

fore, the dependences $\chi'(\Delta T)$, $\chi''(\Delta T)$, and $t_0(\Delta t)$ are given in this case for a few frequencies.

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Dielectric-metal phase transition in V_3O_5

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Results are presented of a comprehensive investigation of a phase transition in V_3O_5 , which is identified on their basis as dielectric-metal phase transition (DMPT). The entire investigated aggregate of properties (kinetic, magnetic, optical, structural) is interpreted in best fashion within the framework of a model with strong electron-electron correlations of the Mott-Hubbard type in both the low- and the high-temperature phases. Above the phase-transition temperature, V_3O_5 is a poor metal with a strong degree of disorder, a small mean free path, and localized magnetic moments. The DMPT that takes place at 430 K is apparently connected with differentiation of the charge and with the spatial localization of the vanadium ions with different valences.

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1. INTRODUCTION

Dielectric-metal phase transitions (DMPT) have been observed in many transition-metal compounds.^[1] In particular, they are typical of vanadium oxides. By virtue of the variable valence (2-5), vanadium forms an entire series of oxides with both integer valence (VO , V_2O_3 , VO_2) and with intermediate valence, such as the Magneli phase V_nO_{2n-1} ($n=3-9$). DMPT take place in almost all the oxides. The only exceptions have up to now been taken to be V_7O_{13} , which remains metallic down to the lowest temperatures, and V_2O_5 , which exhibits semiconductor properties.

In this paper we summarize the results of a comprehensive investigation of the phase transition previously observed^[2] in V_3O_5 and interpret this transition as a DMPT. We study the kinetic characteristics (resistivity, thermoelectric power, Hall effect), the magnetic properties, and the optical characteristics (reflection coefficient in the visible and infrared), carry out structural investigations, and determine from differential thermal analysis (DTA) data the thermodynamic characteristics of the transition. We investigate also the influence of doping on the V_3O_5 properties.

An analysis of the entire aggregate of obtained data allows us to conclude that at 430 K a dielectric-metal phase transition takes place in V_3O_5 . It is apparently similar in character with that of the transitions in other Magneli phases and is due mainly to spatial ordering of the V^{+3} and V^{+4} ions (the analog of Wigner crystallization). Thus, V_3O_5 can be regarded on the basis of its properties as belonging to the common series of vanadium oxides that undergo DMPT.

We report here successively the results of an experimental investigation of various properties of V_3O_5 (Secs. 3, 4) and then carry out a theoretical analysis that allows us to draw conclusions concerning the behavior of V_3O_5 at $T < T_c$ and $T > T_c$ and concerning the mechanism of the transition (Sec. 5). We formulate also a number of questions that remain unanswered to this day.

2. TECHNOLOGY OF PRODUCTION OF V_3O_5 CRYSTALS

The V_3O_5 single crystals were grown by the method of chemical transport reaction in a closed volume, using $TeCl_4$ as the carrier.^[3] To obtain single crystals of V_3O_5 of the lower limit of the homogeneity region the

V_3O_5 powder was mixed with a small amount of V_2O_3 powder. Initially only V_2O_3 single crystals of the upper limit of the homogeneity region were initially transported and the V_3O_5 single crystals were transported only later, when the oxygen partial pressure in the system reached a value corresponding to the lower region of homogeneity of the V_3O_5 phase. As a net result we had in the crystallization zone V_2O_3 single crystals of the upper limit of the homogeneity region and V_3O_5 single crystals of the lower homogeneity region. We obtained in similar fashion the V_3O_5 single crystals of the upper homogeneity region, by starting with a mixture of V_3O_5 and V_4O_7 powders. The single crystals were sorted by measuring the resistivity at room temperature. At these temperatures the V_3O_5 is in a semiconducting state and has appreciable resistivity compared with the neighboring phases V_2O_3 and V_4O_7 , which are metallic at room temperature.

The phase homogeneity of the obtained single crystals was confirmed by an x-ray structure analysis. In^[4-6] the V_3O_5 homogeneity region was determined only on the basis of an x-ray phase analysis method. In these investigations, however, sight can be lost of an admixture of another phase amounting to as much as several percent. This is why there are as yet no published exact data on the homogeneity region of V_3O_5 . The stoichiometry of the V_3O_5 single crystals was determined by oxidizing them in an oxygen atmosphere to the oxide limit V_2O_5 , and the stoichiometry of the initial sample was calculated from the added weight. The so-determined homogeneity region of the V_3O_5 single crystals turned out to be quite narrow.

Molybdenum-doped V_3O_5 single crystals were obtained in the same manner.^[7] The additive was the oxide MoO_2 of "chemically pure" grade. The dopant content in the V_3O_5 was determined by an activating analysis method.

3. MEASUREMENT PROCEDURE

The temperature dependence of the resistivity was measured by the usual four-contact method in vacuum. The contacts were deposited by fusing-in silver paste in vacuum at a temperature 380°C, and were also obtained by spot welding. To eliminate surface effects, the V_3O_5 single crystals were etched in boiling HNO_3 . In addition, the surfaces of some samples were polished with diamond paste. In either case, no substantial difference was observed in the temperature dependence of the resistivity. The thermoelectric power was determined relative to copper. In the measurement of the thermoelectric power the dimensions of the V_3O_5 single crystals were 2.5 × 0.5 × 0.5 mm. The temperature gradient at the sample was set within 4–7 degrees.

The magnetic susceptibility was measured by Foner's method^[3] and by the standard balance method. To obtain reflection spectra in the energy interval 0.1–1 eV we used an IKS-11 infrared spectrophotometer with a Ge-Au photocell as the detector, while in the 1–3.5 interval we used an SF-4A spectrophotometer and an FEU-28 photomultiplier. The reflection coefficient was measured relative to an aluminum mirror. The rela-

tive error in the measurement of the reflection coefficient was 3%. In the measurements, the incidence angle was close to normal (11°). The infrared spectra in the energy region 0.05–0.25 eV were obtained with a UR-20 spectrophotometer. The samples were V_3O_5 powder pressed in a KBr matrix. The x-ray structure investigations of the phase transitions were investigated on V_3O_5 single crystals and polycrystals. The single crystals were investigated by the method of Laue and Schiebold at temperatures 300 and 450 K. The dependence of the unit cell on the temperature was investigated on polycrystalline samples in the temperature interval from 300 to 530 K. All the x-ray structure measurements were made with a DRON-2 x-ray diffractometer with the GPVT-1500 temperature attachment.

4. EXPERIMENTAL RESULTS

A. Kinetic properties

Figure 1 shows typical plots of the resistivity and the thermoelectric power of single-crystal V_3O_5 vs temperature. The resistivity curve shows a jumplike rise, by 10–20 times, at 430 K. Above the phase-transition temperature the resistivity has an activation-type dependence with a conductivity activation energy $E_g = 0.13$ eV.

For all the V_3O_5 samples, the thermoelectric power at room temperature is positive. This result contradicts the data of^[9], where a negative sign was obtained for the carriers. At the phase-transition temperature, the thermoelectric power reverses sign and becomes negative. The absolute value of the thermoelectric co-

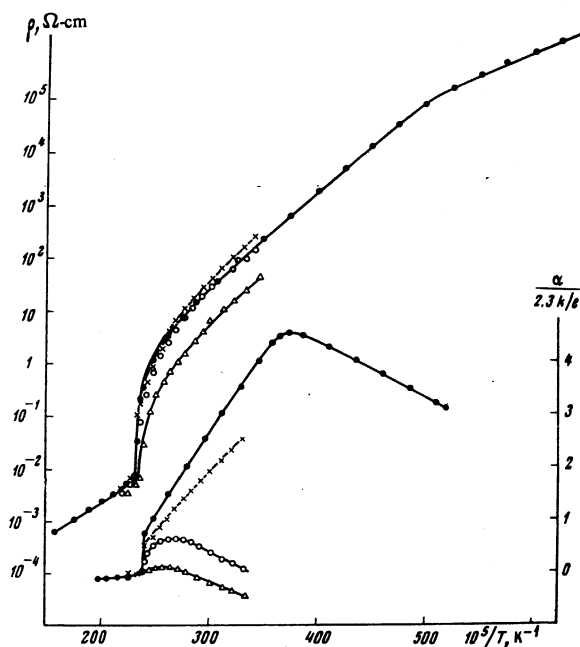


FIG. 1. Temperature dependence of the resistivities of stoichiometric and molybdenum-doped V_3O_5 single crystals: ●— V_3O_5 ; ×— $(V_{0.99998}Mo_{0.00002})_3O_5$; ○— $(V_{0.9996}Mo_{0.0004})_3O_5$; ▲— $(V_{0.9993}Mo_{0.0007})_3O_5$. Lower curves—thermoelectric power $\alpha(1/T)$.

efficient at room temperature fluctuated for different samples in the range from 450 to 700 $\mu\text{V}/\text{deg}$. The thermoelectric coefficient immediately past the phase transition is $\sim 5 \mu\text{V}/\text{deg}$. With further rise of temperature, a slight increase of the thermoelectric coefficient is observed, reaching $\sim 15 \mu\text{V}/\text{deg}$ at 480 K. The increase of the thermoelectric power with temperature, as well as its absolute value at $T > T_c$, are typical of metallic conductivity.

As seen from Fig. 1, in the temperature region below 270 K the thermoelectric coefficient decreases with temperature. The conductivity activation energy remains almost constant in this region at $E_g = 0.3 \text{ eV}$. It begins to decrease at much lower temperatures than the thermoelectric power. The low temperature behavior of $\log \rho(1/T)$ and $\alpha(1/T)$ can be attributed to a transition to impurity conductivity. In fact, the decrease of the thermoelectric power with decreasing temperature can be due only to an increasing influence of carriers of a second type. We defer the interpretation of the data at $T > T_c$ to Sec. 5.

Figure 1 shows also the temperature dependences of $\log \rho$ and α of molybdenum-doped V_3O_5 samples. In this case a pronounced shift of the transition temperature to higher values is observed. At a molybdenum concentration $x = 0.61\%$ the transition temperature is 418 K. An increase of the impurity concentration leads to a small decrease of the resistivity at room temperature without exerting a significant effect on the conductivity activation energy. On the other hand, doping exerts a strong influence on the behavior of the thermoelectric coefficient in the low-temperature phase. Increasing the impurity concentration leads to a decrease of the absolute value of the thermoelectric coefficient at room temperature compared with the stoichiometric V_3O_5 . The maximum of the temperature dependence of the thermoelectric power shifts towards higher temperatures with increasing impurity concentration. The samples doped with molybdenum at an impurity concentration $x = 0.61\%$ have a negative thermoelectric power at room temperature. It must be noted, however, that reversal of the sign of the thermoelectric power does not cause the transition to vanish. Above the phase-transition temperature the molybdenum-doped V_3O_5 samples behave, just as the stoichiometric V_3O_5 samples, independently of the doping level.

Measurements of the Hall coefficient at room temperature have shown that the sign of the carriers in V_3O_5 is positive. This coincides with the thermoelectric-power data. The Hall mobility of the carriers at room temperature was $\mu_H = 0.43 \text{ cm}^2/\text{V}\cdot\text{sec}$.

As the phase transition temperature is approached, a smooth change of the slope of the $\log \rho(1/T)$ curve is observed for single-crystal V_3O_5 , and incidentally also for a number of other vanadium oxides, for example VO_2 , V_4O_7 , and V_8O_{15} . The cause of this behavior is not clear. It is frequently attributed to the presence of traps in the forbidden band. It can be assumed, however, that this is more readily due to a change of the activation energy as the critical temperature is approached. In fact, taking into account the dependence

of the activation energy of the conductivity $\rho = \rho_0 \times \exp(E_g/kT)$ on the temperature we get

$$\frac{d \ln \rho}{d(1/T)} = E_g(T) - \frac{T dE_g(T)}{dT}.$$

If $E_g(T)$ decreases as $T \rightarrow T_c$ then it can be readily seen that the behavior of $\rho(T)$ as $T \rightarrow T_c$ can be of the form obtained above (Fig. 1).

B. Magnetic properties

The magnetic properties of the Magneli series, and in particular of V_3O_5 , were investigated in^[10,11]. It was established with the aid of the Mössbauer effect that V_3O_5 is an antiferromagnet below 70 K. The magnetic susceptibility of V_3O_5 has a smooth maximum in the region of 130 K. Above this temperature V_3O_5 is paramagnetic. The magnetic susceptibility is well described in this case by the expression

$$\chi(T) = \chi_{\text{VV}} + \chi_d(T), \quad (1)$$

where χ_{VV} is the temperature-independent Van Vleck orbital paramagnetism, $\chi_d(T)$ is the temperature-dependent of the d -electron paramagnetism and satisfies the Curie-Weiss law:

$$\chi_d(T) = C/(T - \Theta), \quad (2)$$

where C is the Curie-Weiss constant and Θ is the molecular-field constant.

The ions in V_3O_5 can be in two states, V^{+3} and V^{+4} , in a ratio 2:1, and there is no pairing in this substance in the semiconductor state, unlike in other Magneli phases that have DMPT.^[12] This makes it possible to estimate the Van Vleck contribution to the magnetic susceptibility in the free-ion approximation, using the NMR data for VO_2 and V_2O_3 , in which the vanadium ions are respectively in the oxidation states V^{+3} and V^{+4} .^[13,14] The value obtained for V_3O_5 is $\chi_{\text{VV}} = 4.9 \times 10^{-6} \text{ cgs emu/g}$. Assuming that χ_{VV} is not altered by the phase transition, we can determine with the aid of (1) the magnitude and the temperature dependence of $\chi_d(T)$.

Figure 2 shows a typical temperature dependence of $1/\chi_d$ for V_3O_5 single crystals. In the considered temperature interval the magnetic susceptibility is well described by the Curie-Weiss law. In the phase-transition region one observes a small jump of the magnetic susceptibility, amounting to $0.20 \pm 0.02 \text{ cgs emu/g}$.

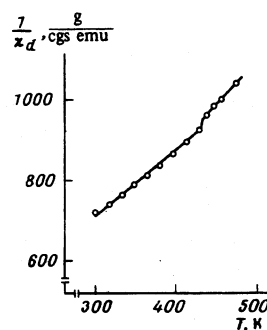


FIG. 2. Dependence of the reciprocal magnetic susceptibility of the spin paramagnetism of d -electrons of V_3O_5 single crystals on the temperature.

TABLE I. Physical properties of V_3O_5 .

Investigated quantity	Values of quantity	
	$T < T_c$	$T > T_c$
Structure	Monoclinic $a = 9.870 \text{ \AA}$ $b = 5.052 \text{ \AA}$ $c = 7.012 \text{ \AA}$ $\beta = 109^\circ 6'$ $V = 330.2 \text{ \AA}^3$	Monoclinic $a = 9.850 \text{ \AA}$ $b = 5.042 \text{ \AA}$ $c = 7.022 \text{ \AA}$ $\beta = 109^\circ 18'$ $V = 329.2 \text{ \AA}^3$
	Paramagnet	Paramagnet
Magnetic order		
Effective magnetic moment	$2.26 \mu_B$	$2.06 \mu_B$
Curie-Weiss constant	0.64	0.53
Molecular-field constant	-338 K	-256 K
Conductivity activation energy	0.3 eV	0.13 eV
Absolute value of thermoelectric coefficient	400-700 V/deg	10-15 V/deg
Sign of thermoelectric power	Plus	Minus
Width of forbidden band at room temperature (from optical data)	0.62 eV	
Hall mobility at room temperature	0.43 $\text{cm}^2/\text{V}\cdot\text{sec}$	
Effective mass		$(2-10)m_0$
Homogeneity region	$\text{VO}_{1.666} - \text{VO}_{1.668 \pm 0.002}$	
Phase-transition temperature	430 K	
Néel temperature	70 K ^[11]	
Resistance jump in phase transition	10-20 times	
Change of magnetic susceptibility in phase transition	$0.20 \pm 0.02 \text{ cgs emu/g}$	
Change in volume of unit cell	0.5 cal/mole-deg	
Change of unit cell volume in phase transition	0.3%	
Change of phase-transition temperature with changing pressure	-2.1 deg/kbar	
Width of hysteresis loop	< 0.5 deg	

The values of C , Θ , and $\mu_{\text{eff}} = 2.84\sqrt{C} \mu_B$ at $T < T_c$ and $T > T_c$ are respectively $C = 0.64$ and 0.53 ; $\Theta = -338$ and -256 K; $\mu_{\text{eff}} = 2.26 \mu_B$ and $2.06 \mu_B$.

Assuming that all the vanadium ions V^{+3} and V^{+4} are in a localized paramagnetic state, we can estimate for V_3O_5 the theoretically expected value $\mu_{\text{eff}}^{\text{theor}} = 2.46 \mu_B$. The obtained $\mu_{\text{eff}}^{\text{theor}}$ is close in value to the experimental data, thus confirming the strong localization of the vanadium ions in the absence of pairing in this substance, since the pairing would greatly decrease the magnetism.

It follows from Table I that in the high-temperature phase there is a certain decrease of μ_{eff} , due in our opinion to delocalization of the d -electrons in the phase transition.

C. Optical properties

The reflection spectra were measured on V_3O_5 single crystals of the lower limit of the homogeneity region. The sample was a mosaic made up of natural unoriented faces of single crystals. The investigation of the electric and magnetic properties attests to absence of noticeable anisotropy in V_3O_5 . This gives grounds for hoping that the optical properties of V_3O_5 do not depend

strongly on the orientation. The finished samples had a reflecting surface measuring 2×4 mm.

The reflection spectra were measured at two temperatures corresponding to the state of V_3O_5 before and after the transition ($T = 296$ and 460 K, respectively). The measurement results are shown in Fig. 3. As seen from the figure, the reflection spectrum of V_3O_5 at $T < T_c$ is of the typical semiconductor form. To determine the size of the forbidden band it was recalculated in terms of the absorption spectrum, using the oscillator method^[15] for this purpose. The position of the absorption edge was determined graphically from the $[\alpha(\omega)\hbar\omega]^2 = A(\hbar\omega - E_g)$ plot. Extrapolation of the linear section of the $[\alpha(\omega)\hbar\omega]^2$ curve gives the approximate value of the energy of the direct interband transition. The value $E_g = 0.62$ eV determined in this manner is in good agreement with the forbidden band width E_g obtained from the temperature dependence of the resistivity.

At $\hbar\omega > E_g$, an increase of the reflection is observed in the low-temperature phase and can be attributed to interband transitions. At $\hbar\omega < E_g$ a tightened low-frequency "tail" is observed and is apparently due to the formation of impurity levels in the forbidden band. A feature of the spectrum is also the presence of two peaks on the edge at $\hbar\omega \approx 0.24$ and $\hbar\omega \approx 0.38$ eV. At $T > T_c$ the peak at $\hbar\omega \approx 0.38$ eV vanishes, but the peak at $\hbar\omega \approx 0.24$ eV remains also in the high-temperature phase. The nature of these peaks is unclear and may be due to impurity or exciton levels.

With increasing temperature, a gradual increase of the reflection coefficient takes place at $\hbar\omega \gg 1$, and is due to the increased concentration of the free carriers. Figure 3 shows also the temperature dependence of the reflection coefficient at $\hbar\omega = 0.14$ eV. It is obvious that the strongest change of the reflection coefficient is observed in the phase-transition region.

Figure 4 shows the transmission spectra of V_3O_5 in the infrared region. As seen from the figure, at $T > T_c$ the spectrum loses the structure due to absorption by phonons. This can be attributed to screening of the lat-

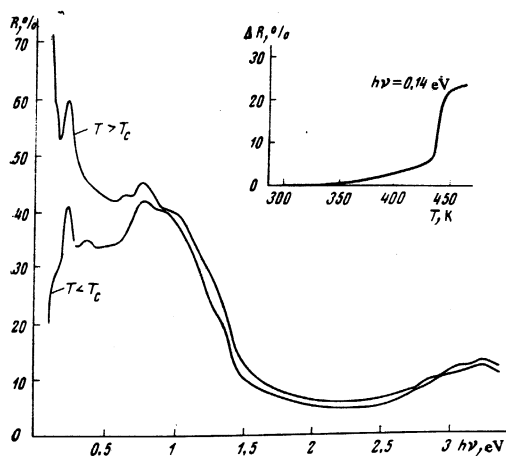


FIG. 3. Reflection spectra of V_3O_5 single crystals before and after the phase transition.

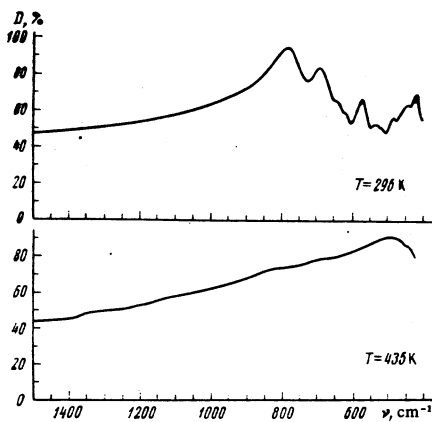


FIG. 4. Transmission spectra of V_3O_5 in the infrared region before and after the phase transition.

tice vibrations by the free-electron plasma. In fact, a reduction of the reflection spectra at $T > T_c$ by the theory of reflection from free electrons (the Drude theory) has shown that the spectrum has a metallic character. A computer reduction has shown that the calculated reflection spectrum agrees within 6% with the experimental data if the plasma frequency is assumed to be given by $\omega_p = 1$ eV and the collision frequency is $\nu = 0.8 \times 10^{15}$ sec^{-1} . Using the formula $\omega_p = (4\pi N e^2 / m^* \epsilon_\infty)^{1/2}$ for the plasma frequency and substituting the value $\epsilon_\infty = 3.3$ obtained from a reduction of the reflection spectrum of the low-temperature phase, we can determine the ratio of the free-carrier concentration to the effective mass N/m^* . The obtained value is $N/m^* = 2.94 \times 10^{48}$. Knowing the carrier mobility at room temperature and assuming that the temperature dependence of the resistivity is governed by the change of the carrier density, we can use the formula $\sigma = eN\mu$ at a constant mobility $\mu = 0.43$ $\text{cm}^2/\text{V-sec}$ to estimate N in the high-temperature phase. The value obtained is $N = 6 \times 10^{21}$ cm^{-3} . Using this value, we have for the effective carrier mass in the high temperature phase $m^* = 2m_0$. Using the collision frequency obtained from optical data we can estimate the carrier mobility at $T > T_c$ from the formula $\mu = e\tau/m^*$. The resultant value $\mu \approx 1$ $\text{cm}^2/\text{V-sec}$ is close to the mobility at $T < T_c$.

It seems more natural, however, that in the metallic phase the number of conduction electrons is equal to the total number of d -electrons ($5d$ electrons per formula), i. e. $N = 1.2 \times 10^{22}$ cm^{-3} . In this case we would obtain from the values of σ and N a mobility $\mu \approx 0.2$ $\text{cm}^2/\text{V-sec}$, which is somewhat lower than in the semiconductor phase, and $m^* = 10m_0$. Some decrease in the mobility at $T > T_c$ agrees with the general picture of the phase transition in such systems (Sec. 5).

Using the obtained collision frequency and effective mass, we can estimate the mean free path $l \approx v_F \tau \approx \hbar \tau / am$, where a is of the order of the lattice parameter. Depending on the assumed value of m^* , we get $l \sim 0.5 - 2.5$ \AA , i. e., $l \leq a$. It is clear therefore that strictly speaking the Drude theory does not hold for the systems under consideration. By way of estimate, however, the results seem quite reasonable.

D. Structural investigations^[16]

The V_3O_5 unit-cell parameters obtained at room temperature agree well with the data of^[17]. Above the phase transition temperature, at $T = 440$ K, we were unable to observe a change in the symmetry of the crystal lattice of V_3O_5 . The Laue patterns attest to preservation of the diffraction symmetry $2/m$. Figure 5 shows the V_3O_5 unit-cell parameters as functions of the temperature. As seen from the figure, the monoclinic unit cell does not undergo substantial changes. The change of the unit-cell parameters in the phase transition decrease the cell volume by $\sim 0.3\%$.

The latent heat of the phase transition was determined with the aid of a differential thermal analysis and a standard. The latter was single-crystal VO_2 , whose latent heat of transition was assumed to be $Q = 1020$ cal/mole.^[18] The approximate value of the latent heat of the phase transition in V_3O_5 turned out to be $Q = 200$ cal/mole, corresponding to an entropy change $\Delta S = 0.5$ cal/mole-deg in the transition.

The main results of the physical investigations of the V_3O_5 single crystals are summarized in the table.

5. DISCUSSION OF EXPERIMENTAL RESULTS

A. Nature of the high-temperature phase

The first question that arises in the analysis of the experimental data is how to classify the high temperature phase, meaning therefore the phase transition itself. Initially,^[2] on the basis of the behavior of $\log\rho(1/T)$, the transition was characterized as a semiconductor-semiconductor phase transition. The low value of the thermoelectric coefficient at $T > T_c$ obtained in this approach can be explained within the framework of the two-band conduction mechanism.

Judging from the large group of V_3O_5 properties obtained in the present article, we favor now another interpretation, namely that the phase transition in V_3O_5 at $T = 430$ K is a dielectric-metal transition. Within the framework of this interpretation, we get a natural explanation of the metallic character of the temperature dependence and of the absolute value of the thermoelec-

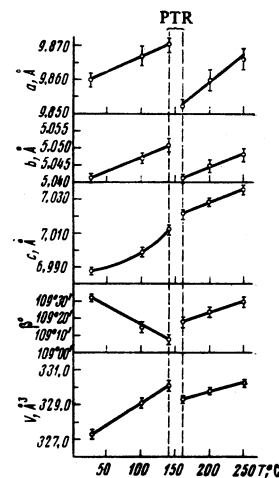


FIG. 5. Temperature dependence of V_3O_5 unit-cell parameters. PTR—phase transition region.

tric power, as well as its independence of the doping at $T > T_c$ whereas the thermoelectric power is quite strongly altered by doping at $T < T_c$.

The strongest argument in favor of this interpretation are the optical properties. As shown in Sec. 4C, they can be explained in natural fashion if account is taken of the appearance at $T > T_c$ of reflection from the free carriers. The vanishing of the IR spectrum structure at $T > T_c$ also agrees with this interpretation.

B. The character of the DMPT

Various mechanisms were proposed to explain the DMPT in transition-metal compound.^[18] As applied to V_3O_5 , it can be assumed that the transition can hardly be caused simply by lowering of the lattice symmetry. According to x-ray structure data, the crystal symmetry is not altered by the transition and remains monoclinic. Nor is the transition connected with the appearance of long-range magnetic order. The Néel temperature of V_3O_5 is 70 K, i. e., it is much lower than T_c . Nor can we hardly identify this transition with the Mott-Hubbard transition. There is no doubt that strong Coulomb correlations of the Mott-Hubbard type play a decisive role in this compound. However, as follows from the magnetic data (weak change of the magnetic susceptibility in the transition, conservation of the localized magnetic moments (LMM) at $T > T_c$), V_3O_5 should apparently be considered to have a strong inter-electron correlation not only at $T < T_c$ but also in the metallic phase. The DMPT itself, however, is not governed by this factor. Judging from NMR data, the transition is likewise not accompanied by electron pairing.^[12]

It is most natural to seek the explanation of the phase transition in the principal singularity of mixed oxides of the Magneli-type phases—in the fact that they contain ions with different valences, V^{+3} and V^{+4} . In such materials the DMPT can be due to segregation of the charges and to the spatial ordering of ions of different valence, i. e., with a phenomenon of the type of Wigner crystallization of the “excess” electrons. A similar reasoning is contained in^[12]. We note in this connection the close analogy between the properties of V_3O_5 and Fe_3O_4 , in which a DMPT transition due to the mechanism described above takes place at $T_V = 120$ K.^[1,19] Indeed, the conductivity, the thermoelectric power, and the optical properties of Fe_3O_4 behave in the manner observed in the present paper for V_3O_5 . Just as in our case, the thermoelectric power reverses sign at $T > T_V$ and immediately assumes a small constant value, while the electric conductivity continues to increase up to $T = 3T_V$, and only then does it assume the normal metallic character.^[19]

The above-noted similarity of the properties of V_3O_5 and Fe_3O_4 can serve as an argument favoring similarity of the nature of the DMPT itself and that of the high-temperature phase. It appears that in other Magneli phases the DMPT are of similar nature, as if confirmed by direct investigations.^[20,21] The high-temperature phase in such a picture is described as a phase with

fast exchange of the V^{+3} and V^{+4} states, i. e., with fast transitions of the “excess” electrons from center to center. This process leads to properties of the type of those of a poor metal with mean free path of the order of the interatomic distances and conductivity of the diffusion type (mobility ≤ 1 cm²/V-sec), as is in fact observed in experiment.

The noticeable correlation between electrons, which can be preserved at $T > T_c$, and the strong electron-phonon interaction can explain qualitatively the increase of the conductivity with rising temperature at $T > T_c$ both in V_3O_5 and in Fe_3O_4 . The metallic phase can in this case have the properties of a disordered system. Also in agreement with an interpretation that connects the semiconductor-like behavior with the disorder (due respectively to strong electron-electron or electron-phonon interaction, or else due to impurities, defects, etc.) is the similar behavior of a number of other oxides, in which the conductivity increases with temperature in those cases when the absolute value of the conductivity turns out to be less after the transition than the minimal metallic conductivity $\sigma_{min} \sim 10^{-3}(\Omega\text{-cm})^{-1}$ of transition-metal oxides.^[22]

We note also that in such systems one frequently encounters a situation wherein the thermoelectric power assumes the metallic behavior ahead of the conductivity.^[1,19,22,23] This is possibly connected with the singularities of the disordered systems near the percolation threshold.^[23]

The spatial ordering of the electrons can itself be governed by two mechanisms, direct Coulomb repulsions of electrons at different centers, and interaction of the electrons with the phonons (polaron effects). The relative roles of these factors are at present unclear and are the task of further research. It is most likely that, just as in Fe_3O_4 , both factors acting jointly are of importance.

C. Localization of electrons and magnetic properties of metallic phase

The magnetic properties of the metallic phase are a separate problem; their analysis can deduce the state of the electrons in V_3O_5 . A common property of all Magneli phases, and particularly V_3O_5 , is the presence of localized magnetic moments (LMM) even in the metallic phase. This manifests itself in the fact that the magnetic susceptibility obeys the Curie-Weiss law with a Curie-Weiss constant corresponding practically to the total spin angular momentum for localized spins.^[11] In this respect, quite unexpectedly, mixed oxides turn out to be more magnetic, i. e., the electrons in them are more localized than the outermost compounds of the series, VO_2 and V_2O_3 , which contain vanadium ions of only one valence. This behavior can be qualitatively understood from the following: In oxides with integer valence, a Mott-Hubbard transition must be accompanied by formation of new polar states (pairs and holes), and in the simplest case of a nondegenerate band this process is accompanied by the vanishing of a fraction of the LMM. The susceptibility of the metallic phase of such compounds therefore has a Pauli character, albeit

with a noticeable exchange enhancement. In compound with mixed valence the number of electrons per center is not an integer, for example $5/3$ electrons in V_3O_5 . In this situation it is possible, while preserving the full correlation of the electrons in one center and correspondingly the LMM, to ensure conductivity via motion of the carriers (electrons or holes) over the empty sites, so that in such systems it is not necessary to produce excess pairs or holes to obtain the metallic state, and by the same token decrease the electron localization. Even in the limit of a very strong repulsion of the electrons at the centers, at $n \neq 1$ there can exist a metal with LMM, so to speak a Mott-Hubbard metal. It appears that the Magneli phases belong in fact to this class.

One can ask why the interelectron correlations in these substances are in fact stronger than in oxides with an integer number of electrons per center. One of the contributing factors may be the nonequivalence of the centers, which is preserved at $T > T_c$ and leads to an effective narrowing of the bands,^[12] as well as polaron effects. Another possible explanation is the following.^[24] It is known that the criterion of localization of Mott-Hubbard electrons is that the Coulomb repulsion U of the electrons at the center exceeds the electron kinetic energy, $U/W > 1$ (W is the width of the d band). A more accurate measure of the electron kinetic energy, however, is not W but the Fermi energy ϵ_F . It is of course of the order of W , but in the case of partial filling of the band, $n < 1$, it can be several times smaller, $\epsilon_F \approx nW < W$. It is natural to assume that the criterion of electron localization should more readily be the condition $U/\epsilon_F \approx U/nW > 1$ (for a nondegenerate band at $n < 1$ we deal with the whole Fermi energy $\epsilon_{Fh} \approx W(1-n) < W$). As a result, at close values of the parameters U and W (and it appears that these parameters are approximately equal for all vanadium oxides, both with integer valence and for Magneli phases), substances with noninteger n will be characterized by a higher degree of interelectron correlation. This conclusion is confirmed also by the results of a theoretical calculation.^[24] Within the framework of the usual Hubbard model with partially filled band, it is possible to show by the Gutzwiller variational method that, in analogy with the case $n = 1$ ^[25] the number ν of pairs at $n < 1$ decreases with increasing U/W more rapidly than at $n = 1$, i. e., the degree of electron correlation increases at lower values of U/W . The critical value U_c decreases with decreasing n even more rapidly than the value $U_c = nW$ obtained above from qualitative considerations.

The presented arguments show why the electrons in the metallic phase of Magneli phases with noninteger valence, including V_3O_5 , are more localized than in V_2O_3 and VO_2 even at close values of the parameters U and W . A similar situation is observed also in titanium oxides. The general value of the parameter U/W is smaller for them than for vanadium oxides, and they are closer in their properties to normal metals. However, within this series of compounds itself the mixed oxides Ti_nO_{2n-1} are "more magnetic" in the metallic phase than Ti_2O_3 .^[1]

A question in itself, as already noted in^[12], is the antiferromagnetic character of the exchange interaction in the metallic phase. A possible explanation is the preservation of a strong short-range order in this phase. Another contributing factor may be the decrease of the width of the band and the strong suppression of the ferromagnetic double exchange on account of polaron effects, whereas the antiferromagnetic superexchange is not affected by them.^[26]

6. CONCLUSION

On the whole, in our opinion the entire investigated aggregate of properties of V_3O_5 is best interpreted within the framework of a model with strong interelectron correlations of the Mott-Hubbard type both in the low-temperature and in the high-temperature phases. At $T > T_c$ the substance is a poor metal with strong degree of disorder, short mean free path, and LMM. The metal-dielectric phase transition that takes place at $T = 430$ K is apparently connected with segregation of the charge and spatial localization of the V^{+3} and V^{+4} ions. Thus, V_3O_5 , as other Magneli phases, is a substance of Mott-Hubbard type in both the dielectric and metallic phases, with a DMPT of the Wigner-crystallization type.

Of course, we have described above only a qualitative scheme. Many questions still remain unanswered. One of them is the structure and degree of degeneracy of the electron bands. The $3d$ levels of the V^{+3} and V^{+4} ions in a regular octahedral surrounding are triply degenerate in the orbital quantum number, so that arguments based on a nondegenerate Hubbard model are not rigorous. It appears, however, by virtue of the low symmetry of V_3O_5 , that the oxygen octahedra are strongly distorted^[27] and the orbital degeneracy is lifted. Favoring this assumption is the value of the effective magnetic moment, which is close to the pure spin value and shows that the orbital angular momentum and the spin-orbit interaction are quenched. It is possible that the optical-absorption peak at $\hbar\omega = 0.24$ eV, which is preserved also in the metallic phase, corresponds to transitions between such sublevels, split by the crystal field, of the t_{2g} level. To confirm this interpretation, however, additional research is necessary.

Many questions have already been mentioned in the above discussion of the kinetic properties, particularly the cause of the increased conductivity when the temperature is raised in the high-temperature phase. The properties of a metal, if such a phase can be legitimately called a metal, with a mean free path on the order of interatomic and strong electron-electron and electron-phonon interactions, are very little understood. It is also necessary to shed light on the relative roles of these interactions in DMPT.

Nonetheless, however, the picture described above provides in general a satisfactory description of the behavior of the V_3O_5 compound, which is thus made to fit in the general series of compounds with intermediate valence and with a dielectric-metal phase transition.

In conclusion, the authors consider it their pleasant

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Generation of high-frequency magnons by nonequilibrium electrons polarized opposite to the direction of magnetization

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A theoretical investigation is made of the generation of high-frequency magnons by nonequilibrium electrons with spins directed opposite to the magnetization in wide-band ferromagnets. It is shown that the isotropic case is characterized by narrowing of the magnon generation range at high electron pumping rates: the range of momenta of the generated magnons decreases either exponentially with increase in the electron pumping rate or is inversely proportional to this rate, and the number of magnons in this range rises exponentially with the pumping rate in the first case and quadratically in the second. Typical momentum of the generated magnons is of the order of the momentum of an electron whose kinetic energy is equal to the s - d exchange interaction energy. If the magnon spectrum depends strongly on the angle between the magnon momentum and magnetic moment of a crystal, an increase in the pumping rate gradually produces an almost monochromatic beam of magnons whose momenta are directed along the magnetization. At a certain critical pumping rate the generation of magnons becomes avalanchelike and the magnon system becomes unstable.

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1. INTRODUCTION

Electromagnetic methods for the excitation of the spin system of a ferromagnet, capable of generating low-frequency spin waves with wave vectors $q < 10^6 \text{ cm}^{-1}$, are widely known.^[1] We shall consider the process of gen-

eration of magnons by nonequilibrium electrons with \uparrow spin ("against the field"), which—under certain conditions—can produce high-intensity beams of high-frequency almost monochromatic magnons.

We shall consider the process of relaxation of non-