

ELECTRON STRUCTURE AND PHASE TRANSITIONS IN LOWER VANADIUM OXIDES IN AN ELECTRIC FIELD

K. A. VALIEV, Yu. V. KOPAEV, V. G. MOKEROV, and A. V. RAKOV

Submitted November 5, 1970

Zh. Eksp. Teor. Fiz. 60, 2175–2187 (June, 1971)

The electric reflection (ER) and ordinary reflection spectra of VO_2 and V_2O_3 single crystals are measured at temperatures between 296 and 360°K. The optical transitions in VO_2 and V_2O_3 are identified for photons with energies between 1.1 and 5.6 eV. Information is obtained regarding the temperature dependence of the VO_2 electron structure in the semiconducting phase and the nature of its variation during the thermal semiconductor-metal phase transition. A metal-insulator phase transition induced by an electric field occurs under the action of a high stationary voltage applied to the sample ($F = 10^6$ v/cm). The shape of the dependence of the ER signal on applied voltage is explained by the static dielectric constant ϵ_0 passing through a maximum during the phase transition. At $T = 296^\circ\text{K}$, an electric-field induced semiconductor-metal phase transition which possesses strong field hysteresis (memory effect) is observed in VO_2 ; with further increase of the electric field strength a less pronounced metal-semiconductor transition is observed. A number of phase transformations induced by an electric field are observed in VO_2 in the metallic state ($T = 348^\circ\text{K}$). Possible mechanisms of field switching are discussed, and it is shown that the most probable cause of the transformations induced in VO_2 and V_2O_3 by an electric field is the inverse piezoeffect.

THE oxides V_2O_3 and VO_2 go over from the semiconducting state into the metallic state when the temperature is raised to a certain critical value T_t ,^[1] with a jumplike change of the electric conductivity by several orders of magnitude. The transition temperatures T_t for V_2O_3 and VO_2 are 150 and 340°K, respectively. The symmetry of the crystal lattice of both oxides also changes in the phase transitions. The symmetry of VO_2 changes from monoclinic to tetragonal, and that of V_2O_3 from monoclinic to rhombohedral on going from the semiconducting to the metallic state. The phase transitions are accompanied by a jumplike change of the volume and are phase transitions of the first kind with temperature hysteresis of several degrees. In V_2O_3 there is also observed a second and weaker anomaly of the temperature dependence of the electric conductivity near 530°K. In^[2] they observed in V_2O_3 samples doped with chromium, besides the transition at $T = 150^\circ\text{K}$, also a second phase transition from the metallic state into the insulator state, occurring with increasing temperature near 530°K, and connected with a change of the volume of the crystal.

The optical^[3, 4] properties of VO_2 are also abruptly altered by the phase transition, a fact attributed to the change of the electronic structure of this material. The oxide V_2O_3 is transparent at $T > T_t$ in a wide range of photon energies, but at $T < T_t$ an absorption edge is observed near 0.1–0.4 eV,^[1] as a result of the occurrence of a gap in the energy spectrum of the low-temperature phase.

Several models have been proposed to explain the phase transitions in vanadium oxides. According to^[5] the transition to the metallic state can be due to a distortion of the crystal lattice owing to excitation of the carriers via the energy gap, and it is shown in^[6] that the crystalline distortion that leads to the phase transition can occur also in the case of current-free excitations—excitons. On the other hand, the semiconductor-

metal transition is connected in the "exciton insulator" model with the Coulomb interaction between the electrons and the holes.^[7–9] It has been shown that distortion of the crystal lattice can occur in this case, too, at sufficiently strong electron-phonon interactions.^[10]

To determine more accurately the mechanism of the phase transitions it is necessary to note the electronic structure of these oxides, and the data concerning this structure are as yet insufficient. We present here the results of an investigation of the optical and electric properties of VO_2 and V_2O_3 in an external electric field. Some preliminary data were reported earlier.^[11]

EXPERIMENTAL PART

The optical properties of VO_2 and V_2O_3 in an electric field were investigated by the electric reflection (ER) method.^[12] The electric field was produced on the samples by placing the crystals in an electrolyte and applying a constant bias U_C in the barrier direction, since the semiconductor-electrolyte interface behaves like a metal-semiconductor diode. The constant and alternating voltages U_C and U_ω were applied through a platinum electrode, also situated in the electrolyte, in such a way that the sum $U_C + U_\omega$ was always less than the value corresponding to the breakdown of the diode. The electrolyte was a weak solution of KCl in water (0.1 M). The sample plane opposite the reflecting surface was secured with silver solder to a copper bus. All the parts of the sample and the contact leads in the electrolyte, with the exception of the reflecting surface, were then covered with epoxy resin.

The ER spectra of VO_2 were measured in polarized light for $E \parallel a_m(c_r)$ and $E \perp a_m(c_r)$, where E is the light polarization direction and a_m and c_r are respectively the crystallographic directions of the monoclinic and tetragonal phases. The ER was recorded with an MDR-2 diffraction-grating monochromator for photon energies

$\hbar\omega$ from 1.1 to 5.5–5.8 eV in the temperature interval 296–360°K. The light source was a 500-W xenon arc and the reflected-signal receiver was a photomultiplier. Separation of the alternating component of the reflected signal was by a phase-sensitive method using a selective amplifier and a synchronous detector. All the measurements were performed at 700 Hz. For direct registration of the quantity $R^{-1}dR/dU$ (R —reflection coefficient), the high-voltage supply of the photomultiplier was regulated with a servomechanism in such a way that the constant signal at the photomultiplier output was maintained at the same level (1 V) over the entire spectrum.

To measure the electric resistance of the samples in the electric field, two contacts were fastened to the reflecting surface and connected to an ohmmeter. The temperature in the cell with the electrolyte was varied by introducing a heat duct. The procedure for obtaining the crystals was described earlier.^[4]

RESULTS AND DISCUSSION

1. ER spectra of VO₂ single crystals in a weak electric field. The ER spectra of VO₂ were measured for normal incidence of light at two directions of the light polarization vector and at different values of the temperature for $U_C = 0$. For comparison, we also registered the spectra of the ordinary reflection R . At small U_C ($U_C < 1.3$ V) and $T = 296$ °K, the most characteristic features of the spectra are as follows: a) a large amplitude of the ER signal in the entire spectral range (larger by almost one order of magnitude than in ordinary semiconductors^[12]), b) there are no sharp oscillations in the ER spectrum near the characteristic critical points of the band structure and no zeroes in the remaining intervals of $\hbar\omega$; c) with increasing U_C (for $U_C \leq 1.2$ –1.3 V), there is observed a monotonic increase of the amplitude of the positive peaks and a weakening of the amplitude of the negative ones, and weak shifts along the $\hbar\omega$ scale appear ($\Delta\hbar\omega \leq 0.1$ eV).

By way of an example, Fig. 1 shows the ER and R spectra for the case $E \perp a_m(c_T)$. It is seen from Fig. 1 that the singularities in the ER spectra coincide with the main singularities of R . But since ER is a differential method, an additional structure missing from R is also observed in these spectra. Apparently, at small U_C the ER spectrum of the low-temperature phase of VO₂ is due to the Franz-Keldysh effect in ER^[13] with allowance for damping, a fact manifest in the broadening of the structure and in the absence of satellite oscillations. As seen from Fig. 1, an analogous interpretation of the ER spectrum is obviously valid also at $T = 348$ °K ($T > T_t$).

At $T > T_t$, the maximum of R near 3 eV corresponds to the ER maxima at 2.92 eV for $E \perp a_m$ and 3.1 eV for $E \parallel a_m$. The strong ER peak at 4.75 eV for the two polarization directions is manifest in the change of the slope of $R(\hbar\omega)$. For $E \perp c_T$, a "weak shoulder" is observed in ER at 2.2 eV. The positions of the main peaks of ER also agree well with the three strong thresholds in the VO₂ absorption spectrum: 2.2, 3, 4.7–4.8 eV,^[4] which are connected with optical transitions between the 2p band of oxygen and the empty 3d subbands of vanadium. This confirms the connection between the ER peaks and the critical points of the band structure.

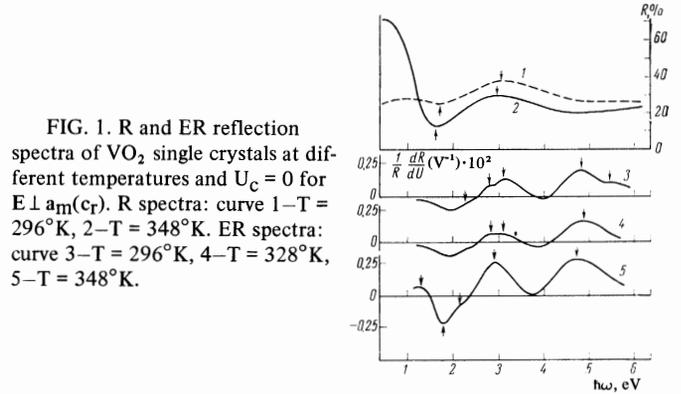


FIG. 1. R and ER reflection spectra of VO₂ single crystals at different temperatures and $U_C = 0$ for $E \perp a_m(c_T)$. R spectra: curve 1— $T = 296$ °K, 2— $T = 348$ °K. ER spectra: curve 3— $T = 296$ °K, 4— $T = 328$ °K, 5— $T = 348$ °K.

The optical properties of VO₂ ($T > T_t$) at $\hbar\omega < 2$ eV are determined by the electronic transitions between the filled and empty 3d subbands of vanadium, and also by the intraband optical transitions, in view of the absence of an energy gap at $T > T_t$. The minimum in the spectrum of R at 1.65 eV corresponds approximately to negative maxima at 1.8 eV for $E \perp a_m$ and 1.9 eV for $E \parallel a_m$. In addition, there are observed in the ER spectra maxima at 1.3 eV ($E \perp a_m$) and 1.4 eV ($E \parallel a_m$), which are missing in the R spectrum. However, in the absorption spectrum of VO₂ at $T > T_t$ there are observed two peaks: 1.5 eV ($E \perp a_m$) and 1.55 eV ($E \parallel a_m$), which can be set in correspondence with these ER maxima.^[4]

The sharp plasma edge ($\hbar\omega \approx 1.65$ eV) and the minimum in the R spectrum at 1.65 eV for $T > T_t$ were previously attributed to the metallic behavior of the free carriers,^[4] an assumption which is apparently not quite correct. Indeed, if we use the carrier effective mass $m^* = 2.5 m_0$ obtained in^[4] from an estimate of the width of the 3d subbands, and the free-carrier density $n_C = 3 \times 10^{21}$ cm⁻³ obtained in^[14] from Hall-effect measurements, then we get for the Fermi energy $E_F = 0.2$ eV. It is known, however, that $E_F \sim p_F v_F$ and $\omega_p \sim \kappa_D v_F$, where p_F and v_F are the momentum and velocity of the electrons on the Fermi surface and κ_D is the reciprocal Debye radius. And since, by definition, $p_F > \kappa_D$, the inequality $E_F > \omega_p$ must be satisfied, and the minimum in the R spectrum at 1.65 eV cannot be ascribed to the conduction-electron plasma. At the same time, at $\hbar\omega$ larger than the average distance between the valence band and the conduction band (with allowance for the band widths), optical transitions are possible between the band sections with identical curvature, and in this case the plasma of the valence electrons will behave in analogy with the plasma of the conduction electrons.

Let us estimate the plasma frequency for the valence 3d electrons of VO₂, using $m^* = 2.5 m_0$, $n_V = 3 \times 10^{22}$ cm⁻³, and $\epsilon = 4$; we then obtain $\hbar\omega_p = [4\pi e^2 n_C \hbar^2 / m^* \epsilon]^{1/2} = 1.85$ eV. This value of ω_p agrees well with the spectral position of the R minimum, the negative ER maxima, and the estimate of the 3d valence subband of VO₂ ($E_V \approx 1.5$ eV) given in^[4]. We note that for Si, for example, when $E_V \approx 15$ eV, the plasma effects of the valence electrons come into play at $\hbar\omega > 13$ eV.^[15] The strong infrared reflection of VO₂ ($R \approx 90\%$)^[14] at $T > T_t$ is due to the conduction electrons. For $n_C = 3 \times 10^{21}$ cm⁻³, the plasma frequency corresponds to 0.5 eV, which agrees with the presence

of a "shoulder" in the R spectrum near 0.5 eV for $T > T_t$.^[3]

On going over to the superconducting state ($T < T_t$) the overlap of the filled and empty 3d subbands is lifted, owing to the occurrence of an energy gap in the semiconducting phase of VO₂, and the contribution made to R and ER by the free carriers vanishes. However, just as when $T > T_t$, we should expect the optical spectra to have a structure connected with the interband transitions, and also metallic behavior of the valence 3d electrons. As seen from Fig. 1, the plasma minimum remains at $T < T_t$ ($\hbar\omega = 1.7$ eV), and in ER, just at $T > T_t$, this minimum corresponds to a negative maximum at 1.9 eV. A similar picture was also observed in the case $E \parallel a_m$. When $E \perp a_m$, there appears at 1.3 eV an ER maximum which apparently corresponds to the absorption peak at 1.4 eV.^[4] In the R spectrum there is observed a peak near 1.0 eV, which is apparently connected with a superposition of the interband and plasma reflections of the 3d valence electrons. The presence of the R minima at 1.65–1.7 eV and of the negative ER maxima at 1.8–2.0 eV for both phases of VO₂ is an argument favoring the assumption that they are connected with the plasma of the valence electrons and not of the free 3d electrons. The quantitative difference between the values of this effect for $T > T_t$ and $T < T_t$ may be connected with the appearance of an energy gap and with the change of the crystal-lattice symmetry during the phase transition. The former leads to a shift of the bands and to elimination of the contribution from the free carriers, and the doubling of the periodicity of the crystal lattice and the corresponding reduction of the dimensions of the Brillouin zone changes the conditions for the indirect optical transitions, owing to the change of the momentum transfer

For the region $\hbar\omega > 2$ eV, which corresponds to $2p \rightarrow 3d$ interband optical transitions, significant changes likewise occur at $T < T_t$. The ER peak at 2.9 eV ($T > T_t$) splits into two peaks at 2.8 and 3.15 eV ($T < T_t$), and the ER maximum at 4.75 eV also splits at $T < T_t$ into two maxima, 4.9 and 5.4 eV. This is obviously connected with doubling of the period of the crystal lattice and illustrates clearly the influence of the periodicity of the crystal on its electronic energy spectrum. The lowering of the crystal symmetry is manifest also in the change of the ratio of the ER intensities for different polarizations. Thus, for $T < T_t$ the ER signal near 4.9 eV is much larger for $E \parallel a_m$ than for $E \perp a_m$, and at $T > T_t$ they are practically equal. We note that the change of the ratio of the ER intensities for different polarizations during the temperature phase transition agrees with the changes occurring in the ordinary reflection spectrum (with zero field). This fact, and also the agreement between the principal ER and R peaks, indicates that a weak electric field ($U_c = 0$), which always exists on the surface barrier, exerts practically no influence on the phase transition. The differential character of the ER method simply makes it possible to observe the finer structure of the optical spectrum.

The presence of distinct extrema in the ER spectrum makes it possible to obtain information on the temperature dependence of the energy spectrum of VO₂. Thus, for $E \perp a_m$ the maxima at 2.8 and 3.15 eV ($T = 296^\circ\text{K}$) correspond to weaker maxima at 2.82 and 3.1 eV in the

case of $T = 328^\circ\text{K}$, and for $E \parallel a_m$ the maxima at 2.65 and 3.42 eV ($T = 296^\circ\text{K}$) correspond to the maxima at 2.7 and 3.3 eV ($T = 328^\circ\text{K}$). Such appreciable changes in the intervals between the ER peaks ($\Delta\hbar\omega = 0.1$ eV) for $\Delta T = 30^\circ\text{K}$ point to strong shifts of the energy bands in VO₂ with changing temperature near T_t . This can serve as an argument in favor of the nonlinear temperature variation of the energy gap E_g , the possibility of which was discussed in^[4] on the basis of an analysis of the temperature dependence of the electric conductivity.

2. ER spectra of V₂O₃ in a weak electric field. The R and ER spectra in a weak constant electric field at $T = 296^\circ\text{K}$ ($T > T_t$) are shown in Fig. 2. The main features of the ER are the presence of broad bands without satellite oscillations and the large signal amplitude. In the R spectrum at $\hbar\omega \leq 1.3$ eV there is observed a typical plasma edge, which is apparently connected with the presence of free carriers ($n_c = 3 \times 10^{22}$ cm⁻³^[16]). At $\hbar\omega > 1.3$ eV, the main singularities of R and ER approximately coincide. The maxima of R at 1.45 and 1.9 eV can be set in correspondence with the maximum at 1.4 eV and the "shoulder" at 2.0 eV in the ER spectrum. For $\hbar\omega > 2$ eV, the R spectrum exhibits a decrease of the reflection, which is characteristic of metals, with increasing quantum energy, corresponding, as in the case of VO₂, to the negative ER maximum at 2.9 eV. At $\hbar\omega > 3$ eV, the reflection coefficient again increases and two maxima appear at 4.6 and 5.6 eV. In the ER spectrum, they can be set in correspondence to the 4.5 eV maximum and to the weak "shoulder" at 5.5 eV. In the ER spectrum there also appears an additional maximum near 4 eV, which is missing from the reflection spectrum.

The energy spectrum of V₂O₃ near the Fermi level consists of empty and filled 3d subbands, which overlap partly at $T > T_t$, and at $T > T_t$ V₂O₃ is a semimetal with 0.6 quasifree carriers per vanadium atom. From a comparison of the ER spectra of VO₂ and V₂O₃ it can be assumed that the 1.45 and 1.9 eV peaks are connected with direct optical transitions between the filled and empty 3d subbands, while the drop of R at $\hbar\omega > 2$ eV and the negative maximum of ER at 2.9 eV are due to the metallic behavior of the valence 3d electrons, just as in the VO₂ case. Starting from two 3d electrons per vanadium atom, $n_v = 10^{23}$ cm⁻³, we get $\hbar\omega_{p_v} = 3$ eV. This agrees well with the positions of the minimum in the R spectrum and of the negative maximum in ER.

The increase of reflection at $\hbar\omega > 3$ eV is obviously connected with the start of the optical transitions between the 2p band of the oxygen and the empty 3d subbands of the vanadium, and the maxima of R at 4.6 and 5.6 eV correspond to the energy gaps at the critical points of the band structure. It is interesting to note that the strong extrema of ER and R for the $2p \rightarrow 3d$ optical transitions are observed at an energy 1 eV higher than in VO₂. This may be connected with the presence of two 3d electrons in the shell of the vanadium ion, compared with the single 3d electron in the case of VO₂. As a result, the distance between the Fermi level and the 2p band of the oxygen in V₂O₃ may be larger than in VO₂.

3. Metal-insulator phase transition in V₂O₃ in a strong electric field. Figure 3 shows the ER spectra of V₂O₃ at different values of U_c for $T = 296^\circ\text{K}$

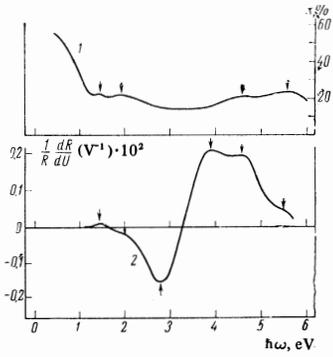


FIG. 2. R (curve 1) and ER (curve 2) spectra of V_2O_3 single crystals at $T = 296^\circ K$ and $U_C = 0.4 V$ (the polarity of U_C is opposite to the barrier direction of the diode made up by the V_2O_3 and the electrolyte).

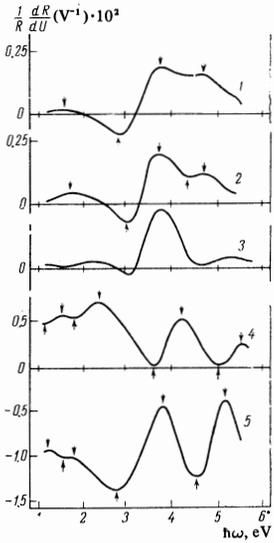


FIG. 3. ER spectra of V_2O_3 single crystals at different values of the constant bias U_C : 1-0, 2-1.5V, 3-1.7V, 4-2.2V, 5-2.5V.

($T > T_t$). As seen from Fig. 3, at $U_C < 1.5 V$ no noticeable changes of the signal intensity occur, but shifts of the ER peaks are observed ($\Delta \hbar \omega \approx 0.1 eV$) when U_C changes from zero to 1.5 V. When U_C increases from 1.5 to 1.7 V, a decrease of the signal occurs at $\hbar \omega < 4.5 eV$, and the minimum at 4.4 eV ($U_C = 1.5 V$) shifts to 4.7 eV for $U_C = 1.7 V$. This shift, in terms of $\hbar \omega$, is larger by one order of magnitude than the shifts of the peaks in the corresponding U_C interval for $U_C < 1.5 V$. With further increase of U_C , the amplitude of the ER signal increases (especially for $\hbar \omega < 3 eV$), and at $U_C = 2.2 V$ the signal becomes positive in the entire experimental interval of $\hbar \omega$, and reaches the maximum value. From a comparison of the ER spectra at $U_C = 1.5$ and 2.2 V, we see that when account is taken of the shifts along the $\hbar \omega$ scale, the ER maxima at $U_C = 1.5 V$ correspond to the maxima at $U_C = 2.2 V$, and vice versa. For example, the 3.7 eV maximum and the 4.4 eV minimum for $U_C = 1.5 V$ can be set in correspondence with the 3.6 eV minimum and 4.3 eV maximum in the case of $U_C = 2.2 V$. When U_C changes from 2.2 to 2.5 V, the ER signal decreases, passes rapidly through zero and becomes negative in the entire spectral interval, reaching a maximum value at $U_C = 2.5 V$ (and the maxima turn into minima), and when U_C increases to 3 V the ER signal decreases.

Figure 4a shows the dependence of the ER signal on U_C for $\hbar \omega = 2.3 eV$; this dependence reflects the general character of the ER variation. As seen from Fig. 4a, when U_C changes from zero to 1.5 V, the ER signal re-

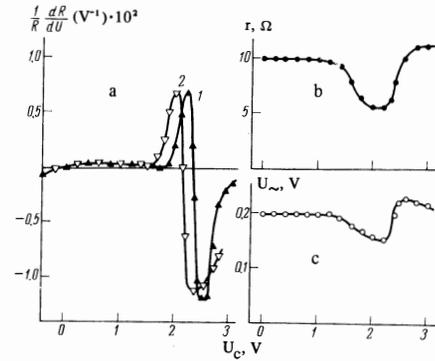


FIG. 4. Dependence of the ER signal amplitude, of the surface resistance r , and of the amplitude of the alternating voltage U_{\sim} on the cell with the electrolyte on U_C for V_2O_3 : a—value of $R^{-1}dR/dU$ at $\hbar \omega = 2.2 eV$ for $T = 296^\circ K$ (curve 1) and $T = 360^\circ K$ (curve 2); b—dependence of r on U_C ($T = 296^\circ K$); c—dependence of U_{\sim} on U_C ($T = 296^\circ K$).

mains practically constant; then a weakening of the signal is observed around $U_C = 1.7 V$, and in the narrow interval of U_C between 1.7 and 2.2 V the signal increases by almost 30 times. An even sharper (jumplike) change of the signal occurs near $U_C = 2.3 V$, where the signal amplitude changes by two orders of magnitude in an interval $\Delta U_C = 0.1 V$. At $U_C = 2.3 V$, there is also observed a jump in the surface resistance (Fig. 4b), and the amplitude of the alternating voltage on the cell with the electrolyte increases sharply (Fig. 4c). The results allow us to assume that the metal-insulator phase transition observed in [21] for V_2O_3 with chromium admixture following changes in the pressure and temperature takes place at $U_C = 2.3 V$. As seen from Fig. 4a, with increasing temperature the anomaly of $R^{-1}dR/dU$ shifts towards smaller U_C . This corresponds to the insulator phase assuming a high-temperature character, as in [21], and the action of the electric field is analogous to expansion of the crystal (negative pressure).

Let us examine in greater detail the relation $R^{-1}dR/dU \equiv f(U_C)$. The ER amplitude is quite sensitive to the ratio of the penetration depths of the light and of the electric field. The field controls only part of the reflected light:

$$R_{eff} \sim \rho_0 d_0, \quad (1)$$

where ρ_0 is the reflection coefficient per unit thickness of the surface layer; $d_0 \sim (\epsilon_0/n)^{1/2}$ is the depth of penetration of the electric field; ϵ_0 is the static dielectric constant; n is the free-carrier concentration. Substituting in (1) the value of d_0 and differentiating, we obtain

$$\frac{1}{R} \frac{dR}{dU} \sim \frac{1}{2\epsilon_0} \frac{d\epsilon_0}{dU} - \frac{1}{2n} \frac{dn}{dU} + \frac{1}{\rho_0} \frac{d\rho_0}{dU} \quad (2)$$

In ordinary semiconductors ϵ_0 does not depend on the external field, while n depends on it weakly; the first and second terms of (2) make no contribution to the ER. These terms, however, may turn out to be significant if $\epsilon_0 = \epsilon_0(U)$, for example in the case of ferroelectrics, and $n = n(U)$ in a metal-insulator transition under the influence of an electric field. The jump of $n(U)$ in the phase transition leads only to a burst of the ER amplitude at $U_C = U_{CR}$, but produces no change in sign. The

anomalous behavior of $R^{-1}dR/dU = f(U_C)$ can be explained if $\epsilon_0(U_C)$ goes through a maximum in the interval of variation of U_C . Then the observed course of the ER amplitude will correspond to the character of the dependence of $d\epsilon_0/dU$ on U_C . The presence of a maximum of $\epsilon_0(U_C)$ and its shift with changing temperature were observed in a first-order phase transition in ferroelectric materials.^[17] In our case, the critical field also depends on the temperature (Fig. 4a). The temperature shift of the ER anomaly corresponds to the case when the high-temperature phase is ferroelectric and the low-temperature phase is paraelectric (antiferroelectric).^[17]

In addition to being connected with the ferroelectric transformation, the maximum of $\epsilon_0(U_C)$ with changing U_C can be connected with the collapse (occurrence) of an energy gap E_g in the electronic spectrum during the insulator-metal (metal-insulator) phase transition. Since ϵ_0 increases with decreasing E_g in the insulator phase, ϵ_0 will decrease in the metallic phase because of the negative contribution from the free carriers.

The variation of the ER signal with increasing U_C depends on $\hbar\omega$ (see Fig. 3). As indicated above, the ER in V_2O_3 at $\hbar\omega > 3$ eV is determined by the $2p \rightarrow 3d$ optical transitions. For such optical transitions, the depth of penetration of the light is $l \sim 10^{-6}$ cm.^[4] The weaker dependence of the ER signal on U_C in this region of the spectrum is obviously connected with the fact that d_0 and l are of the same order, i.e., $d_0 \approx 10^{-6}$ cm. We can then estimate the average value of the electric field in our experiment: $F = U_C/d_0$, and for $U_C = 1-2$ V we obtain $F = 10^5$ V/cm.

We note that in view of the difficulty of working with the electrolyte at $T < 140^\circ$ K we did not investigate the influence of the electric field on the semiconducting phase of V_2O_3 . In addition, there is already a published report of a jump of the resistance of V_2O_3 under the influence of an electric field at $T < T_t$.^[18]

4. ER spectra and phase transitions in VO_2 single crystals in a strong electric field.

a) Let us consider the case $T > T_t$. An investigation of the spectral distribution of the ER of VO_2 at $T = 348^\circ$ K for different values of U_C has shown that the amplitude and the positions of the maxima of ER depend strongly on U_C . The character of the variation of ER, just as in the case of V_2O_3 , is conveniently traced by means of the U_C dependence of the amplitude of the positive maximum, which is located at 1.3 eV in the case $U_C = 0$ ($\mathbf{E} \perp \mathbf{c}_R$) and is connected with optical transitions between the 3d subbands (see Fig. 5).

Figure 5a shows distinctly three characteristic regions of variation of the ER signal. In region I, where U_C changes from zero to 0.9 V, the ER signal reaches a maximum near 0.75 V, and then drops to zero at $U_C = 0.9$ V. Variation of the ER is also observed in the remaining sections of $\hbar\omega$ in this interval of U_C . Thus, the maxima at 2.9 eV ($\mathbf{E} \perp \mathbf{c}_R$) and 3.1 eV ($\mathbf{E} \parallel \mathbf{c}_R$) for $U_C = 0$ shift to 3.1 eV ($\mathbf{E} \perp \mathbf{c}_R$) and 3.5 eV ($\mathbf{E} \parallel \mathbf{c}_R$) at $U_C = 0.4$ V. The ER maximum which lies at 4.75 eV ($\mathbf{E} \parallel \mathbf{c}_R$) shifts in the case of $U_C = 0$ by 0.35 eV with increasing U_C from 0.4 to 0.8 V. These shifts are accompanied by broadening of the maxima, and a change takes place also between the ER spectra in the ratio of intensities corresponding to different directions of polariza-

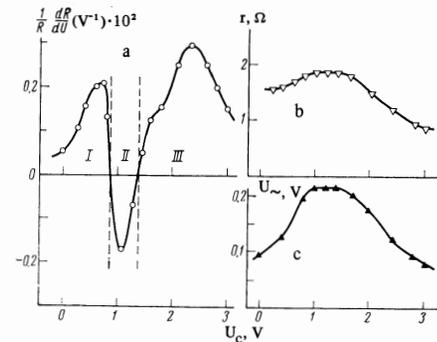


FIG. 5. Dependence of the ER signal amplitude (a), of the surface resistance r (b), and of the alternating voltage U_{\sim} on the cell with the electrolyte (c) on the constant bias U_C for VO_2 at $T = 348^\circ$ K ($T > T_t$).

tion of the light. Since such variations of the ER in the thermal phase transition ($U_C = 0$) are due to the crystal-lattice distortion, it can be assumed that the changes of the ER at $U_C > 0$ are connected with deformation of the crystal lattice by the electric field. At the same time, the observed result cannot be explained within the framework of the Franz-Keldysh effect,^[19, 20] according to which the ER maxima corresponding to the vertical optical transitions at the critical points of the band structure hardly shift with increasing electric field.^[12] Displacements of the ER extrema by several tenths of an eV were observed earlier in $KTaO_3$ ^[21] for $2p \rightarrow 3d$ optical transitions and were attributed to the displacement of the oxygen ions relative to the transition-metal ions under the influence of an electric field (the inverse piezoeffect). For VO_2 , the maximum shift of the ER peaks appears also for $2p \rightarrow 3d$ optical transitions ($\hbar\omega > 2$ eV). At $\hbar\omega < 2$ eV, corresponding to optical transitions between and within the 3d subbands, the shifts in the spectrum are smaller.

On going over to region II (see Fig. 5a), the ER amplitude passes sharply through zero and becomes negative. Then, with increasing U_C , the ER signal, remaining negative, reaches the maximum value near $U_C = 1.1$ V, and at $U_C = 1.35$ V it again passes through zero with another reversal of the sign. Just as in the already discussed phase transition in V_2O_3 , such an anomaly in the dependence of the ER on U_C can be due to variation of the depth of penetration of the electric field, when the static dielectric constant passes through a maximum with increasing U_C . We performed parallel measurements of the U_C dependence of the alternating voltage on the cell with the electrolyte (VO_2 -electrolyte barrier layer) and of the resistance of the crystal surface in contact with the electrolyte (see Fig. 5). It is seen from Fig. 5 that here, too, it is possible to separate three analogous regions of U_C , which are characterized by sharp variations of the resistance on each of the boundaries. The double passage of the ER signal through zero with simultaneous change of the entire spectrum, and also the presence of resistance jumps, point to the possible existence of two phase transitions (of the metal-insulator-metal type) with realignment of the crystal lattice at $T > T_t$ under the influence of the electric field.

For region III, the most characteristic features of the ER are the increase of the amplitude of the given maximum to $U_C = 2.3$ V and the subsequent decrease as

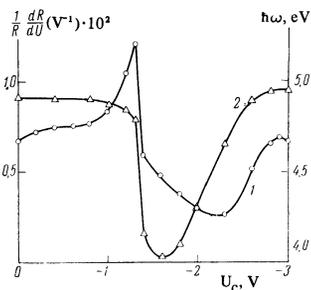


FIG. 6. Dependence of the ER signal amplitude (curve 1) and of the spectral position (curve 2) of the most intense ER peak ($\hbar\omega = 4.9$ eV at $U_C = 0$) on the constant bias U_C for VO_2 at $T = 296^\circ\text{K}$.

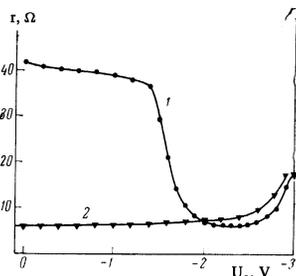


FIG. 7. Dependence of the resistance r of the oxide VO_2 on the applied constant bias U_C at $T = 296^\circ\text{K}$: 1— $r(U_C)$ with U_C increasing from zero to 3V; 2— $r(U_C)$ with U_C decreasing from 3V to zero.

U_C increases to 3 V. When U_C decreases from 3 V, a weak hysteresis takes place for the transition from the region III to II, but when U_C decreases to zero (see Fig. 5), the sign of the ER corresponds to region II. Thus, during the reversal of U_C there is no transition from region II to region I, indicating a strong field hysteresis for this phase transition. The spectrum corresponding to region I can be reconstructed by applying a sufficiently strong constant bias of the opposite polarity. We note that the phase transformations for VO_2 at $T > T_t$ were not observed earlier in investigations of the influence of the temperature or pressure.

b) Let us consider the case $T < T_t$. We shall describe below phase transitions of VO_2 under the influence of an electric field at $T = 296^\circ\text{K}$. A study of the ER spectra of VO_2 at $T = 296^\circ\text{K}$ ($T < T_t$) for different values of U_C has shown that their main features are the conservation of the general form and of the ratio of the ER signal amplitudes for different light polarization directions up to $U_C = 1.3$ V. However, when U_C changes from 1.3 to 1.4 V, the entire spectrum experiences qualitative changes: a change takes place in the form of the spectral distribution and in the ratio of the amplitudes for both directions of light polarization. The character of the variation of the ER is seen clearly in Fig. 6, which shows the U_C dependences of the amplitude and of the spectral position of the most intense ER peak located at $\hbar\omega = 4.9$ eV for $U_C = 0$ and $\mathbf{E} \parallel \mathbf{a}_m$.

We also measured the resistance of the sample surface in contact with the electrolyte at different values of U_C (see Fig. 7). It is seen from Fig. 7 that at $U_C = 1.4$ V a sharp decrease of the VO_2 resistance takes place. The simultaneous jump of the ER spectrum and of the sample resistance at $U_C = 1.4$ V points to a semiconductor-metal phase transition under the influence of the electric field at $T = 296^\circ\text{K}$ ($T < T_t$). It is interesting to note that the ER spectrum for $T = 296^\circ\text{K}$ ($T < T_t$) and $U_C = 1.4$ –1.6 V is not at all similar to the ER spectrum of the metallic phase corresponding to thermal switching, i.e., at $U_C = 0$ and $T = 348^\circ\text{K}$ ($T > T_t$), but resembles the ER spectrum at $U_C = 1.4$ V and $T = 348^\circ\text{K}$. This may be connected with the fact that

switching by means of the electric field and by temperature occurs in different metallic phases.

With further increase of U_C ($U_C > 2$ V), strong changes of the ER again occur (see Fig. 6) up to $U_C = 2.6$ –2.7 V. Near $U_C = 3$ V there again appear in the ER spectral distribution, just as at $U_C = 0$, characteristic maxima and minima, and an increase of the electric resistance of the sample takes place (see Fig. 7), possibly in connection with a metal-semiconductor transition in this interval of U_C . However, as seen from a comparison of the ER spectra at U_C equal to zero and 3 V, the initial and final semiconducting phases are different. When U_C decreases from 3 V, a weak hysteresis is observed for the second phase transition ($U_C \approx 2.6$ V), but the measured resistance still corresponds to the metallic state down to $U_C = 0$ (see Fig. 7). In the ER spectra during the rise and fall of U_C there is also observed agreement in the section 1.4–3 V, but in the 0–1.4 V interval, the ER spectra during the increase and decrease of U_C are noticeably different. The ER spectra during the decrease of U_C at $U_C = 0$ correspond to the case of $U_C = 1.4$ –1.6 V during the increase of U_C .

The observed results points to a strong field hysteresis in the semiconductor-metal phase transition, in contrast to the weak temperature hysteresis in the thermal phase transition.^[4] The initial semiconducting state can be restored by applying a constant bias of opposite sign. It is important to note that the magnitude of the jump of the electric conductivity (resistance) in the case of the field-induced phase transition coincides with the jump of the electric conductivity of the given sample during the thermal phase transition, and corresponds to switching over of the entire volume of the crystal, and not of a thin layer on the order of the field-penetration depth. The result can be attributed to the presence of strong hysteresis in the field-induced phase transition, for when the semiconductor-metal interface moves into the interior of the sample, no inverse switching of the metallic region into the semiconducting state takes place.

CONCLUSION

On the basis of the measurements of the ER spectra and of the electric resistance of VO_2 and V_2O_3 at different values of the electric field, it is concluded that a number of phase transitions take place in these vanadium oxides. The results indicate that the high sensitivity and simplicity of the ER method make it promising for the investigation of phase transformations accompanied by realignment of the crystal lattice and by a jump of the electric conductivity with changing electric field. The specific nature of the application of the field to the sample makes it possible to use the ER to study strongly doped semiconductors and metals.

One of the important results is observation of the switching effect in VO_2 from the semiconducting state to the metallic state under the influence of an electric field with the presence of a strong field hysteresis (a memory effect).

Let us examine the possible mechanisms of such a switching. In ^[22] they proposed a switching mechanism connected with the injection of the carriers. In our experiments, the polarity of the applied constant voltage

corresponded to enrichment of the surface layer with carriers (n-type). Starting from $\epsilon_0 = 41$ and $n = 10^{19} \text{ cm}^{-3}$ for the semiconducting phase of VO_2 ,^[14] we get $d_0 \approx 10^{-6} \text{ cm}$ and an average electric field $F = U_C/d_0 \approx 10^6 \text{ V/cm}$ at $U_C = 1-2 \text{ V}$. The surface capacitance in the experimental interval of U_C was $c_0 = 0.1-1 \mu\text{F}$, and then we obtain for the concentration of the carriers injected from the contact $n_{\text{in}} = 10^{19} - 10^{20} \text{ cm}^{-3}$. However, doping of crystals to 10^{20} cm^{-3} hardly shifts the phase-transition temperature.^[23] The carrier density necessary to close the energy gap $E_g = 0.5 \text{ eV}$ as a result of screening is $\sim 10^{21} \text{ cm}^{-3}$. Such a switching mechanism is therefore little likely.

Since passage of large currents through samples with ohmic contacts gave rise to S-shaped current-voltage characteristics connected with switching into the metallic state as a result of thermal heating, it is of interest to estimate the possibility of the thermal effect in our experiments. The amount of heat necessary for switching is

$$Q_1 = cm(T_t - T_0) + \mathcal{L}m,$$

where $c = 0.2 \text{ cal/g-deg}$ is the specific heat of the VO_2 in the semiconducting phase, $m = 0.026 \text{ g}$ is the mass of the sample, $\mathcal{L} = 10 \text{ cal/g}$ is the latent heat of the transition, $T_0 = 296^\circ \text{K}$ is the temperature of the thermostat, and $T_t = 338^\circ \text{K}$ is the temperature of the phase transition. We then obtain $Q_1 = 0.46 \text{ cal}$. The value of the Joule heat is equal to

$$Q_2 = 0.24UI\tau.$$

where $U = 1.4 \text{ V}$, $I \leq 20 \mu\text{A}$, $\tau = \rho cS/k_0 = 3 \text{ sec}$, $\rho = 4.4 \text{ g/cm}^3$ is the density of the VO_2 in the semiconducting phase, $S = 0.06 \text{ cm}^2$ is the cross section of the sample, $k_0 = 0.015 \text{ cal/cm-deg-sec}$ is the coefficient of thermal conductivity of VO_2 .^[23] Then $Q_2 = 0.26 \times 10^{-4} \text{ cal}$ and $Q_2 \ll Q_1$. Thus, the thermal switching is impossible. As further confirmation, we note that the ER spectra obtained after switching into the metallic state by means of a field and by means of temperature are strongly different.

On the other hand, the results offer evidence that the most probable switching mechanism is the change of the parameters of the crystal lattice in the electric field (the inverse piezoeffect). Let us estimate the possibility of such a deformation, recognizing that the symmetry of the semiconducting phase of VO_2 admits of the piezoeffect. Since strong shifts of the ER bands with changing U_C were observed so far only in the case of ferroelectrics, to estimate the inverse piezoeffect we shall use the piezoelectric constants characteristic of BaTiO_3 , namely $d \approx 5 \times 10^{-8} \text{ cm/V}$. We then obtain for the relative deformation of the lattice parameters $Fd = 5\%$, which agrees with the corresponding value obtained in the temperature-induced phase transition.

In view of the presence of phase transitions at $T > T_t$ for V_2O_3 and VO_2 from the metallic state into the insulator state, transitions which are apparently also connected with deformation of the crystal lattice, it is of interest to discuss another possible mechanism for this case. The influence of the electric field, besides the piezoeffect, may be connected with the difference between the energy of the electric field $F^2/8\pi$ in the metal and in the semiconductor, a difference that manifests itself in expulsion of the field from the metal. This effect is analogous to the influence, due to the Meissner

effect, exerted by the magnetic field on the transition from the superconducting to the normal state of a bulky metal. If at $F = 0$ the energy of the metallic phase is lower than that of the insulator phase, i.e., there is an insulator phase with higher temperature than the metallic phase, then a metal-insulator transition can take place at $F \neq 0$ when $F^2/8\pi = \mathcal{L}\rho$. Using $\mathcal{L} = 100 \text{ cal/mole}$ for the metal-insulator transition in V_2O_3 with chromium admixture,^[21] we obtain for the switching field $F = 2 \times 10^7 \text{ V/cm}$, which, at the utmost, is higher by one order of magnitude than the experimental estimate.

Thus, the main mechanism for all the observed phase transitions in VO_2 or V_2O_3 in the electric field is apparently the inverse piezoeffect.

¹D. Adler, Rev. Mod. Phys. 40, 714 (1968).

²D. B. McWhan, T. M. Rice, and J. P. Remeika, Phys. Rev. Lett. 23, 1384 (1969).

³H. Verleur, A. S. Barker, and C. N. Berglund, Phys. Rev. 172, 788 (1968).

⁴B. S. Borisov, S. T. Koretskaya, V. G. Mokerov, A. V. Rakov, and S. G. Solov'ev, Fiz. Tverd. Tela 12, 2209 (1970) [Sov. Phys.-Solid State 12, 1763 (1971)].

⁵D. Adler and H. Brooks, Phys. Rev. 155, 826 (1967).

⁶A. G. Aronov and E. K. Kudinov, Zh. Eksp. Teor. Phys. 55, 1344 (1968) [Sov. Phys.-JETP 28, 704 (1969)].

⁷L. V. Keldysh and Yu. V. Kopaev, Fiz. Tverd. Tela 6, 2791 (1964) [Sov. Phys.-Solid State 6, 2219 (1965)].

⁸A. N. Kozlov and L. A. Maksimov, Zh. Eksp. Teor. Fiz. 48, 1184 (1965) [Sov. Phys.-JETP 21, 790 (1965)].

⁹B. J. Halperin and T. M. Rice, Sol. Stat. Phys. 21, 115 (1968).

¹⁰Yu. V. Kopaev, Fiz. Tverd. Tela 8, 2633 (1966) [Sov. Phys.-Solid State 8, 2106 (1967)].

¹¹K. A. Valiev, Yu. V. Kopaev, V. G. Mokerov, A. V. Rakov, and S. G. Solov'ev, ZhETF Pis. Red. 12, 18 (1970) [JETP Lett. 12, 12 (1970)].

¹²M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. 154, 696 (1967).

¹³D. E. Aspnes, Phys. Rev. 153, 972 (1967).

¹⁴A. S. Barker, H. W. Verleur, and H. J. Guggenheim, Phys. Rev. Lett. 17, 1286 (1966).

¹⁵H. P. Phillip and H. Ehrenreich, Phys. Rev. 129, 1550 (1963).

¹⁶V. P. Zhuze, A. A. Andreev, and A. I. Shelykh, Fiz. Tverd. Tela 10, 3674 (1968) [Sov. Phys.-Solid State 10, 2914 (1969)].

¹⁷G. S. Zhdanov, Fizika tverdogo tela (Solid-State Physics), MGU, 1962, p. 251.

¹⁸V. N. Andreev, A. G. Aronov, and F. A. Chudnovskii, Fiz. Tverd. Tela 12, 1557 (1970) [Sov. Phys.-Solid State 12, 1230 (1970)].

¹⁹L. V. Keldysh, Zh. Eksp. Teor. Fiz. 34, 1138 (1958) [Sov. Phys.-JETP 7, 788 (1958)].

²⁰W. Franz, Zs. Naturforsch. 13, 484 (1958).

²¹A. Frova and P. J. Boddy, Phys. Rev. 153, 606 (1967).

²²V. B. Sandomirskii, A. A. Sukhanov, and A. G. Zhdan, Zh. Eksp. Teor. Fiz. 58, 1683 (1970) [Sov. Phys.-JETP 31, 902 (1970)].

²³C. N. Berglund and H. J. Guggenheim, Phys. Rev. 185, 1022 (1969).