconductor-metal transition at approximately 68°C, encouraged by the availability of high quality single crystals[4] and sputtered[5] and epitaxial[6,7] thin films. However, the experimental data on the hydrostatic pressure dependence of the electronic properties of VO_2 are limited to rather low pressures[8] and are contradictory.[9] Adler[1] has pointed out that the pressure dependence of the transition temperature measured by Minomura and Nagasaki[9] is inconsistent through the Clausius-Clapeyron equation for first-order phase transitions with the observed volume change at the transition.[10]

In this paper, the hydrostatic pressure dependence of the conductivity of VO_2 and its temperature dependence up to a pressure of 40 kbar will be described. The data will be discussed in terms of an energy-band picture for VO_2 recently described by Berglund and Guggenheim,[11] and the implications of the results with respect to some of the published theories on semiconductor-metal transitions in solids will be pointed out.

2. EXPERIMENTAL DESCRIPTION

Hydrostatic pressures to 40 kbar were generated in a piston-cylinder device using the Teflon-cell technique.[12] A 1:1 mixture of *n*-pentane and isoamyl alcohol was used as a pressure medium. The temperature inside the pressure cell was varied by heating the entire pressure plate with a heating tape wrapped around the cylinder. Temperature was measured by a chromel-alumel thermocouple set inside the Teflon cell near the sample.

The single-crystal samples of VO_2 were grown by Guggenheim from a supersaturated solution of V_2O_5.[4] The samples usually had a conductivity change at the transition of approximately a factor of 10^4, although there was some variation from sample to sample as described by Berglund and Guggenheim.[11] Resistivity measurements were made using bar samples approximately 0.25 in. long and 0.020 in. in cross section. Four copper leads were bonded to the samples using silver paste. A constant current was applied to the two outer leads while voltage measurements were made with the two inner leads. The voltage drop across the sample was continuously recorded as a function of temperature at constant pressure. Also, the resistivity of the samples was measured as a function of pressure at room temperature using a precision millivoltmeter.

Vanadium dioxide is a particularly difficult material to study because of the phase transition near 68°C. Whenever a sample of the material goes through the transition, cracks tend to form in it and the samples sometimes break. The effect of these cracks on measured transport properties has been discussed by Berglund and Guggenheim,[11] and it has been concluded that they

[1] See, for instance, the review by David Adler, Rev. Mod. Phys. **40**, 714 (1968).
[2] Hans W. Verleur, A. S. Barker, Jr., and C. N. Berglund, Phys. Rev. **172**, 788 (1968).
[3] P. F. Bongers, Solid State Commun. **3**, 275 (1956).
[4] H. J. Guggenheim and J. B. MacChesney (unpublished).
[5] D. H. Hensler, J. Appl. Phys. **39**, 2354 (1968).
[6] H. Takei and S. Koide, J. Phys. Soc. Japan **21**, 1010 (1966).
[7] S. Koide and H. Takei, J. Phys. Soc. Japan **22**, 946 (1967).
[8] C. H. Neuman, A. W. Lawson, and R. F. Brown, J. Chem. Phys. **41**, 1591 (1964).
[9] S. Minomura and H. Nagasaki, J. Phys. Soc. Japan **19**, 131 (1964).
[10] T. Kawakubo and T. Nakagawa, J. Phys. Soc. Japan **19**, 517 (1964).
[11] C. N. Berglund and H. J. Guggenheim, preceding paper, Phys. Rev. **185**, 1022 (1969).
[12] A. Jayaraman, A. R. Hutson, J. H. McFee, A. S. Coriell, and R. G. Maines, Rev. Sci. Instr. **38**, 44 (1967).

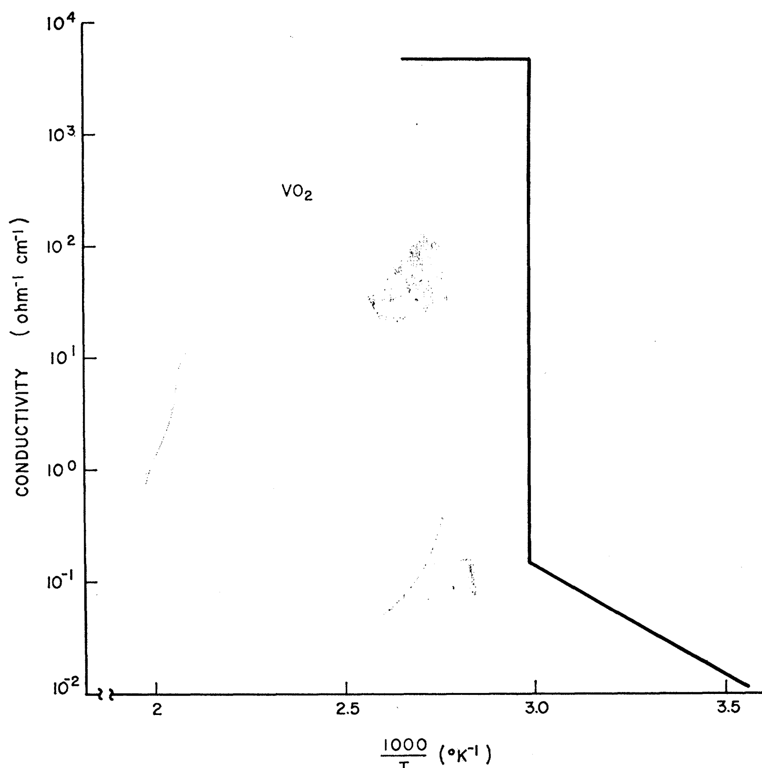

FIG. 1. Temperature dependence of the conductivity of a typical VO_2 sample used in the pressure measurements.

will rarely alter significantly experimental results from the semiconductor phase of VO_2. However, in the metallic phase the presence of cracks may tend to make the measured resistivity somewhat higher than the true bulk resistivity. Since the cracks are nearly always aligned along the crystal (rutile phase) c axis, this source of error has been effectively eliminated in our experiments by measuring resistivity only along the c axis. The resistivity of several samples with various thermal histories in the metallic phase was measured as a function of pressure at a constant temperature of about 74°C. Since the resistivity in the metallic phase is approximately four orders of magnitude less than in the semiconductor phase, the current through the sample had to be increased by several orders of magnitude over that used at lower temperatures and care had to be taken to eliminate stray thermal voltages.

3. RESULTS AND DISCUSSION

Figure 1 shows a typical conductivity-versus-temperature curve for VO_2 at zero applied pressure. The discontinuity in conductivity at the transition temperature of 65.8°C is approximately 10 000. The conductivity varies nearly exponentially with reciprocal temperature in the semiconductor phase from 0°C to the transition temperature with a constant activation energy of approximately 0.4 eV and the thermal hysteresis is about one degree. Most of the data to be described were obtained from samples with characteristics similar to those shown in Fig. 1, but with variations from sample to sample in conductivity at room temperature of over an order of magnitude.

The hydrostatic-pressure dependence of the transition temperature to about 40 kbar is shown in Fig. 2 for both increasing and decreasing temperature. The difference in transition temperature is due to the thermal hysteresis associated with the transition in the VO_2. There is no measurable change in the hysteresis with pressure.

The magnitude of the measured pressure dependence of the transition temperature is consistent with the work of Neuman *et al.*,[8] since it is within their experimental error, but it is opposite in sign and much smaller than that measured by Minomura and Nagasaki.[9] The transition temperature increases linearly with pressure, and the slope dT_t/dp is $+0.082\pm0.005$ deg/kbar. This value is sample-independent. The measured volume expansion at the transition of approximately 0.1%[10] and the measured latent heat[11] of 1020 cal/mole of VO_2 using the Clausius-Clapeyron equation gives agreement in sign and agreement within 50% in magnitude. The discrepancy between the experimentally measured slope and the predicted value is probably due to the uncertainty in magnitude of the volume change. However, the measured positive slope appears to resolve the anomaly referred to by Adler,[1] namely, the observed volume expansion[10] on the one hand and a negative dT/dp measured by Minomura and Nagasaki[9] on the other.

The fact that the transition temperature increases with pressure, while consistent with thermodynamic ex-

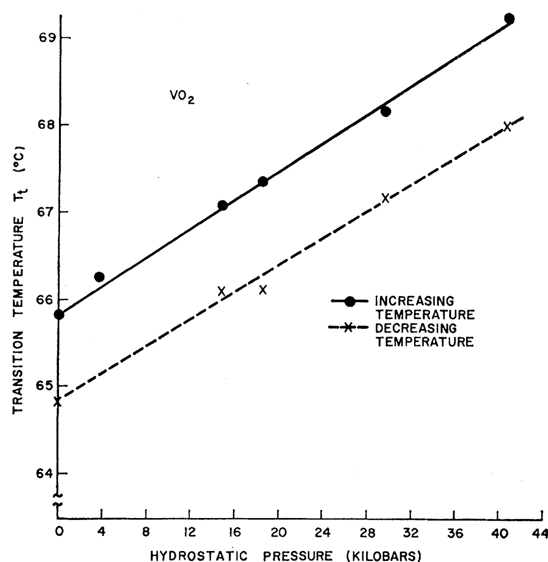

FIG. 2. Hydrostatic-pressure dependence of the transition temperature of VO_2 for increasing and decreasing temperature.

pectations, seems inconsistent with several theories of semiconductor-metal transitions in solids which view the electronic energy bands as very narrow. For example, Mott's early theory on metal-nonmetal transitions predicts that the transition temperature will decrease as the interatomic spacing decreases.[13] However, the lattice distortion, the atomic displacements induced by the transition and the electronic band structure of VO_2 are sufficiently complex that definite conclusions on the validity of any theory cannot be made using this fact alone. The pressure dependence of the band structure and the carrier concentration are also required.

A band model for VO_2 on the basis of optical measurements has been proposed by Verleur, Barker, and Berglund,[2] and discussed in more detail by Berglund and Guggenheim.[11] In this model there is a nearly fully occupied band at the Fermi surface in metallic VO_2 which overlaps slightly one or more partially occupied bands. A similar model has recently been proposed for V_2O_3 by McWhan and Rice.[14] The pressure dependence of the conductivity in the metallic phase of VO_2 (74°C) for two typical samples is shown in Fig. 3. Although there was some slight variation from sample to sample, all showed a relatively rapid increase of conductivity with pressure at low pressures similar to that measured by Neuman *et al.*,[8] with a saturation effect setting in at pressures about 15–20 kbar and a much slower increase in conductivity at higher pressures. The magnitude of the pressure dependence of the conductivity is similar to that measured by McWhan and Rice in V_2O_3.[14] The nonlinearity in the pressure dependence of the conductivity cannot be unambiguously attributed to either a mobility change or to a carrier concentration change, but it seems unlikely to be primarily due to a mobility change. The pressure dependence of the mobility of most metals is nearly linear,[15] as is that of the mobility of materials closely related to VO_2, such as $SrTiO_3$ and $BaTiO_3$.[16] Thus, even if both the mobility and the carrier concentration are pressure-dependent, the nonlinearity is more likely to be primarily due to a carrier concentration change. Such a change is qualitatively consistent with the small-band-overlap model of VO_2. If the overlap of the bands increases under hydrostatic pressure, the occupancy of the partially filled bands will increase, resulting in an increasing conductivity. Further, with increasing overlap, the dependence of the conductivity on the amount of overlap will decrease and the pressure dependence of the conductivity will exhibit a saturation similar to that observed. For this reason, it can be concluded that the pressure data at 74°C are consistent with a two-band model in which the energy overlap of the bands at the Fermi surface in metallic VO_2 is small compared to the bandwidth at zero pressure, and increases with hydrostatic pressure.

In the monoclinic state, an energy gap of approximately 0.6–0.7 eV appears.[2,17] This gap energy should also be pressure-dependent. However, in addition to the tendency for the bands to increase their overlap with pressure noted above the transition temperature (which would correspond to an energy gap decreasing with pressure below the transition temperature) it is likely that the degree of monoclinic distortion will be a function of pressure. Since the energy gap is of necessity a strong function of the monoclinic distortion, the pressure dependence of the band overlap in the metallic state of VO_2 may not be similar either in magnitude or sign with the pressure dependence of the energy gap in the semiconductor state.

Experimentally, it was found on our VO_2 samples that the conductivity in the semiconductor state varied exponentially with the reciprocal of the absolute temperature T from the transition temperature down to at least 0°C,[11] and that a conductivity activation energy E_a could be defined over this range with sufficient accuracy to measure its pressure dependence. At somewhat lower temperatures a departure from simple exponential behavior occurred qualitatively similar to that observed by other workers.[1,3,10] One possible explanation for the observations is that in its semiconducting state VO_2 is an intrinsic semiconductor with mobilities which are sufficiently temperature-dependent to account for the observed departure from an ideal exponential relationship. If this is the case, then the

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

[14] D. B. McWhan and T. M. Rice, Phys. Rev. Letters **22**, 887 (1969).

[15] See, for instance, A. W. Lawson, Progr. Metal Phys. **6**, 1 (1956); F. B. Bundy and H. M. Strong, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 13, p. 81, or William Paul in *High Pressure Physics and Chemistry I*, edited by R. S. Bradley (Academic Press Inc., New York, 1963), p. 299.

[16] M. Di Domencio, S. H. Wemple, and A. Jayaraman, Ninth International Conference on the Physics of Semiconductors, Moscow, July 1968 (unpublished).

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

carrier-density activation energy will correspond approximately to one-half the band gap energy E_g, and a measurement of the pressure dependence of the carrier activation energy should provide a direct measure of the pressure dependence of the band gap energy. However, a recent work by Berglund and Guggenheim[11] indicates that the VO_2 samples studied here contain donor- and/or acceptorlike states within the energy gap to a density greater than that of the carriers. Hence, measured conductivity and carrier density activation energies may not be simply related to E_g, and they will depend on a number of other parameters including the relative densities of donors and acceptors, their binding energies, the relative magnitudes of electron and hole mobilities, and the conduction-band and valence-band densities of states. The values of conductivity and carrier density activation energies may be less than or larger than one-half the band gap energy depending on the sample, but their pressure dependences will not generally be simply related to the pressure dependence of E_g. Nevertheless, the pressure dependence of E_a is important from the point of view of examining the applicability of existing theories to the semiconductor-metal transition, since one quantity of interest nearly as important as the pressure dependence of the band gap energy is the pressure dependence of the density of carriers in the semiconducting phase. If the activated conductivity noted in VO_2 is caused by an activated density of carriers rather than an activated mobility, it will be shown that the pressure dependence of E_a will provide sufficient information to determine the pressure dependence of the density of carriers relative to its density at zero applied pressure.

Since only electrons contribute to the measured conductivity,[5,18] the conductivity of VO_2 in its semiconductor state is

$$\sigma = q\mu_n n\,, \quad (1)$$

where q is the electronic charge, μ_n is the electron mobility, and n is the electron density in the conduction band

$$n = N_c e^{-E_F/kT}\,, \quad (2)$$

where N_c is the effective density of states in the conduction band, 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 at temperature T. Since the mobility is essentially temperature-independent over the temperature range from 0°C to the transition temperature,[5,18] and since a unique conductivity activation energy E_a is observed over this same range, E_F must contain a temperature-independent term over this range equal to E_a provided only that N_c has no anomalous temperature dependence. The pressure dependence of E_a can be determined independent of the pressure dependence of the mobility by plotting the logarithm of the measured conductivity versus reciprocal temperature at each pressure. Even though the magnitude of the conductivity is dependent on both mobility and E_a, the slope of such a plot depends only on E_a. Thus, the pressure dependence of E_a coupled with the fact that N_c is expected to have negligible pressure dependence will yield through Eq. (2) a reasonable estimate of the relative pressure dependence of the electron concentration. Given this relative change in n, the pressure dependence of the conductivity can be used with Eq. (1) to provide some information on the pressure dependence of the electron mobility. In this way, careful measurements of conductivity as a function of temperature from 0°C up to the transition temperature at various pressures can provide information on the pressure dependences of both the electron concentration and the mobility.

[18] I. Kitahiro, T. Ohaski, and A. Watanabe, J. Phys. Soc. Japan 21, 2422 (1966).

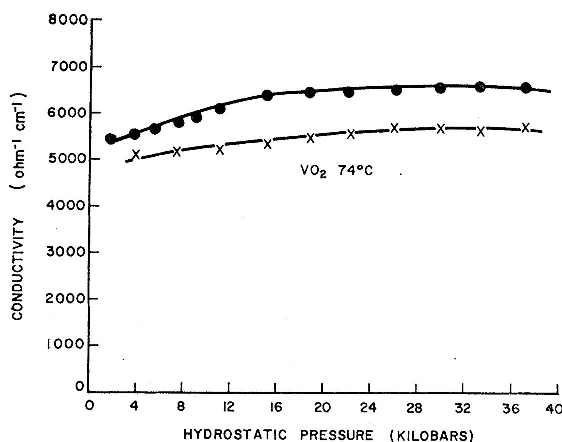

FIG. 3. Hydrostatic-pressure dependence of the metallic VO_2 conductivity (74°) for two samples.

The results of measurements on one typical sample are shown in Fig. 4. For this particular sample, care was taken not to allow the sample to transform to the tetragonal metallic state during the measurements. Figure 5 shows the activation energy versus pressure for this sample, and for another sample which was allowed to pass through the transition at each pressure. While there is some disagreement in the pressure dependence between the two samples and more scatter in the points from the sample which passed through the transition, both indicate that the activation energy decreases with pressure. For all samples measured the activation energy was found to decrease with pressure, usually between 1 and 2 mV/kbar. This is a significant enough change to result in at least a factor of 10 increase in n at a pressure of 40 kbar and temperatures near the transition. Thus, it is reasonable to conclude that the carrier concentration in our samples increases with hydrostatic pressure.

As pointed out previously, given the pressure dependence of the activation energy, and the pressure dependence of the conductivity at a fixed temperature, Eq. (1) can provide an estimate of the pressure dependence of the mobility. However, the rather large activation energies and the limited temperature range of measurement make such an estimate quantitatively unreliable. It can only be stated on the basis of Fig. 4 that

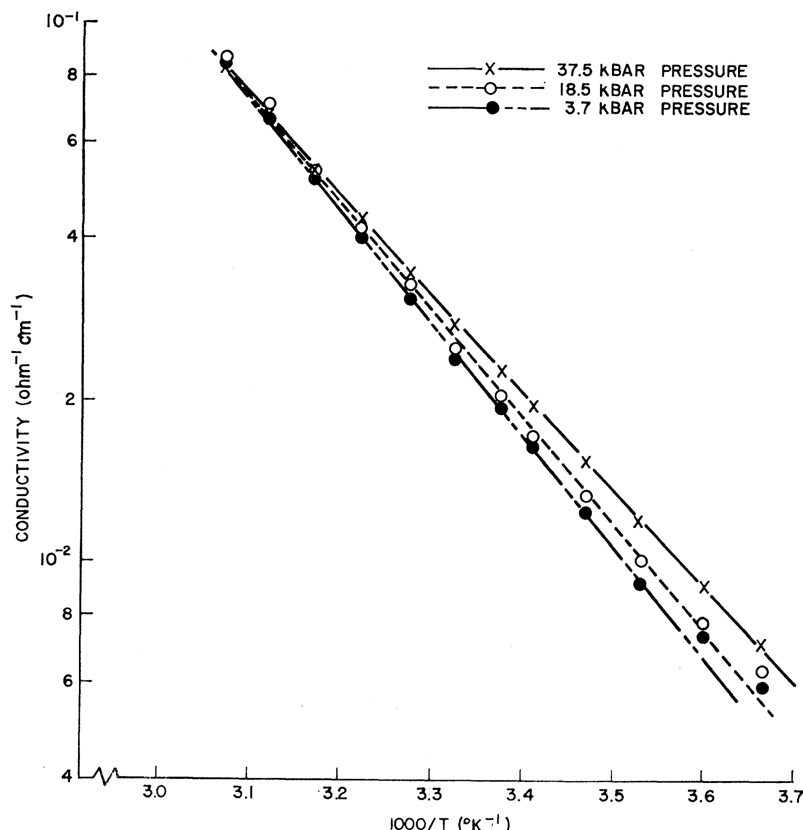

Fig. 4. Typical log-conductivity versus $1/T$ plots for the semiconductor phase of VO_2 at three hydrostatic pressures.

the mobility must decrease with increasing pressure. This fact is illustrated in Fig. 6, where the measured conductivity at room temperature for one sample is shown as a function of hydrostatic pressure. Also shown is the pressure dependence of the conductivity that would result owing only to the change in carrier concentration accompanying the change in E_a. A comparison shows that the mobility must decrease with pressure and the change must be rather large. In fact, for this particular sample the opposing effects of the decreasing mobility and increasing n with pressure results in a nearly pressure-independent conductivity at room temperature.

Several theories of semiconductor-metal transitions in solids, for example that by Adler and Brooks[19] and that by Mott,[20] make use of the concept that there is a critical carrier concentration in the semiconductor state above which the energy gap collapses and the material transforms discontinuously to a metal. The present work shows that in VO_2 the transition temperature increases with pressure while the carrier concentration at a fixed temperature below T_t also increases (carrier activation energy decreases). Thus, it can be concluded that if a theory based on such a concept applies, the critical carrier concentration must have a significant pressure dependence.[21] More important, however, is the fact that measurements on samples with differing conductivities in the semiconductor state result in pressure dependences of this critical carrier density which vary noticeably from sample to sample, whereas the pressure dependence of the transition temperature is sample-independent within experimental error. This result suggests that the transition temperature in VO_2 is independent of the density of carriers in the semiconductor state just below the transition. While it is possible that such behavior can be explained within the framework of existing theories, it is interesting to note that there are other experimental data which also seem inconsistent with this particular concept of an electronically induced transition.[11] Some of the more recent theories, such as that by Mott[22] or by Halperin and Rice,[23] may provide a basis on which to explain the results, but there is also the possibility, pointed out by Berglund and Guggenheim,[11] that the transition in VO_2 is primarily lattice dominated similar to crystalline phase transitions in many solids which do not exhibit striking changes in electronic properties. The metal-semiconductor transi-

[19] David Adler and Harvey Brooks, Phys. Rev. **155**, 826 (1967).
[20] N. F. Mott, Phil. Mag. **6**, 287 (1961). It is shown in Ref. 8 that this theory leads to an energy gap proportional to the transition temperature.
[21] J. Feinleib and W. Paul, Phys. Rev. **155**, 841 (1967).
[22] N. F. Mott, Rev. Mod. Phys. **40**, 677 (1968).
[23] 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.

tion is then best approximated as being a consequence of the fact that the band overlap is a function of the lattice distortion rather than being considered a cause of the crystalline phase transition. Such an explanation for VO_2 would be consistent with the hydrostatic-pressure dependences of the electronic properties presented here.

4. CONCLUSIONS

The semiconductor-metal transition temperature in VO_2 has been found to increase linearly with hydrostatic pressure at a rate of approximately 0.08 deg/kbar up to the highest limit of pressure, namely, 40 kbar in the present study, and to be reproducible from sample to sample. This pressure dependence is in disagreement with the results of Minomura and Nagasaki[9] both with respect to the sign and magnitude. Neuman *et al.*[8] could not detect any shift in the transition temperature with pressure, but this is due to the limited pressure range of their study and the fact that dT/dp is quite small. The measured slope is in good agreement through the Clausius-Clapeyron equation with the measured volume[10] and entropy changes[11] at the transition.

The conductivity activation energies for the samples studied are not simply related to the energy gap of VO_2 in the semiconductor state. They appear to arise as the result of a high density of donorlike and/or acceptorlike states within the gap. As a result, measurements of the pressure dependence of these conductivity activation energies provide no unambiguous information on the pressure dependence of the energy gap. However, such measurements do provide information on the pressure

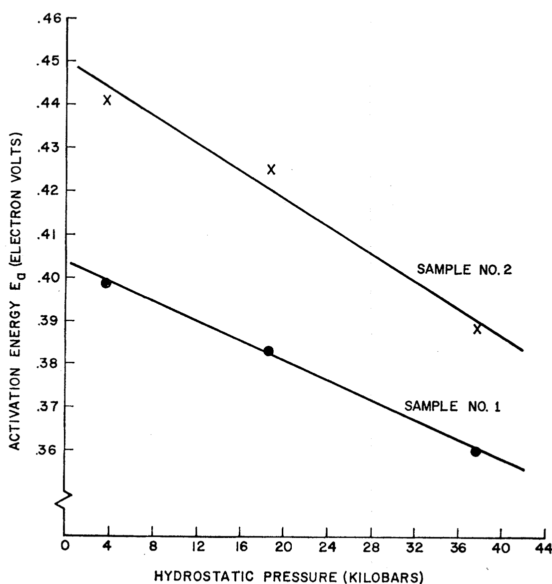

FIG. 5. Conductivity activation energy dependence on hydrostatic pressure for two samples. Sample number 1 was not allowed to pass through the transition during the measurements, while sample number 2 passed through the transition during each measurement.

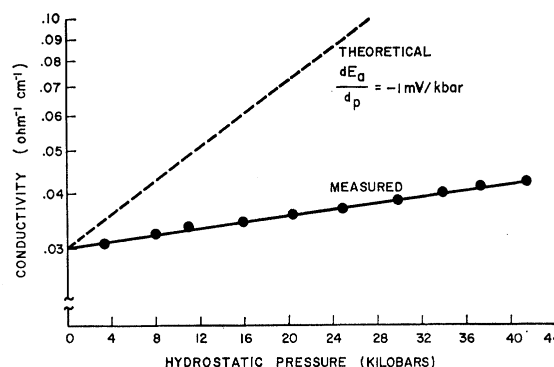

FIG. 6. Room-temperature dependence of VO_2 conductivity on hydrostatic pressure. Also shown (dashed curve) is the change in conductivity which would result from the observed activation energy change alone.

dependence of the carrier concentration. It was found that the activation energies decreased with hydrostatic pressure typically at a rate in the range from 1 to 2 mV/kbar but varying noticeably from sample to sample. The presently observed reproducible pressure dependence of the transition temperature on the one hand and the sample-dependent decrease in the conductivity activation energy on the other appears to be an important result. It indicates that the concept of a critical density of carriers in the semiconductor state above which the material will transform discontinuously into a metal is not a useful one for VO_2. Although it is possible that these data may be explained either by some of the more recent theories of semiconductor-metal transitions or by modifying existing theories, another possibility that should not be overlooked is that the crystalline transition in VO_2 is a lattice-dominated one similar to ferroelectric or other phase transitions common in many solids.[11] If this is the case, the change in electronic properties in VO_2 at the transition can probably be looked upon as a consequence of the crystalline distortion rather than a cause of it.

In the metallic state, the hydrostatic-pressure dependence of the conductivity is consistent with a band model proposed by Verleur *et al.*,[2] in which there is a nearly fully occupied band at the Fermi level having small overlap with one or more partially occupied bands. The experimental data indicate that the overlap at zero pressure is relatively small compared to the bandwidth, and that it increases with hydrostatic pressure. The magnitude of the pressure dependence of the metallic conductivity is similar to that measured in V_2O_3.[14]

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