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Metal–Insulator Transition in Disordered VO_2

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Disordered VO_2 films were prepared by electrochemical anodic oxidation of vanadium. The crystallinity, stoichiometry, conductivity, Hall effect, ESR, and optical adsorption data in disordered VO_2 films have been studied. The main result of this work is that metal–insulator phase transition (MIT) has been preserved in the absence of long-range crystallographic order. A Peierls-like instability which is required for the realization of long-range crystallographic order is therefore not the driving force of the MIT in VO_2. The properties of the disordered VO_2 are compared to those of crystalline VO_2 in metallic and semiconductor phases. The essential role of electron localization in influencing the behavior of the disordered VO_2 is shown. Possible mechanisms of electron localization in the semiconductor and metallic phases are discussed.

There are two main points of view concerning the driving forces of the metal–insulator transition (MIT) in VO_2. First, so-called Peierls-like instability is caused by electron–phonon interactions involving charge-density wave formation. Second, the Mott–Hubbard MIT is based on electron–electron correlations. If parts of the electron and hole Fermi surfaces fulfill the nesting conditions, Peierls-like instability occurs.

Thus, the electron dispersion law for the metallic phase has to fulfill the electron–hole resonance condition (*1, 2*).

$$\varepsilon(\mathbf{K} + \mathbf{Q}) - \varepsilon_F = -\varepsilon(\mathbf{K}) + \varepsilon_F, \quad (1)$$

where **K** is the electron wave vector, **Q** is the reciprocal-lattice wave vector, and ε_F is the Fermi energy level.

A Peierls-like MIT is dependent on structural features and requires long-range crystallographic order for realization. Condition (1) has to be satisfied only for certain atomic configurations. On the other hand, the Mott-type phase transition does not depend on the crystalline structure of the material. Thus, the problem of whether long-range crystalline order is required for the existence of an MIT in VO_2 is particularly interesting.

Numerous experimental attempts have been made to prepare VO_2 in a disordered state (*3–6*). However, in examining this work, it is impossible to state anything definite about the influence of the disorder on the properties of VO_2 due to the uncertainty in stoichiometry and because the degree of crystallinity of the samples was not specifically studied.

In this paper we discuss the preparation of disordered VO_2 films, the characterization of stoichiometry and crystallinity as well as conductivity, Hall effect, ESR, and optical absorption data. The unusual behav-

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ior of metallic and semiconductor phases of the disordered films is compared to those of crystalline VO_2. The essential role of electron correlation of the MIT in VO_2 is also emphasized.

Experimental

Disordered VO_2 films were prepared by electrochemical anodic oxidation of vanadium. Metal films were initially vaporized on several substrates: alumina, silicon, and quartz. Anodic oxidation was used for preparing VO_2 films from the deposited metal films as well as from vanadium foil. More details on film preparation are provided in Ref. (*7*). Conductivity and Hall effect measurements were made using the Van der Pauw four-contact method. A magnetic field of 1.8 T was used. Measurements were limited to temperatures below ~100°C because of the onset of disordered state crystallization. ESR was measured in a quartz cryostat at 9.45 GHz. The number of spins, N, was calculated in comparison with the standard ESR signal ($G = 2.0023$, $N = 10^{13}$ spins). Spectroscopic investigations were made on thin film samples (film thickness was ~1000 Å) in reflecting geometry. The spectral region from 250 to 2000 nm was used.

Investigations of short-range order in the atomic structure of disordered VO_2 were carried out with a monochromatic X-ray diffractometer, DRON-3.0. The experimental method and analysis of the results are reported in detail in Ref. (*8*).

Results

Figure 1 shows the typical thickness dependence of the oxygen (C_0) to vanadium (C_v) concentration ratio in a disordered VO_2 film. These data were obtained by Auger spectroscopy. Assuming a constant rate of etching by Ar ions, the etching time is directly proportional to the thickness of the film. Thus, from the experimental data in Fig. 1, it can be seen that the majority of the film is stoichiometric vanadium dioxide. A thin layer near the surface of the film contains more oxygen than the bulk. The material near the substrate is slightly deficient in oxygen. In X-ray analysis (*8*) of our specimens, the best agreement with the experimental distribution of intensities may be obtained by modeling the disordered VO_2 as a random assembly of spherical clusters with a radius of 5 Å. Thus, the size of the region with an ordered distribution of atoms in disordered VO_2 did not exceed 10 Å. The distribution of atoms in clusters in disordered VO_2 was considerably different compared to that in crystalline material and did not change during the MIT. Thus, there was no pairing of V atoms in the semiconductor phase of the kind observed in the transition from the rutile to the monoclinic lattice in crystalline VO_2. The transition to the high temperature phase in disordered VO_2 corresponded to a reduction in the size of the ordering region to about 1 Å.

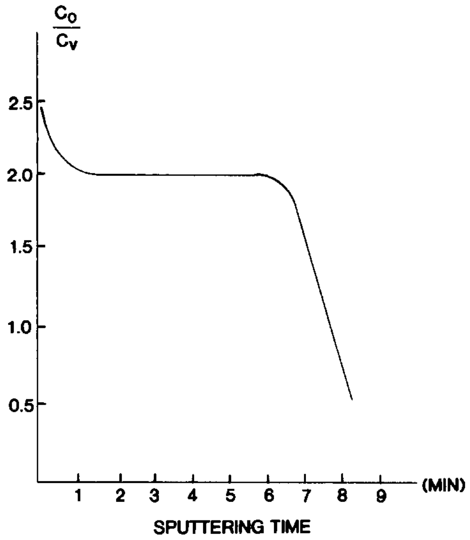

FIG. 1. Typical thickness dependence of the oxygen (C_0) to vanadium (C_v) concentration ratio in the disordered VO_2 film. From Auger spectroscopy data.

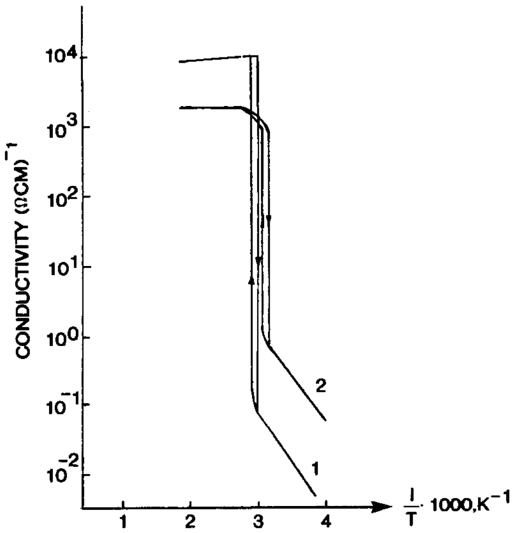

FIG. 2. Temperature dependence of the conductivity for (1) crystalline film and (2) disordered film.

We plot in Fig. 2 the temperature dependence of the conductivity of disordered VO_2 in comparison to that of crystalline VO_2 film. The crystalline VO_2 film was prepared by gas-phase thermal decomposition of vanadium alcoholates (*9*). Therefore, we conclude from these data that the MIT was not suppressed in disordered VO_2. The phase transition temperature, T_c, shifted to lower temperatures by about 10°C. The jump in resistivity at T_c decreases from $\sim 10^5$ ohm · cm for the crystalline film to $\sim 10^3$ for the disordered film. The activation energy in the disordered semiconductor phase is close to 0.5 eV. In the metallic phase, the value of the conductivity is 2×10^3 $(\text{ohm} \cdot \text{cm})^{-1}$ and is temperature independent. The Hall mobility is 10^{-2} $\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$ and does not change during the phase transition. The value of the Hall mobility was at the limit of our experimental detection, so we cannot say anything definite about its temperature dependence.

ESR measurements show a wide peak with $g = 1.951$. The number of localized spins deduced from the ESR results is large, of the order of 10^{22} cm^{-3}. The ESR peak width is temperature independent and its intensity, J, decreased with increasing temperature. Thus, we can assume that J is directly proportional to the magnetic susceptibility, χ (*10*). Figure 3 shows the temperature dependence of the ESR peak intensity. The temperature dependence is consistent with the Curie–Weiss law.

In Fig. 4 we compare the crystalline and disordered VO_2 spectroscopic data. The major feature of the absorption bands in disordered VO_2 are similar to those of crystalline VO_2. Therefore, we conclude that the optical energy gap in disordered VO_2 is roughly 1 eV, about the same as that for crystalline VO_2. The results of our experimental data are summarized in Table I.

Discussion of Results

The most significant aspect of our work is that the MIT has been conserved in the absence of long-range crystallographic order. Also, the MIT in disordered VO_2 is sharp and its transition width is almost the same as that in crystalline films.

Nevertheless, the features of the metallic and semiconductor phases in disordered

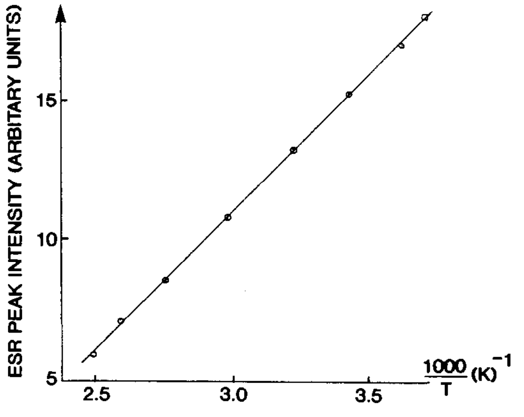

FIG. 3. Temperature dependence of the ESR peak intensity.

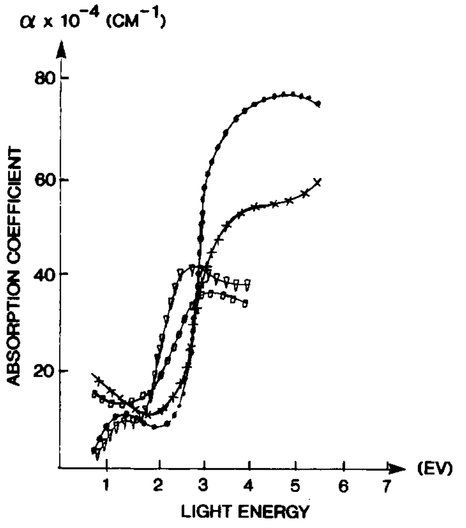

FIG. 4. Optical absorption data: (●, ×) crystalline film; (□, ▽) disordered film; (●, ▽) $T < T_c$; (×, □) $T > T_c$.

VO_2 are unusual and differ from those of crystalline VO_2. The Hall mobility of the disordered VO_2 phase is much smaller in comparison to that of the crystalline material, both for the metallic and the semiconductor phases. The drift mobility is similar in disordered and crystalline VO_2 and is equal to approximately 1 $cm^2/V \cdot s$ (see Table I). Thus, the Hall mobility of disordered VO_2 is about two orders of magnetic smaller than the drift mobility. The observed features are most readily explained by a localization of the electron gas establishing the hopping conductivity mechanism.

In the pure crystalline semiconductor phase of VO_2, no ESR signal is observed due to singlet-pairing of electrons on neighboring V^4 ions. Nevertheless, in crystalline Cr-doped VO_2 two new semiconductor phases were found (*12*). In one of those, only half of the vanadium atoms are paired and a large ESR signal is observed. Thus, a strong ESR signal in disordered VO_2 again confirms the conclusion reached in the X-ray diffraction experiments concerning the absence of V–V pairing in disordered VO_2. The estimation of magnetic susceptibility from ESR shows that the high and low temperature phases of disordered VO_2 are Curie–Weiss paramagnets with spin concentrations of $\sim 10^{22}$ cm^{-3}. Thus, the large susceptibility is the result of strong electron localization which nearly produces the atomic magnetic moment.

The gaps obtained from optical and conductivity measurements on crystalline and disordered VO_2 are nearly coincident; this indicates the prevalence of electron–electron correlations. It should be pointed out that, according to Ref. (*11*), the major contribution to the energy gap of crystalline VO_2 is the Coulomb interaction.

We now comment about the mechanism of MIT in VO_2. Much work has been done on the nature of the MIT in VO_2, in which the nesting condition of Eq. (1) has been applied (*13–15*). Band calculations of the generalized susceptibility $\chi(\mathbf{Q}, o)$ showed the existence of a maximum at $\mathbf{Q} = (\Pi/a, o, \Pi/c)$ (*13*). This leads to phonon instability of the metallic state with a half-filled band and to transition to the dielectric phase accompanied by the appearance of an interband electron–hole condensate. It is doubtful whether condition (1) is fulfilled in the disordered phase.

Nevertheless, even if condition (1) in disordered VO_2 is satisfied, the Peierls-like instability caused by the existence of a Fermi step in the electron energy dispersion law lattice disorder may suppress this instability. According to Ref. (*16, 17*) the Peierls-like instability can be suppressed if the inequality

$$T_c = \frac{\hbar}{t_{imp}} \qquad (2)$$

is satisfied, where $t_{imp} = l/V_F$—the time scattering of electrons by impurities (l is the mean free path of the electrons, and V_F is the Fermi velocity).

Our X-ray diffraction data show that the

TABLE I

Comparison Properties for Disordered and Crystalline Films

	Disordered film	Crystalline film
Temperature of the MIT (°C)	60	68
Jump of conductivity	10^3	10^5
Hysteresis loop width	$\sim 10°$	5°
Metallic phase $T > T_c$		
Conductivity $(\Omega \cdot \text{cm})^{-1}$	$2 \times 10^{-3} = \sigma$ min Mott temperature independent	10^{-4} metallic-like
Hall mobility ($cm^2/V \cdot sec$)	10^{-2}	~ 1
Drift mobility ($cm^2/V \cdot sec$)	~ 1	~ 1
Concentration of the electrons ($1/cm^3$)	10^{22}	10^{22}
Temperature dependence of the magnetic susceptibility	Curie–Weiss	Between Pauli and Curie–Weiss
Semiconductor phase $T < T_c$		
Energy gap (eV)		
From temperature dependence of conductivity	0.5	~ 0.5
From optical data	~ 1	~ 1
Hall mobility ($cm^2/V \cdot sec$)	10^{-2}	1
Magnetic susceptibility	Curie–Weiss	Temperature independent

size of the region with an ordered distribution of atoms does not exceed 1 or 2 interatomic distances. Assuming the mean free path of electrons in disordered VO_2 is $l = 10^{-7}$ cm and an electron velocity $V = V_F \sim 10^8$ cm · sec^{-1}, we obtain $t_{imp} \approx 10^{-15}$ sec. For VO_2, $T_c \sim 0.1$ eV, and inequality (2) is satisfied. Thus, we suggest that the energy gap in disordered VO_2 is the result of the Mott–Hubbard correlations.

The standard Mott–Hubbard model cannot describe all the details of the experimental behavior in disordered VO_2. In particular, the existence of localized magnetic moments in the metallic phase indicates that electron correlations are important in both the semiconductor and the metallic phases of disordered VO_2. Moreover, the MIT in disordered VO_2 accompanies some changes in the phonon subsystem; thus we cannot exclude electron–phonon interactions which are not included in the traditional Mott–Hubbard model.

The unusual experimental behavior of the high temperature phase of disordered VO_2 provides strong evidence for Anderson localization: a temperature independent conductivity of the order of the Mott minimum metallic value, hopping mobility, and spin susceptibility behavior in accordance with the Curie–Weiss law. However, no theory of the degenerate electron gas with Anderson localization and strong electron–electron correlation exists.

For metallic systems with strong electron correlation, even for ideal crystals, localization is possible. This type of localization is more probable in compounds with narrow bands, which are electron Wigner crystals at low temperatures. If electron–electron interactions are sufficiently strong, the situation when $U > B$ (B is the band width and U is the energy for Coulomb interactions) may be realized. In this case, if a chaotic distribution of particles exists, dynamic shifting of electron levels appears, which is the analog of Anderson-type static shifting. As $\mathbf{T} \to 0$, the band character of electron motion is suppressed and localization sets in. This kind of localization was investigated in Ref. (*18*). However, the major features of the metallic phase in disordered VO_2 are quite different. In particular, in the systems with this kind of localization, a conductivity of less than the Mott minimum metallic value can be expected.

We may also suppose that electron correlations, though strong, do not lead to complete localization. Thus we expect significant enhancement of the electron mass. The heat capacity measurements on the W-doped stabilized metallic phase of VO_2 indicate a high effective mass in the metallic state (*19*).

All highly correlated metals, in particular heavy fermion systems, behave in a universal manner. This has raised considerable theoretical and experimental interest; for example, in Ref. (*20*) the behavior of the highly correlated metals is described. According to the authors (*20*), if the spectrum of one-electron states in a metal has a relatively narrow density-of-states peak due the presence of a narrow band of hybridization, an electron–polaron effect is generated. In this case, two electron subsystems may exist: One with $m^* \gg m$ and the other with $m^* > m$. As compared to "light" electrons ($m^* > m$) the "heavy" ones ($m^* \gg m$) are quasilocalized and randomly located. This leads to quasilocalized behavior of the thermodynamic and kinetic characteristics. In crystalline VO_2 energy band calculation indicates the hybridization of a wide Π^* band and narrow *d*-band; so the model of Ref. (*20*) may be applicable. But for disordered VO_2 the existence of a density-of-state peak on the Fermi level has not been established.

It is important to note that the abovementioned special conditions for electron spectra near the Fermi level in describing the behavior of strongly correlated systems are not necessary (*21*). According to Ref. (*21*) the properties of strongly correlated metals can be described in terms of a semiquantum liquid model proposed (*22*) earlier for ^3He. In many systems because of the large effective mass (m^*), the quantum degeneracy temperature, $T_d = P_F^2/2m^*$ (where $P_F = (3\pi^2h^2n)^{1/2}$ is the Fermi momentum and n is the electron density), is anomalously low. This is not only well established for heavy Fermi-ion metals (UPt_3, UBe_{13}, and $CeAl_3$) where $T_d \sim 10$ K (*23*), but also for V_2O_3 in the metallic phase at pressure $p > 18$ kbar where $T_d \sim 100$–600 K (*24*). VO_2 electrons in the metallic phase have an effective mass one or two orders of magnitude larger than those of "bare" electrons.

On the other hand, the plasma frequency

$$\Omega_p = \left(\frac{4\Pi e^2 n}{m}\right)^{1/2}$$

is high and there are two characteristic energies for these compounds, T_d and $\hbar\Omega_p$, where $\hbar\Omega_p \gg T_d$. If $T \ll T_d$, Fermi-liquid behavior with $m^* \gg m$ can be expected.

In the temperature region $T_d \ll T \ll \hbar\Omega_p$ the electron liquid is nondegenerate and the electron spins are disordered. The inequality $T \ll \hbar\Omega_p$ implies that, at times shorter than the lifetime near equilibrium positions, the electrons are still localized near these positions and only oscillate with their characteristic frequency Ω_p. As a result, we obtain the Curie–Weiss susceptibility. The temperature dependence of conductivity is governed by electron–electron collisions. An estimate of the mean free path at $T = T_d$ is the same order as electron–electron distances; as a result one anticipates a Mott minimum metallic value. In Ref. (*21*) the influence of disorder on the thermodynamic and transport parameters is not discussed, but it may be inferred that disorder renders the inequality $m^* \gg m$ stronger, and quasilocal behavior of the electrons is anticipated.

The many features predicted in the model proposed in Ref. (*21*) coincide with those elaborated by Brinkman and Rice (*25*), using the variational method of Gutzwiller for the

Hubbard model in the vicinity of the MIT. However, the model of Ref. (*25*) is applicable only at $T = 0$ K.

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References

1. D. C. Mattis and W. O. Langer, *Phys. Rev. Lett.* **25,** 375 (1970).

2. Yu. V. Kopaev and R. Kh. Timerov, *Zh. Eksp. Teor. Fiz.* **63,** 290 (1972) [*Sov. Phys. JETP* **36,** 153 (1972)].

3. T. N. Kennedy and G. O. Mackenzie, *J. Non-Cryst. Solids* **1,** 326 (1969).

4. K. O. Ufret and E. I. Terukov, *Phys. Status Solidi A* **40,** K157 (1977).

5. A. R. Begishev, G. B. Galiev, A. S. Ignatev, and V. G. Mokerov, *Fiz. Tverd. Tela* **20,** 1643 (1978) [*Sov. Phys. Solid State* **20,** 951 (1978).]

6. V. G. Mokerov, A. R. Begishew, and A. S. Ignatev, *Fiz. Tverd. Tela* **22,** 92 (1980) [*Sov. Phys. Solid State* **22,** 53 (1980)].

7. V. P. Malinenko, G. B. Stefanovich, and F. A. Chudnovskii, *Pisma Zh. Tekn. Fiz.* **9,** 754 (1983) [*Sov. Tech. Phys. Lett.* **9,** 325 (1988)].

8. L. A. Aleshina, V. P. Malinenko, G. B. Stefanovich, and F. A. Chudnovskii, *Fiz. Tverd. Tela* **30,** 914 (1988) [*Sov. Phys. Solid State* **30,** 531 (1988)].

9. G. I. Makin, Yu. Yu. Baryshnikov, O. N. Oruzhkov, and M. Yu. Terman, *in* "Proceedings, Fourth All-Union Conference on the Chemistry, Technology, and Application of Vanadium Compounds [in Russian]," p. 97, Nizhnii Tagil (1982).

10. G. Lancaster, "Electron Spin Resonance in Semiconductors," Plenum, New York (1967).

11. A. Zyllersteein and N. F. Mott, *Phys. Rev. B* **11,** 4383 (1975).

12. D. Heanens, D. Kaplan, and P. Merenda, *J. Phys. C* **8,** 2267 (1975).

13. M. Gupta, A. T. Freeman, and A. T. Ziolkewicz, *J. Phys. Lett.* **38,** L25 (1977).

14. Yu. V. Kopaev and V. G. Mokerov, *Sov. Phys. Dokl.* **27,** 487 (1982).

15. B. G. Idlis and Yu. V. Kopaev, *Solid State Commun.* **45,** 301 (1983).

16. L. N. Bulaevskii and M. V. Sadovskii, *Fiz. Tverd. Tela* **16,** 1159 (1974) [*Sov. Phys. Solid State* **16,** 773 (1974)].

17. G. V. Loseva, S. G. Ovchinnikov, and G. A. Petrakovskii, "Metal–Insulator Transition in Sulfide 3-D Metals [in Russian]," Nauka, Novosibizsk (1983).

18. Yu. Kagan and L. A. Maksimov, *Zh. Eksp. Teor. Fiz.* **86,** 992 (1985) [*Sov. Phys. JETP* **61,** 583 (1985)].

19. D. B. McWhan, T. B. Remeika, and J. P. Maita, *Phys. Rev. B* **7,** 326 (1973).

20. Yu. Kagan and N. V. Prokofev, *Zh. Eksp. Teor. Fiz.* **93,** 366 (1987) [*Sov. Phys. JETP* **66,** 211 (1987)].

21. B. Z. Spivak, *Zh. Eksp. Teor. Fiz.* **90,** 1299 (1986) [*Sov. Phys. JETP* **63,** 759 (1986)].

22. A. F. Andreev and Yu. A. Kosevich, *Zh. Eksp. Teor. Fiz.* **77,** 2518 (1979) [*Sov. Phys. JETP* **50,** 1218 (1979)].

23. G. R. Steward, *Rev. Mod. Phys.* **56,** 7555 (1984).

24. D. B. McWhan, Mench, T. P. Remeika, W. F. Brinkman, and T. M. Rice, *Phys. Rev. B* **7,** 1920 (1973).

25. W. F. Brinkman and T. M. Rice, *Phys. Rev. B* **2,** 4302 (1970).