critical velocity goes to zero. If one uses their formula for E when a vortex is near the wall [their Eq. (14)], but uses the value I_1 [Eq. (8)] which assumes that the vortex was created at the wall, then the limiting value of E/I_1 for a ring at the wall is $\kappa/2\pi a \simeq 1.6\times10^4$ cm/sec for $\kappa = h/m$ and a (the core radius) $= 10^{-8}$ cm. As pointed out by Vinen, this eliminates the problem, even classically, that the critical velocity for the creation of vortex rings at the wall is predicted to be zero. However, the value $\kappa/2\pi a$ is a maximum value of E/I_1 for rings near the wall and should not represent a critical velocity.

In a quantum calculation Fetter[9] showed that the energy of a ring does not go to zero as it approaches the wall. If one does the injustice of dividing the quantum value of E by the classical value I_1, one gets $E/P \to (11/12)\kappa/8\pi b$, where b is the distance from the ring to the wall. Again this is a maximum as $b \to 0$, but the result is not meaningful since I_1 should also be calculated quantum mechanically. Because the impulse required to create a ring is not unique, some care should be exercised before one substitutes I for P in Landau's formula.

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INFRARED OPTICAL PROPERTIES OF VANADIUM DIOXIDE ABOVE AND BELOW THE TRANSITION TEMPERATURE

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We have measured the infrared reflection and transmission spectra of crystals of VO_2 both above and below its transition temperature $T_t = 68°C$. Since the work of Morin[1] which showed the transition as an abrupt change of resistance there have been many recent speculations on the nature of the transitions in $3d$ transition-metal oxides[2,3]: whether they are metallic $\rightleftharpoons$ antiferromagnetic, and/or metallic $\rightleftharpoons$ semiconducting, and whether the conduction in the more insulating state below T_t is band-type or hopping-type. In a recent communication Adler[4] has discussed a model for Ti_2O_3 with a gap which goes rapidly to zero at T_t because of an exchange interaction. A somewhat different model[5] gives a rapidly disappearing gap as a result of a crystalline structure distortion. We have investigated the conduction properties using analysis of infrared reflection and transmission, and we present the first Hall data in VO_2 both above and below T_t. We have also examined the question of lattice stability and conclude that there is not a Cochran-type ferroelectric mode[6] connected with the transition. The crystals used were grown by decomposing V_2O_5 in a temperature-difference system. Chemical analysis showed the stoichiometry to be VO_x with $x = 2.01 \pm 0.01$.

Group theory applied to monoclinic (m) VO_2 shows that in the long-wavelength limit there are eight infrared-active modes for the electric vector $\vec{E}$ parallel to the b_m axis and seven infrared-active modes for $\vec{E}$ in the plane perpendicular to the b_m axis. In addition, there

are 18 Raman-active modes. In VO_2 for $T > T_t$ (rutile structure r) there are three infrared-active modes perpendicular to the c_r axis and one parallel to the c_r axis.

The reflectivity spectra were measured in the usual manner[7] both below and above T_t, as well as at a temperature near T_t. The range of frequencies covered was from 100 to 20 000 cm^{-1}. The spectra at room temperature were measured with all possibly distinct orientations of the crystal. However, distinct spectra were obtained only with $\vec{E}$ parallel or perpendicular to the a_m axis. Figure 1 shows the $E \| a_m$ spectra. The lack of a unique $E \| b_m$ spectrum below T_t leads to an interesting conclusion concerning the crystal structure. At T_t, the crystallographic transformation is[8]

$$a_m \leftarrow 2c_r, \quad b_m \leftarrow a_r, \quad c_m \leftarrow a_r - c_r.$$

Furthermore, the distortion is slight, so that $|c_m|_{T<T_t} \simeq |a_r - c_r|_{T>T_t}$. If one views the crystal in the low-temperature phase in reflection using a polarizing microscope, one observes a domain pattern.[9] The reflectivity measurements suggest that these domains are the result of the monoclinic b_m axis choosing one a_r axis to point along in one region and choosing the other a_r axis in another region when the crystal is cooled through T_t. Typical domains are about 40 μ across the narrow dimension; thus we have not been able to measure the reflectivity spectrum of a single domain.

We have used the classical oscillator expression for ϵ, the dielectric function, to fit the reflectivity spectra below and above T_t. The oscillator parameters for $E \| a_m$ and $E \perp a_m$ are listed in Table I. We have fitted nine modes to the $E \|$ spectrum. We assume that the highest frequency "mode" simulates the band-to-band transitions. Newman, Lawson, and Brown[3] have observed an activation energy in conductivity measurements of 4000 cm^{-1}, suggesting a gap at 8000 cm^{-1}. However, activation energies as low as 1600 cm^{-1} have also been observed.[10] Preliminary transmission measurements on our single-crystal samples show an onset of absorption near 2500 cm^{-1} which may

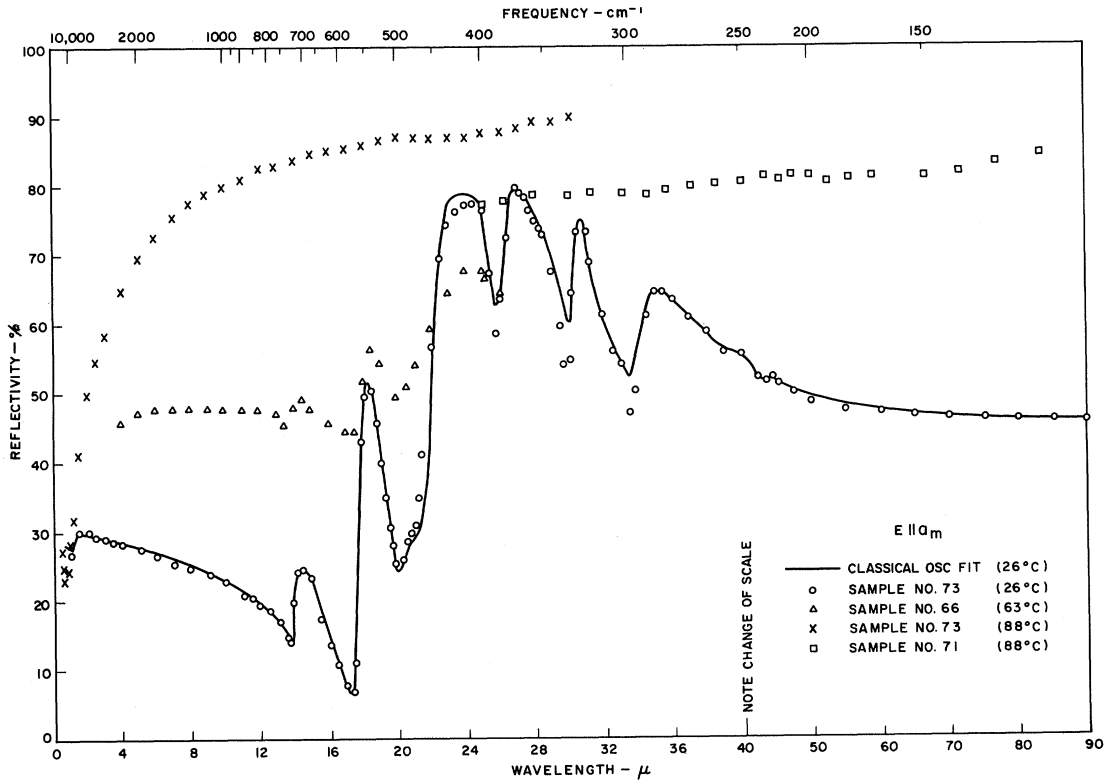

FIG. 1. Reflectivity of VO_2. The solid curve is a fit for $T < T_t$ using eight phonon modes and one band-structure mode. The crosses and squares show the data above T_t. The squares are low because of sample cracking; however, they illustrate the monotonic rise expected of free carrier reflection. The triangle points were taken on cooling. Because of thermal hysteresis, $T_t \simeq 63°C$ for this run.

Table I. VO_2 classical oscillator parameters for the dielectric function above and below T_t.

Mode no.	$E \perp a_m$ ω (cm^{-1})	$4\pi\rho$	γ	$E \parallel a_m$ ω (cm^{-1})	$4\pi\rho$	γ
		$T = 26°C$, primitive cell V_4O_8 (monoclinic)				
1	189	0.54	0.012	227.5	0.1	0.02
2	270	13.0	0.07	285	3.3	0.06
3	310	7.0	0.05	324	1.95	0.018
4	340	0.7	0.024	355	7.4	0.08
5	505	3.1	0.07	392.5	1.0	0.03
6	600	4.8	0.074	478	0.2	0.08
7	710	0.15	0.06	530	0.65	0.045
8	10 000	1.3	0.4	700	0.25	0.055
9				10 000	1.3	0.4
		$\epsilon_\infty = 10.0$, $\epsilon_0 = 40.6$			$\epsilon_\infty = 9.7$, $\epsilon_0 = 25.9$	
		$T = 80°C$, primitive cell V_2O_4				
		$E \parallel c_r$ (rutile)				
		$\omega_p = 8000$ cm^{-1}, $\omega_c = 10\,000$ cm^{-1}, $\epsilon_\infty = 9$				

be the band gap. The remaining optical phonon modes have strengths typical of ionic crystals.

Because of the domain problem, the $E \perp a_m$ spectra can exhibit up to 15 optical phonon modes with strengths which depend on the angle between the E vector and the dipole moment of the normal modes, some of which lie along b_m and some of which are perpendicular to b_m. While there is much fine structure, the data are adequately fit by the seven modes listed in Table I plus a band-structure mode near 10 000 cm^{-1} similar to that for $E \parallel a_m$. Neither polarization shows a strong low-frequency mode such as might be expected if the transition were caused by a Cochran-type infrared-active mode, though such a mode may exist above T_t and change its character completely below T_t. We note, however, that the ion shifts[8] at T_t are typical of a $(101)_r$ or a $(011)_r$ zone-boundary phonon and thus not likely to show up even for $T > T_t$ in the first-order spectrum.

Figure 1 shows a typical reflectivity spectrum for $T > T_t$. Two samples were used for this run. After the long-wavelength data were taken, the sample appeared to be cracked, which probably caused the discontinuity between the low- and the (more reliable) high-frequency measurements. The spectra for all other polarizations with $T > T_t$ show similar high reflectivity typical of metallic or free carrier behavior, except that the reflectivity spectrum for $E \perp c_r$ (not shown) has some additional structure near 660 cm^{-1}. We hesitate to interpret this as being due to an optical phonon in the rutile phase because it was not reproduced in all other crystals we measured.

We list in Table I the dielectric-function parameters ω_p and ω_c, the plasma and collision frequencies, where $\epsilon(\text{carriers}) = -\omega_p^2\epsilon_\infty/(\omega^2 - i\omega\omega_c)$ for one $E \parallel c_r$ spectrum. For $T \simeq T_t$ we see both the semiconducting-phase phonons and the metallic-phase phonons and the metallic-phase plasma. We interpret this spectrum (Fig. 1) as arising from the coexistence of regions of both phases. Table II shows the Hall effect data on samples from the same growth batch as those studied in the infrared. The only measurement of a Hall voltage detectable above noise (for $T > T_t$) gives $n \sim 30 \times 10^{20}$ electrons/cm^3. This represents only 0.1 electron per vanadium ion and raises the question of whether we actually have simple "metallic" conductivity. Proceeding, however, and using $n \sim 30 \times 10^{20}$ combined with the infrared results, we deduce an optical mass of $m^* \sim 0.5 m_e$ and an optical mobility of $\mu_{\text{opt}} = e/\omega_c m^* \sim 2$ cm^2/V sec for the metallic phase.

The d.c. mobility in the semiconducting phase (Table II), though small, is many orders of magnitude larger than in NiO, a hopping-type conductor.[11] Rough fits to the infrared free-carrier absorption measured by transmission at 25°C in the 1000- to 5000-cm^{-1} region combined with the Hall measurements suggest that m^* is greater than m_e, and may be as large as $4m_e$. Recent nuclear magnetic resonance

Table II. Hall effect and resistivity of VO_2.

Sample	Temperature (°C)	Current direction	ρ (Ω cm)	$n = 1/R_H c$ (10^{20} cm^{-3})	μ (cm^2/V sec)
78	22	$\perp a_m$	1	0.09[a]	0.7
78	80	$\perp c_r$	0.000 14	>23	>19
80	22	$\perp a_m$	1.2	0.09[a]	0.6
80	81	$\perp c_r$	0.000 24	>17	>15
80	22	$\parallel a_m$	1.4	0.086[a]	0.52
80	79	$\parallel c_r$	0.000 13	~30[a,b]	~16[b]

[a]Hall voltage corresponds to electrons.
[b]Factor of 2 uncertainty.

measurements[12] show that VO_2 does not become antiferromagnetic at T_t. Our crystals show a constant magnetic susceptibility of 0.88×10^{-6} emu/g from room temperature down to 100°K, where a Curie-law behavior sets in ($T_C \sim 0$°K) which may be due to impurities. It appears then that a gap opens up on cooling through T_t causing a transition to a nonmagnetic semiconducting phase.

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