SEMICONDUCTOR-METAL PHASE TRANSITION IN A STRONG ELECTRIC FIELD IN V_2O_3

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Submitted February 16, 1971

Zh. Eksp. Teor. Fiz. 61, 705–717 (August, 1971)

The electric conductivity in a strong electric field in V_2O_3 is studied experimentally in the temperature range from 4.2 to 150°K. A shift is observed in the phase transition point in an electric field down to helium temperatures. It is found that magnetic field strengths up to 240 kOe do not affect the phase transition temperature. The research results are discussed on the basis of the exciton model with strong electron-phonon coupling. The transition point shift in an electric field is ascribed to the effect of deformations that arise as a result of the piezoeffect.

INTRODUCTION

We have previously reported[1] the effect of an electric field on phase transitions in V_2O_3. It was surmised in that paper that the shift of the transition point in the electric field was connected with the piezoeffect.

A large number of papers devoted to V_2O_3 have, in our opinion, not yet reached an understanding of the nature of the semiconductor-metal phase transition and the mechanism of conductivity. Models of the Hubbard type, of an exciton dielectric in a weak electron-phonon coupling, encounter a number of serious difficulties because of the need to explain both the anomalously large jump in the electric conductivity and the lattice distortion that arises in the phase transition. At the same time, the Adler-Brooks model, which actually uses the strong coupling of current excitations with the lattice, cannot explain quantitatively the jump in the electric conductivity observed in V_2O_3.

We present here the experimental results in terms of the effect of the field on the phase transition in V_2O_3 over a wide range of temperatures, carry out a proof of the fact that the effect observed by us is due to the effect of the electric field and is not a change-over connected with Joule heating, as, for example, in amorphous semiconductors;[2] we also attempt to analyze the results obtained on the basis of a model of the phase transition proposed by Kudinov together with one of the authors.[3]

I. EXPERIMENTAL METHOD AND THE EXPERIMENTAL RESULTS

1. Samples and the Methodology of the Measurements

The effect of a strong electric field on phase transitions has been studied on V_2O_3 single crystals, cut by the method of Verneuil. The shape of the samples is shown in Fig. 1 (a, b, c). All the samples were cut so that the applied field was oriented along the crystal axis. The electrical contacts were made with "kontaktol" on a base of colloidal silver and, in individual cases, with indium-gallium eutectic. Samples in the shape of washers (Fig. 1a) had thicknesses from 0.5 to 1.5 mm, and those in the shape of washers with a slots (Fig. 1b) were much thinner—down to about 40 microns.

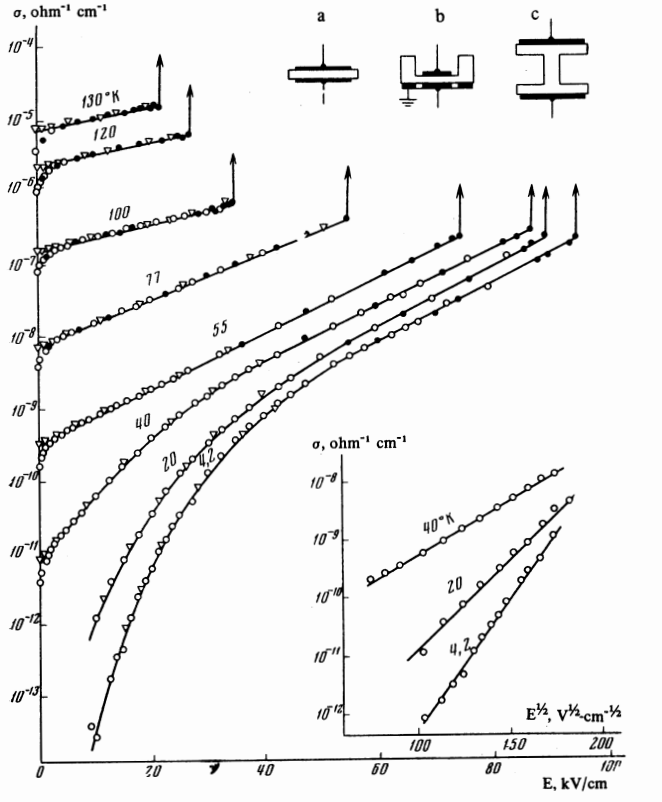

FIG. 1. Dependence of log σ on E. In the right upper corner are given the shapes of the samples; O—measurements at constant current for samples of shape b, ●—measurements on microsecond pulses for samples of shape b, ∇—measurements at constant current and on microsecond pulses for samples of shape c. At the lower right, the dependences of log σ on $E^{1/2}$.

A guard ring was employed to remove currents from the surface. It turned out that the surface component of the current could also be removed by etching the samples in concentrated HNO_3. For reduce to a minimum the contact phenomena, such as contact rectification and space-charge-limited currents, samples were prepared in the form of a "dumbbell" (Fig. 1e). The geometry of the dumbbell was so chosen that the resistance of the wide contact portions of the sample was much less than the resistance of the narrow part.

The measurements were performed in a regime of given voltage at constant current and with pulses of

rectangular shape, the length of which varied from 4 to 2000 μsec, while the repetition rate varied from one to 5000 pulses/sec.

The V_2O_3 crystal experiences in the transition a volume change of 0.6 to 3.5%, according to the different published values, and disintegrates after several temperature phase transitions. Therefore, all the measurements were carried out on samples that were reduced temperature to the semiconductor state. In most cases, the samples were sealed in wax, which made it possible to obtain stable characteristics, although significant differences relative to the free sample were not noted.

2. Experimental Results

A. Dependence of the electric conductivity on the field strength E. Figure 1 shows the dependence of $\log \sigma$ on E in the temperature range from 4.2 to 130°K. It is seen that at helium temperatures, a sharp rise is observed in $\log \sigma$ with respect to E for fields ~40 kV/cm. Upon increase in temperature, the portion of strong increase is gradually eliminated. This portion of the curve is satisfactorily described by the law $\log \sigma \sim E^{1/2}$ (see Fig. 1). After the portion with the law $\log \sigma \sim E^{1/2}$, there is a region of linear dependence of $\log \sigma$ on E, and the slope of the latter portion is almost temperature-independent. For temperatures above 60°K, the dependence of $\log \sigma$ on E is linear over the entire region of change of field, and the slope of these characteristics is proportional to 1/T. For small fields, a sharp increase in the electric conductivity, independent of the temperature region, is observed on all the characteristics $\log \sigma$ (E). This increase is associated with contact phenomena, since it disappears almost completely in samples of the "dumbbell" shape (Fig. 1c).

The dependences of $\log \sigma$ on E are symmetric over the entire range of electric fields studied.

B. Relaxation oscillations (generation). When the field on the sample reaches the critical value E_c, there is a sharp increase in the current and a corresponding decrease in the voltage. Figure 2a shows oscillograms of the pulses of current and voltage at the instant of switching. It is seen that the switching is characterized by a time delay τ_d which falls off with increase in the voltage. This is observed only during the first 50–100 switchings, after which relaxation oscillations (generation) appear upon application of the critical field E_c (see Fig. 2b). The quantity E_c decreases several fold; nevertheless, the electric conductivity in zero field σ_0 and the electric conductivity σ_c before switching do not change. The $\log \sigma$ (E) curves depend more sharply on the field; however, their character remains unchanged.[1)]

The lowering of the critical field is evidently connected with resultant inhomogeneity of the field in the sample because of its cracking as a consequence of the strong deformation at the instant of switching. Generation was observed on the samples studied at a specified current with a frequency which was determined by the parameters of the external circuit and the applied voltage. The generation frequency easily reached 10 MHz.

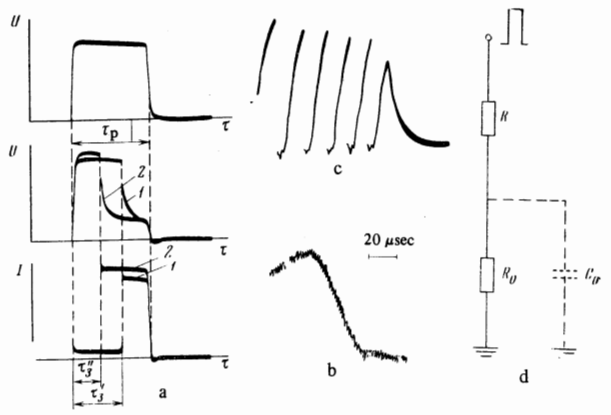

FIG. 2. a–Oscillograms of voltage pulses U and current pulses I. Above is the voltage pulse up to switching (τ_p is the length of the pulse, equal to 10 μsec). In the middle and below are the pulses of voltage and current at the moment of switching. Curves 1 and 2 correspond to an increase in the voltage applied to the sample, which leads to a decrease in the time delay of switching, τ_d; b–is the oscillatory regime, the oscillation frequency being 10 MHz, c–the shape of the front of reverse switching; d–equivalent circuit.

One can understand the reason for the appearance of the relaxation oscillations by representing the equivalent circuit of the sample in the form of Fig. 2d. The rise time of the voltage is determined by the time constant for charging the equivalent capacitor C_0 by means of the load resistance R. The decay time is determined by the time of discharge of C_0 through the small resistance of the sample in the metallic state. Figure 2c shows the oscillogram of the front of the reverse transition, taken by means of a stroboscopic oscillograph. The decay time is equal to 30 sec and is determined by the rather high resistance of the contacts and also by the parasitic capacitances and inductances of the circuit. In fact, in the metallic state, the resistance of samples with contacts amounted to 0.5 ohm, whereas the characteristic resistance of thick samples was lower by several orders of magnitude. The problem of the true time of phase transition requires further investigations.

C. Temperature dependence of σ_0 and σ_c. Figure 3 shows the dependences of the electric conductivities σ_0 (as $E \to 0$) and σ_c (as $E \to E_c$) on the reciprocal of the temperature. The activation energy ϵ_a amounts to 0.12 eV for the various samples above 100°K and is equal to 0.053 ± 0.003 eV below this temperature. The dependence of $\log \sigma_c$ on 1/T at $T > 100$°K has a slope of 0.09 eV and ceases to depend on T as one approaches helium temperatures. The value of σ_0 for $T > 100$°K agrees with the data of[4] and, if we take it into account that in this region the conductivity is intrinsic, the value of the energy gap $\epsilon_g = 2\epsilon_a$ amounts to 0.24 eV. Continuing the curves $\sigma_0(1/T)$ and $\sigma_c(1/T)$ into the region of higher temperatures until they intersect, we find that the temperature of the intersection point ~150°K agrees with the phase transition point.

[1)] We note that the $\log \sigma$ (E) characteristics taken up to the first switching and after a small number (up to 20-50) switchings, are practically identical. The form of the characteristics does not depend on whether they are taken at constant current or in a regime of microsecond pulses (see Fig. 1).

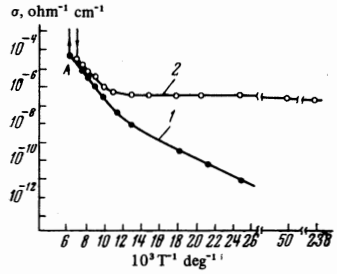

FIG. 3. Temperature dependence of σ_0 (curve 1) and σ_C (curve 2).

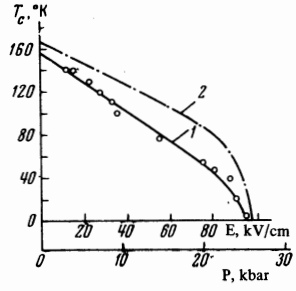

FIG. 4. Dependence of T_C on P (curve 2 [5]).

This agreement shows that the transition in the electric field and the temperature transition are mutually connected.

D. Dependence of the transition temperature on the external field. The graph of the dependence of T_C on E is represented in Fig. 4. In the temperature range above ~40°K, the dependence of T_C is linear with slope $dT_C/dE \sim 1.36 \times 10^{-3}$ deg-cm/V. For temperatures below 40°K, T_C depends weakly on E. We note that the behavior of $T_C(E)$ recalls the dependence of the transition temperature on uniform pressure, obtained in[5] (see Fig. 4). For a large number of switching cycles, the slope of the linear part of $T_C(E)$ decreases; however, the character of the dependence remains unchanged.

E. Switching in the region of temperature hysteresis ("the memory effect"). Upon application of an electric field in the region of temperature hysteresis (point A on Fig. 3), the switching takes place irreversibly, i.e., after switching, the sample remains in the metallic state indefinitely. It would appear that it could be returned to the semiconductor state only by cooling. However, this can be done another way—by applying an excess pressure to the sample in the metallic phase. The mechanism of this phenomenon is not understood by us at the present time and requires further study.

F. Effect of a magnetic field on the transition temperature. The effect of a strong magnetic field on the metal-semiconductor transition temperature has been studied in V_2O_3. The single crystal had random orientation relative to the magnetic field. A pulsed magnetic field with intensity up to 240 kG did not change the transition temperature, with accuracy to within 1°.[2)] In our opinion, this can be taken as an indication of the absence of a direct connection between magnetic order and the mechanism of the metal-semiconductor phase transition in V_2O_3.

G. The absence of effect of heating by Joule heat. The effect of a strong electric field on the metal-semiconductor phase transition in VO_2 and Fe_3O_4 was studied in[6] and[7], respectively. In these papers, the observed effects are attributed to current heating; actually, the low resistance of VO_2 and Fe_3O_4 in the semiconducting phase in comparison with V_2O_3 did not permit the separation of the effect of Joule heating from the other effects. The effect of an electric field on the metal-semiconductor phase transition was observed only in[1] on V_2O_3, and later under the conditions of the field effect on VO_2[8].

The absence of any sort of significant thermal effect in our experiments was connected, as pointed out above, with the high resistance of the V_2O_3 single crystals in the semiconducting phase (at helium temperatures it was greater than 10^{14} ohm-cm as $E \to 0$). We observed in practice a complete agreement of the volt-ampere characteristics, taken at constant current and with single pulses of duration ranging from several microseconds upward (Fig. 1) (especially good agreement was obtained on samples which experienced a small number of switchings). Furthermore, the volt-ampere characteristics are entirely independent of the repetition frequency of the pulses in the range from 0.1 Hz to 5 kHz. The existence of a horizontal portion on the current and voltage pulses, right up to the switching fields, indicates the absence of any significant heating by the current during the time of action of the pulse. Therefore, all the nonstationary processes associated with current heating should terminate at least within the time of the leading front of the pulse, i.e., in a time no greater than 1 μsec.

Neglecting the processes of thermal conductivity for such times, knowing the heat capacity of V_2O_3,[9] and assuming that all the energy of the passing current is isolated in some sort of "channel," it is easy to calculate, from the equation of heat balance, that the diameter of the "channel" which can be heated to the transition temperature (~150°K) in a time of 1 μsec, is no greater than 6 μ for the entire range of temperatures measured. However, for such narrow "channels," it is already impossible to neglect the processes of thermal conductivity, which can only decrease the diameter. It is easy to understand that the heating of such a narrow "channel" cannot explain the behavior (Fig. 1) of the electric conductivity as a function of the electric field. Moreover, the electrical resistance of a "channel" of radius 6 μ, which undergoes transition to the metallic state, amounts to 89 kohm, which is two orders of magnitude greater than that which we observed experimentally. At T = 130°K, it is a simple matter to estimate the diameter of the region entering the metallic state from the values of the jumps in current and voltage, assuming that the resistance of the contacts is ~0.5 ohm. This diameter turns out to be approximately 0.15 mm. Thus the electric power is too small, by several orders of magnitude, to heat such a massive "channel." For a more exact calculation of the heating, with account of the exponential decrease in the resistance,[10] we can show that for the thermal transition mechanism the value of the switching field should be significantly larger than the observed value. It should be noted that, in the case of heating by Joule current, the transition voltage will be an exponential

[2)]The authors thank D. V. Mashovets for making possible the measurements in high magnetic fields.

function of the temperature. In our experiments, this dependence is linear (Fig. 4). If we assume that the heating takes place with the time of linear increase in the leading edge of the pulse, then, as follows from calculations,[10] the dependence of the switching voltage U_c on the thickness of the sample d should be given by $U_c \sim d^{2/3}$. In our case, U_c depends linearly on d to a high degree of accuracy.

Thus neither the qualitative nor the quantitative picture of the transitions corresponds to the thermal nature of the transition, as is the case in switching on amorphous glasses.[2] Along with this, some small heating exists nevertheless. The appearance of this heating is seen in the emergence of a delay time τ_d. As is seen from Fig. 4, the switching field decreases with increasing temperature. Therefore, if the field E applied to the sample differs by a small value from the critical field, then the temperature of the sample increases, because of the heating within the time τ_d, the switching field decreases, and the transition takes place.

II. DISCUSSION OF THE EXPERIMENTAL RESULTS

At the present time, a large number of models have been proposed for the explanation of phase transitions, including models in which the transition appears because of the interaction of the current carriers, and models in which the phase transition (the instability of the system) is due to interaction of non-current excitations.[11-14]

In the present section, an analysis is carried out of the experimental results and the following is demonstrated:

1) the phase transition in V_2O_3 cannot be described in the framework of models where the instability arises as a result of the interaction of the current carriers;

2) a phenomenological model is considered which is a generalization of the model proposed in[3,14], where, along with current excitations, certain excitations whose nature is not specified in the model are considered;

3) from the analysis of the experimental results it follows that certain excitations should rather have an electronic nature (Frenkel excitons);

4) a comparison is carried out of the experimental results with the model.

Let us consider the dependences of the electric conductivities $\sigma_0(1/T)$ and $\sigma(1/T)$ (Fig. 3). In the temperature region $T > 100°K$, the most characteristic mark is the difference in the activation energies. We shall show that models in which the instability is connected with the interaction of the current carriers cannot explain this fact. Actually, the width of the energy band ϵ_g in these models is a function of the carrier concentration and the concentration itself can be represented in the form

$$n = f(T)\exp\left\{-\frac{\varepsilon_g - K\varphi(n)}{2T}\right\},$$

where K is a constant of the self-consistent field and $\varphi(n)$ is a function describing the change in the gap with increasing number of carriers; $\varphi(n) > 0$ and $\varphi'(n) > 0$. At the instability point $dn/dT \to \infty$, and one can show that the condition

$$(n\partial\varphi/\partial n)_{n=n_c} = 2T_c/K. \quad (1)$$

should be satisfied at this point. If, as is usually the case, $\varphi(n)$ is a power-law function, then the relation (1) shows that the carrier concentration at the point of transition depends in power-law fashion on the critical temperature, which can change under the action of the effect (for example, it depends on the electric field). Such a power-law dependence contradicts the exponential dependence of $\sigma_c(1/T)$ (Fig. 3).

A model was developed in[3] in which the instability of the system was connected with the interaction of the Frenkel excitons. Phenomenologically, the conclusion of this research can be drawn in the following way. We carry out our analysis in the narrow-band approximation. Then there are Frenkel excitons in the system along with the current carriers; these excitons appear in this approximation as intra-atomic excitations. Let the lattice distortion u lower the energy of excitation of the exciton by an amount $-bu$, and the energy of creation of the electron-hole pair by an amount $-au$. Moreover, if the applied electric field changes the energy of the crystal via the piezoeffect by an amount $-cEu$, then the free energy of the system is

$$\frac{F}{N} = (\varepsilon_g - au)x + (\varepsilon_e - bu)x_e - cEu + \frac{Bu^2}{2} - T[x_e \ln x_e - x_e + 2(x\ln x - x)]. \quad (2)$$

if the carriers and the excitons are nondegenerate. Here x is the carrier concentration divided by the number of metallic ions N, and x_c is the exciton concentration. The term $Bu^2/2$ describes the elastic energy which is due to the lattice distortion, ϵ_g and ϵ_c are the electron-hole pair and exciton production energies for zero concentration and in zero electric field. If we vary F with respect to u and then vary the resultant expression for the free energy with respect to x and x_c, we find that the carrier concentration and the exciton concentration are given by the following expressions:

$$x = \exp\{-(\varepsilon_g - K_o x_e - \alpha_o E)/2T\}, \quad (3)$$

$$x_e = \exp\{-(\varepsilon_e - K_e x_e - \alpha_e E)/T\}. \quad (4)$$

Here we have assumed that it is the excitons that determine the phase transition, i.e., $x \ll x_e$ or $\epsilon_g > 2\epsilon_c$. In (3) and (4) we use the notation

$$\frac{ac}{B} = \alpha_\sigma, \quad \frac{bc}{B} = \alpha_e, \quad \frac{ab}{B} = K_\sigma, \quad \frac{b^2}{B} = K_e.$$

We note that these four quantities are connected by the relation

$$\gamma = a/b = \alpha_\sigma/\alpha_e = K_\sigma/K_e. \quad (5)$$

The quantity α_e characterizes the shift of the transition point, and α_σ the change in the activation energy of the conductivity in the electric field.

We first consider the shift in the transition point. At the point of instability of the system, where $(dx_e/dT)_{T=T_c} \to \infty$, we have

$$x_e(T_c) = T_c/K_e \quad (6)$$

and the transition temperature is connected with the parameters ϵ_e, K_e and the field by the relation

$$\alpha_e E = \varepsilon_e - T_c(1 - \ln(T_c/K_e)). \quad (7)$$

Thus, the critical field and the critical temperature

are connected, with logarithmic accuracy, by a linear relation. Here as $E \to 0$, i.e., $T_c \to T_{c0}$, we have

$$\alpha_c = \left(\frac{dT_c}{dE}\right)_{E\to 0} = \frac{\alpha_\varepsilon}{\ln(T_{c0}/K_c)}. \quad (8)$$

Using (7), (6) and (5), we obtain the result that for $T = T_c(E)$, the current carrier concentration is determined by the expression

$$x(E_c) = \left(\frac{T_c}{K_\varepsilon}\right)^{\gamma/2} \exp\left\{-\frac{\varepsilon_g - \gamma\varepsilon_e}{2T_c}\right\}. \quad (9)$$

Thus, if $\gamma \approx 1$, then σ_c as a function of $1/T_c$ must have a slope equal to $(\epsilon_g - \gamma\epsilon_e)/2 = I/2$ and is different from $\epsilon_g/2$ in zero field.

It is seen from the expressions (3), (7), (9) that qualitatively they describe the fundamental regularities observed experimentally: the difference in the activation energies σ_0 and σ_c, the exponential dependence of the electric conductivity on the field, and the linear relation of the transition temperature with the electric field in the high-temperature region. From the dependence of σ_c on $1/T$ (Fig. 3), we can find $I = 0.18$ eV, and since the activation energy σ_0 is $\epsilon_g/2 = 0.12$ eV (Fig. 3), we obtain $\Delta = \gamma\epsilon_e = 0.06$ eV. From the slope of $\ln\sigma = f(E)$, we get $\alpha_\sigma = 9 \times 10^{-3}$ deg-cm/V and from the $T_c(E)$ dependence we find $\alpha_c = -1.4 \times 10^{-3}$ deg-cm/V. By using the experimental values of the constants we can verify the self-consistency of the initial assumption that the temperature is determined by certain excitations, but the influence of the field on the conductivity and on the transition temperature is due to a common cause. Actually, it follows from (7) that the electric field for which $T_c \to 0$ is determined by the relation

$$E_0 = \varepsilon_e / \alpha_c = \Delta / \alpha_\sigma,$$

where we have used the connection between ϵ_e and Δ and the relation (5).

Substituting the experimental values of Δ and α_σ found from measurements of the conductivity, we obtain $E_0 = 8 \times 10^4$ V/cm; at the same time, by extrapolating the dependence $T_c(E)$ to zero, we get $E_0 \approx 1.1 \times 10^5$ V/cm. To our view, the agreement is better if we take into account the roughness of the model and the large experimental errors in the measurement of α_σ ($\approx$30%) and $T_c(E)$ ($\approx$10%). At the same time, in the model of current excitations the computed and measured values would have differed by a factor of four.

From the expressions (5), (8) and (7) at $E = 0$ we can obtain relations for the parameter γ directly in terms of the experimentally measured quantities:

$$\gamma = \Delta / T_{c0} - \alpha_\sigma / |\alpha_c|. \quad (10)$$

Here, in each case, it is necessary to have the condition $\gamma > 0$ in order that the model have meaning. Unfortunately, the large errors in the measurement of Δ, α_σ, α_c do not allow us to determine the parameter γ from the relation (10). However, we can establish their order of magnitude from the following considerations. With account of the error in the measurements entering into (19), the values of γ should lie in the limits $\gamma = 1.2$–4.8. At the same time, in order that we can say that the carriers do not determine the transition, it is necessary that the condition $\epsilon_e < \epsilon_g/2$ be satisfied, as has already been pointed out above. Using the connection between ϵ_e and Δ, we obtain the result that

$$\gamma > \frac{\alpha_\sigma}{|\alpha_c|}\frac{2T_{c0}}{\varepsilon_g - 2T_{c0}} \approx 0.8 \pm 0.3.$$

Thus the quantity γ is seen to be "locked-in" within the narrow range $1.2 \gtrsim \gamma > 0.8 \pm 0.3$, i.e., $\gamma \approx 1$.[3)]

Making use of the value $\gamma \approx 1$, we can estimate all the parameters that enter into the theory: $\epsilon_e = \Delta = 6 \times 10^{-2}$ eV, $\alpha_e \approx \alpha_\sigma = 9 \times 10^{-3}$ deg-cm/V. The value of the constant of the self-consistent field is best estimated from the expression (7) for $E = 0$, because of the smaller experimental error in the determination of Δ. The estimate gives $K_e \sim K_\sigma \sim 0.6$ eV. Of course, such an estimate can serve only as an illustration of the order of magnitude of K. From the value of α_σ we can estimate the constant of the "deformation" potential of the current carriers, D. Actually, $\alpha_\sigma \sim D\beta$, where β is the piezoelectric modulus. If $\beta \sim 10^{-7}$ cm/V, then $D \sim 10$ eV.

Here one must note one important circumstance. In the phenomenological consideration given above, nothing has been done in the way of making specific the nature of the non-current excitations: these could be phonons instead of excitons, with a frequency dependent on their concentration. However, there are two objections to a phonon nature for the non-current excitations:

1) the same order of magnitude of α_e and α_σ found from the dependence of the electric conductivity on the field and of the transition temperature on the field;

2) the value of the constant of the deformation potential $D \sim 10$ eV, which has an order of magnitude that indicates its electric origin.[4)]

Actually, in the case of phonons, such a constant cannot exceed the maximum frequency of the phonon and would be of the order of 10^{-1} eV. Just these two facts permit us to connect the non-current excitations which lead to the instability of the system with the Frenkel excitons, the energy of the thermal excitation of which is equal to $\approx 6 \times 10^{-2}$ eV, as we have seen above.

We shall now consider the region of low temperatures. It is seen from Fig. 3 that the slope of the curve $\sigma_0(1/T)$ changes rapidly in the temperature region $T \lesssim 100$°K. Here the activation energy is equal to 0.05 eV, which gives us reason to think that we are in transition from the region of intrinsic conductivity for $T \gtrsim 100$°K to the region of impurity conductivity for $T \lesssim 100$°K. The character of the $\sigma_c(1/T)$ curve changes rapidly at the same time; this curve practically ceases to depend on the temperature down to helium temperatures. At the same time, the character of the field dependences of the electric conductivity begins to change and at temperatures below 50°K, a portion $\ln\sigma \sim \sqrt{E}$ is clearly observed, which is characteristic for the Frenkel-Poole law (Fig. 1). The phase

[3)] We note here that $\gamma = 1$ in the model developed in [3].

[4)] It should be noted, however, that the estimates given are rather rough, although they give reasonable orders of magnitude. A final derivation can be made only if accurate values of the piezoelectric modulus are known and there is increased accuracy in the determination of α_c and α_σ.

curve T_C as a function of E does not change at temperatures of the order of 100°K and the noted departures from linearity begin only at temperatures of the order of 30°K. This confirms the assertion made above that the excitations corresponding to a phase transition do not determine the electric conductivity in this temperature range.

The independence of σ_C of the temperature in the region of impurity conductivity can be connected with the decrease in the energy of ionization of the impurity with increase in the electric field (due to the Frenkel-Poole effect and the piezoeffect), so that at $E = E_C$ all the impurities become ionized. Since the dependence $T_C(E)$ is determined by the excitons as before, then it must be described by the relation (7). As $T \to 0$, the curve has a negative derivative and $dE/dT \to -\infty$. It is clear, however, that in the low temperature region it is no longer possible to use the representation of infinitely narrow bands. If this can lead to a small change in the slope at high temperatures, then it leads to a change in the character of the dependence at low temperatures. Actually, if the width of the exciton band is $\Delta E^{(e)}$, then the exciton concentration at low temperatures $T \ll E^{(e)}$ is determined by the relation

$$x_e = \left(\frac{T}{\Delta E^{(e)}}\right)^{3/2} \exp\left\{-\frac{\varepsilon_e - K_e x_e - a_e E}{T}\right\}, \qquad (11)$$

and therefore the critical field is connected with the transition temperature by the relation

$$a_e E = \varepsilon_e - T_c\left(1 - \ln\frac{(\Delta E^{(e)})^{3/2}}{K_e T_c^{3/2}}\right). \qquad (12)$$

The expression (12) correctly describes the character of the experimental curve and allows us in principle to determine the width of the polaron band of excitons for a known value of K_e. The estimate yields $\Delta E^{(e)} \sim 10^{-2}$ eV.

Let us now raise two important questions.

1) With what electronic transitions can the excitons in V_2O_3 be specifically identified?

2) How can such narrow bands of width of the order of 10^{-2} eV arise?

To answer the first question, we consider the V^{+3} level in the Al_2O_3 matrix (point symmetry C_{3V}[15]), which corresponds to the high-temperature phase of V_2O_3. Without account of the trigonal distortion, the ground state has a symmetry $^3T_1(t^2)$. With account of this distortion, the term is split into $^3A_2 + {}^3E$; here the state ^3E is 0.14 eV higher than $^3A_2$. The value of the spin-orbit interaction is small and amounts to no more than 10^{-3} eV for the state $^3A_2$. The investigation of the absorption spectrum of the complex $[V(urea)_6]^{+3}$ in the crystal $V(urea)_6 \times (ClO_4)_3$, where the vanadium ion occupies a site with point symmetry D_3, gives a trigonal splitting 0.148 eV and spin-orbit splitting of the state $^3A_2$ gives 7.5×10^{-3} eV.[16] All this leads us to think that if the upper transition points of the band can be absolutely narrow, then the transition $^3A_2 \to {}^3E$ should correspond to the exciton state in the "metal." A small monoclinic distortion, which appears below the transition point, leads to a small splitting of the states and a change in the distances between the levels. It is clear that the energy of excitation of the exciton in our case depends on the value of the trigonal distortion, but it should be the same in order of magnitude as the data given for the isolated field, which also holds in our case.

The second question—how do the narrow bands arise? In[3] it was shown that the expression for the free energy developed at the beginning of the section is obtained if there is strong electron-phonon coupling and a decrease in the energy of activation of the excitons is the result of their interaction through phonon exchange. Here the constant of the self-consistent field K_e is of the order of magnitude of the polaron coupling of the exciton. Strong coupling leads to a sharp narrowing of the initial bands both of the exciton and the conduction and valence bands. Here the width of the polaron band will be[17,18]

$$\Delta E_p \approx \Delta E e^{-\gamma_0} = \Delta E e^{-E_p/\hbar\omega_0},$$

where E_p is the value of the polaron shift and ω_0 is the frequency of the optical phonon. If we assume, as is the case in 3d-oxides, that the width of the initial bands is of the order of 1 eV,[19-21] and the width of the exciton band with account of the polaron effect is of the order of the widths of the polaron conduction bands and the valence band $\sim 10^{-2}$ eV, we then obtain the result that $\gamma_0 \sim 5$. We remark that, since the widths of the bands are under the logarithm sign in the estimate of γ_0, we can assume that the order of magnitude of γ_0 is correct.

If we use the location of the highest high-energy peak in the lattice reflection spectrum $\hbar\omega_0 \approx 6 \times 10^{-2}$ eV[3)] for estimate of $\hbar\omega_0$, then the polaron shift $E_p \sim \hbar\omega_0\gamma_0 \sim 0.3$ eV, which agrees with the value of the constant of the self-consistent field $K_e \sim 0.6$ eV. The carriers in the narrow band model are the excess electron at the site (i.e., the state V^{+2}) and the hole at the site (i.e., the state V^{+4}). If we start out from the scheme of an ionic crystal and denote the difference of the ionization potentials of the ions V^{+2} and V^{+3} by J, then, with account of the polaron shifts, the width of the forbidden band will be equal to

$$\varepsilon_g = J - E_p^{(c)} - E_p^{(v)}$$

where $E_p^{(e)}$ and $E_p^{(V)}$ are the polaron shifts in the conduction band and the valence band. Assuming that $E_p^{(c)} \sim E_p^{(V)} \sim 0.3$ eV and $\epsilon_g = 0.24$ eV, we obtain the result that $J \sim 0.8$ eV. It is seen that this value is much less than the corresponding differences of the ionization potentials of isolated ions, which amounts to almost 11 eV. Such a large difference between the found value J and the difference in the ionization potentials can be the consequence of the fact that the purely ionic model is unsuitable and in the calculation of the ionization energy it is more correct to assume that the electron is localized not on the ion but within the limits of the unit cell.

We again emphasize that the given estimates have a very approximate character. However, in our opinion, they show that the model can describe the experimental results in non-contradictory fashion.

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5)The authors are grateful to D. N. Mirlin who measured the reflection spectrum of V_2O_3 in the semiconductor phase.

CONCLUSION

The basic results of the result are the following.

1. A shift was observed in the point of the phase transition in V_2O_3 in a strong electric field, down to helium temperatures, as well as a switching effect. The temperature and field dependences of the electric conductivity and also the temperature dependence of the critical field are investigated. It is shown that thermal effects, which are capable of masking the field effect, do not play a role in our experiments.

2. High-frequency generation was observed in the phase transition in a constant electric field in the given-current regime. The generated frequency is determined by the parameters of the external circuit. The transition in the electric field is accompanied in the region of temperature hysteresis by a "memory effect." This indicates the presence of a long-lived metastable metallic phase in this temperature region.

3. No effect of the magnetic field ($B \leq 240$ kG) on the temperature of the phase transition was observed, in spite of the existence of antiferromagnetic ordering below the transition point $T_{C0} = 150°K$.[22]

4. It is shown that the models in which instability arises because of the interaction of the carriers cannot explain the observed experimental results.

5. To explain the experimental results, we used a phase-transition model in which the loss of stability of the system is connected with Frenkel excitons in strong electron-phonon interaction. The model correctly describes the basic regularities observed experimentally. Treatment of the switching effect as the result of a shift in the transition point in the electric field due to the piezoeffect explains the experimental results over a wide range of temperatures.

6. An estimate is given of the parameters entering into the theory on the basis of the experimental data, and it is shown that as a result of the polaron effect bands of width of the order of $\sim 10^{-2}$ eV appear. Here the constant of interaction with phonons is $\gamma_0 \sim 5$. At the same time, the temperature of the phase transition T_{C0} is evidently below the temperature T_0, above which there is a jump mechanism of conductivity.

The proposed model qualitatively explains the temperature and field dependences of the electric conductivity and the $T_C(E)$ diagram.

In conclusion, the authors express their gratitude to V. N. Bogomolov and V. P. Zhuze for discussions of a number of experimental problems, L. V. Keldysh, E. K. Kudinov, I. B. Levinson, D. N. Mirlin, G. I. Pikus, and É. I. Rashba for very useful critical discussions of the conditions of the applicability of the model to the description of the observed effects.

Note added in proof (July 2, 1971) The direct experimental proof of the equivalence of the electric field effect to the pressure effect was given in the work of V. N. Andreev, B. A. Talerchik and F. A. Chudnovskiĭ [ZhETF Pis. Red. 13, 527 (1971), JETP Lett. [3, 376 (1971)].

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Translated by R. T. Beyer
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