[4] G.A. Alers, O. Buck, and B.R. Tittman, Phys. Rev. Lett. 23, 290 (1969).
[5] V.S. Fomenko, V.I. Startsev, V.V. Pustovalov, and D.A. Didenko, Fizika kond. sostoyaniya (Physics of Condensed State; Collection of Papers of the Physico-technical Institute of Low Temperatures), No. 5, 228, 1969, Khar'kov.
[6] V.V. Pustovalov, V.I. Startsev, and V.S. Fomenko, Preprint, Phys.-tech. Inst. Low Temp., 1969; Phys. Stat. Sol. 37, 413 (1970).
[7] J. Giaever and K. Megerle, Phys. Rev. 122, 1101 (1961).
[8] J. Bardeen, L.N. Cooper, and J.R. Schrieffer, Phys. Rev. 108, 1175 (1957).
[9] P. de Gennes, Superconductivity of Metals and Alloys, Benjamin, 1965.
[10] M.I. Koganov and V.D. Natsik, ZhETF Pis. Red. 11, 550 (1970) [JETP Lett. 11, 379 (1970)].
[11] V.Ya. Kravchenko, Fiz. Tverd. Tela 8, 927 (1966) [Sov. Phys.-Solid State 8, 740 (1966)].

METAL-INSULATOR TRANSITION IN V_2O_3 IN A STRONG ELECTRIC FIELD

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Submitted 28 May 1970
ZhETF Pis. Red. 12, No. 1, 18 - 22 (5 July 1970)

The most interesting physical properties of V_2O_3 are the insulator-metal phase transition at T = 150°K and the anomaly of the temperature dependence of the electric conductivity near 530°C [1]. A recent communication reported a metal-insulator transition in V_2O_3 with chromium admixture upon variation of the concentration of the chromium and of the pressure [2].

We have observed a similar metal-insulator phase transition under the influence of an electric field on the V_2O_3 crystal. The influence of the electric field on the properties of V_2O_3 was investigated by the electroreflection (ER) method [3]. The ER spectra was measured in the photon energy interval $1.1 \leq \hbar\omega \leq 6.0$ eV, at different temperatures $300° \leq T \leq 360°$K. For comparison, we recorded the spectrum of the usual reflection $R(\hbar\omega)$ in the region $0.5 \leq \hbar\omega \leq 6.0$ eV (Fig. 1).

As seen from Fig. 1, the ER peaks shift noticeably along the $\hbar\omega$ scale when the fixed bias U_b is varied, but the intensity of the ER spectrum depends little on U_b when $U_b < 1.7$ V. The large amplitude of the signal and the shifts of the ER peaks differ strongly from the corresponding values for typical semiconductors [3], but are in agreement with the ER spectra of ferroelectrics above and below the Curie point [4]. A certain disparity between the structure of the spectra of the ER and $R(\hbar\omega)$ in Fig. 1 at $U_b = 0$ is obviously connected with the shift of the bands in the electric field of the surface barrier. For values $U_b \geq 1.8$ V, the amplitude dR/RdU increases sharply in the ER spectra in the region $\hbar\omega < 2.5$ eV and the shifts of the peaks $\Delta\hbar\omega$ increase appreciably in the region $\hbar\omega > 2.5$ eV. Thus, a change of U_b of 0.1 V near $U_b = 2$ V yields $\Delta\hbar\omega \approx 0.18$ eV, whereas at $0 \leq U_b \leq 1.7$ V the corresponding shift amounts to only 0.025 eV. Near $U_b = 1.8$ V the peaks 1 and 2 (Fig. 1) merge into one, and with further increase the number of peaks remains constant ($\hbar\omega > 3$ eV).

Figure 2b shows the dependence of the interval $\Delta\hbar\omega$ between the peaks 1' and 3 on U_b. The strongest change in the ER signal amplitude with increasing U_b is observed for $\hbar\omega \leq 2.5$ eV (see Figs. 1 and 2). Whereas at $U_b < 1.8$ V the amplitude of the ER is practically independent of U_b, near $U_b = 2$ V it increases by almost one order of magnitude in the narrow interval $\Delta U_b = 0.1$ V.

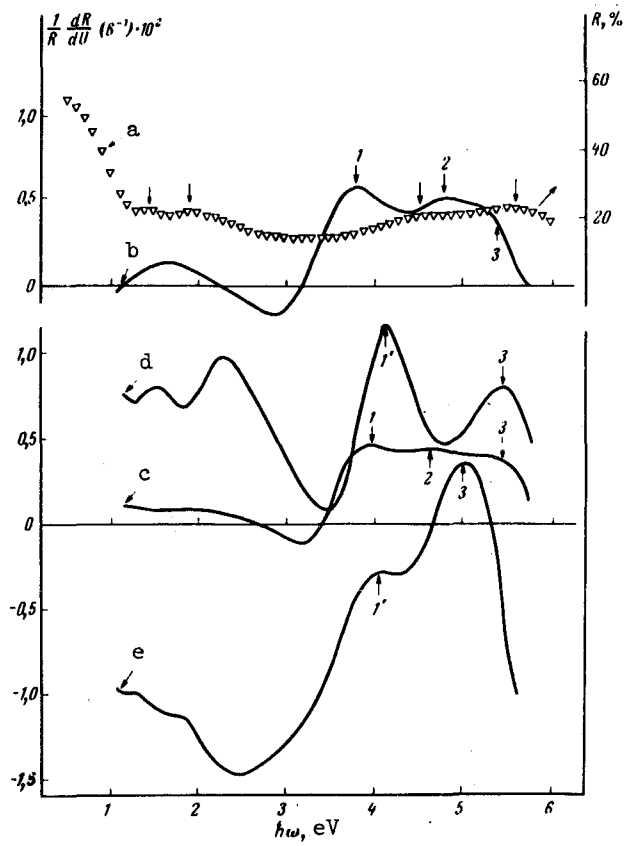

Fig. 1. Spectral distribution of $R(\hbar\omega)$ and ER of V_2O_3 single crystals at T = 300°K: a - $R(\hbar\omega)$, b - ER spectrum at U_b = 0, c - ER spectrum at U_b = 1.6 V, d - ER spectrum at U_b = 2.2 V, e - ER spectrum at U_b = 2.6 V.

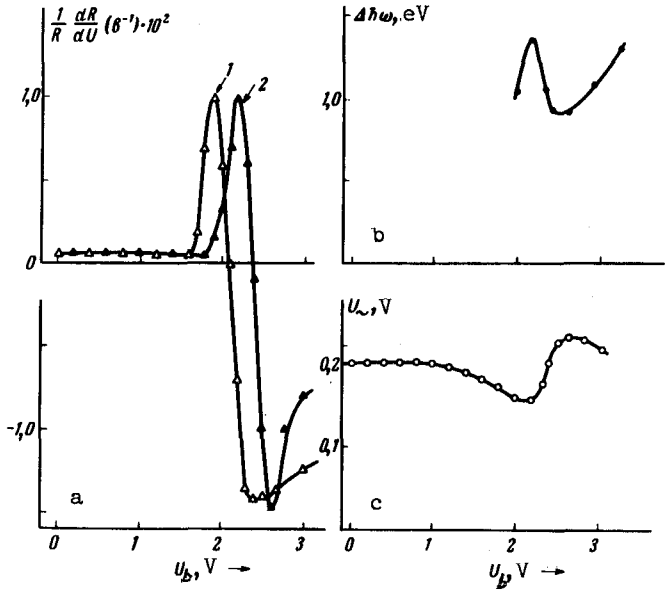

Fig. 2. Amplitude of the ER signal, interval between peaks 1' and 3 ($\Delta\hbar\omega$), and amplitude of the alternating voltage U on the cell with electrolyte vs. the fixed bias U_b: a - (1/R)(dR/dU) at $\hbar\omega$ = 2.2 eV for T = 360°K (curve 1) and T = 300°K (curve 2); b - dependence of $\Delta\hbar\omega$ (peaks 1' and 3) on U_b at T = 300°K; c - dependence of U on U_b at T = 300°K.

It should be noted that the alternating voltage on the cell with the electrolyte increases at values of U_b corresponding to the anomalous change of dR/RdU (Fig. 2c). This indicates a jump of the resistance of the surface layer of V_2O_3.

The results enable us to propose that in this region of U_b there takes place the metal-insulator phase transition observed in [2] for V_2O_3 with chromium admixture upon variation of pressure and temperature. As seen from Fig. 2a, with increasing temperature, the anomaly of $R^{-1}dR/dU$ shifts toward smaller U_b. This indicates that the insulator phase is a high-temperature one, just as in [2], and the action of the electric field is analogous to the expansion of the crystal (negative pressure).

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

$$R_{ef} \sim \rho d_0, \qquad (1)$$

where ρ is the reflection coefficient per unit thickness of the surface layer;

d_0 is the depth of penetration of the electric field. Since the current-voltage characteristic of the electrolyte $+V_2O_3$ system the usual diode form, the Schottky-barrier model is apparently applicable in this case. Then the depth of penetration of the field $d_0 \sim \sqrt{\varepsilon/N}$, where ε is the static dielectric constant and N is the concentration of the free carriers. Substituting in (1) the value of d_0 and differentiating, we obtain

$$\frac{1}{\rho}\frac{dR}{dU} \sim \sqrt{\frac{\varepsilon}{N}}\left[\frac{1}{2\varepsilon}\frac{d\varepsilon}{dU} - \frac{1}{2N}\frac{dN}{dU} + \frac{1}{\rho}\frac{d\rho}{dU}\right]. \qquad (2)$$

In usual semiconductors ε does not depend on the external field, N depends on it weakly, and the first and second terms of (2) make no contributions to the ER. However, these terms may turn out to be significant if $\varepsilon = \varepsilon(U)$, for example in the case of ferroelectrics and $N = N(U)$, and in the 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 $U_b = U_{crit}$, but does not lead to a reversal of the sign.

The anomalous dependence of $R^{-1}dR/dU = f(U_b)$ can be explained if $\varepsilon(U_b)$ goes through a maximum in the interval of variation of U_b. Then the observed course of the ER amplitude will correspond to the dependence of $d\varepsilon/dU$ on U_b. The presence of a maximum of $\varepsilon(U)$ and its shift with changing temperature was observed in a first-order phase transition in ferroelectric materials [5]. In our case the critical field also depends on the temperature (Fig. 2a). The temperature shift of the anomaly of the ER corresponds to the case when the high-temperature phase is ferroelectric and the low-temperature phase is paraelectric (antiferroelectric) [5].

We note that the change of the amplitude of the ER signal with increasing U_b depends on $\hbar\omega$. In analogy with VO_2 [6], it can be assumed that at $\hbar\omega < 2.5$ eV the absorption of the light is connected with optical transitions between the empty and filled 3d subbands, and at $\hbar\omega > 2.5$ eV with optical transitions between the 2p band of oxygen and the 3d band of vanadium. According to the data obtained by us with VO_2, the depth of penetration of light is $\ell \approx 10^{-4}$ cm at $\hbar\omega < 2.5$ eV and $\ell \approx 10^{-5} - 10^{-6}$ cm at $\hbar\omega > 2.5$ eV. Since $N \approx 10^{22}$ cm^{-3} for V_2O_3, the depth of penetration of the field d_0 at small U_b apparently does not exceed 10^{-6} cm. It follows therefore that the maximum change of the ER signal should become manifest at $\hbar\omega < 2.5$ eV, where $d_0 \ll \ell$ (at small U_b), as is indeed observed in the experiment.

In conclusion it should be noted that the observed phase transition in an electric field apparently corresponds to a transition from the metallic state into an insulator with simultaneous transition from a non-ferroelectric into a ferroelectric state. The dependence of the critical electric field on the temperature suggests that the cause of the transition is the ferroelectric transformation.

[1] F.I. Morin, Phys. Rev. Lett. 3, 34 (1959).
[2] D.B. McWhan, T.M. Rice, and I.P. Remeike, Phys. Rev. Lett. 23, 1384 (1969).
[3] K.L. Shaklee, F.H. Pollak, and M. Cardona, Phys. Rev. Lett. 15, 833 (1965).
[4] A. Frova and P.J. Boddy, Phys. Rev. 153, 606 (1967).
[5] G.S. Zhdanov, Fizika tverdogo tela (Solid State Physics), Moscow University Press, 1962, p. 251 - 288.
[6] V.G. Mokerov and A.V. Rakov, Fiz. Tverd. Tela 11, 197 (1969) [Sov. Phys.-Solid State 11, 150 (1969)].