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## Metal-Insulator phase transition in thin films of vanadium dioxide doped with indium

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The electrical conductivity of thin polycrystalline films  $V_{(1-x)}In_xO_2$  has been studied in a wide temperature range covering the regions of existence of both the metallic and insulator phases. It is shown that with increasing indium concentration, the temperature of the metal-insulator phase transition decreases, and the width of the temperature region of phase coexistence monotonically increases. To explain the temperature dependence of the electrical conductivity of the insulator phase  $V_{(1-x)}In_xO_2$ , a model of hopping conductivity is applied, taking into account the effect of thermal vibrations of atoms on the resonance integral. Calculated the values of the parameter  $\varepsilon$  depend on the degree of doping of  $VO_2$ .

**Keywords:** phase transition, vanadium oxides, thin films, polaron, electrical conductivity.

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### 1. Introduction

In single crystals of pure vanadium dioxide ( $VO_2$ ) upon cooling below  $T_c = 340$  K, a first-order structural phase transition from the metallic tetragonal phase (R-phase) into a insulator monoclinic phase ( $M_1$ -phase) is observed [1,2]. The change in the crystal structure proceeds abruptly and is accompanied by a sharp change in the electrical and optical parameters of vanadium dioxide. In the vicinity of  $T_c$ , the temperature dependences of these parameters have the form of a hysteresis loop, which is explained by the martensitic nature of the phase transition. The phase transition in macroscopic samples of vanadium dioxide due to emerging elastic stresses is accompanied by their destruction, therefore, for practical applications based on the fact that the phase transition time is about 100 fs [3], thin films are usually used [4].

The introduction of cation impurities with different valences has a strong effect on the electrical and optical properties of vanadium dioxide. It is assumed that the nature of the  $T_c$  shift upon doping of vanadium dioxide is determined by the impurity valence. There is a possibility that the metal-insulator phase transition (MIT) in vanadium dioxide has a Mott character. If the impurity is a donor, then its introduction leads to an increase in the concentration of „free“ electrons and stabilization of the metal phase. As a result, the temperature of  $VO_2$  transition into the insulator phase decreases. Indeed, introduction of substitutional impurities such as  $Mo^{6+}$  or  $W^{6+}$ , which are donors, is accompanied by a noticeable decrease in the temperature of phase transition  $R \rightarrow M_1$  and gradual degradation of this transition [5]. On the contrary, introduction of acceptor impurities, such as  $Al^{3+}$  or  $Cr^{3+}$ , followed by the replace-

ment of  $V^{4+}$  by  $V^{5+}$ , not only increases the phase transition temperature, but changes its very nature. Instead of the insulator phase  $M_1$ , when cooling, the insulator phase  $M_2$  is formed, which differs from the first one in that only half of the vanadium atoms are paired in it, while the other half only shifts from the center of oxygen octahedra during the phase transition [6]. It should be noted that the formation of the  $M_2$ -phase is not directly related to the acceptor properties of trivalent impurities. The  $M_2$  phase also appears in pure  $VO_2$  when uniaxial mechanical stress [7] is applied to a single crystal. This result supports such an approach, in which impurity cations are considered not just as donors or acceptors, but also as centers of internal expansion or compression of the crystal structure. The presence of internal or external elastic stresses strongly influences the process of metal-insulator transition [8–11]. In the proposed article, on the example of indium-doped vanadium dioxide, this approach receives one more confirmation.

It should be noted that a large number of articles have recently been devoted to studying the effect of impurities on MIT in vanadium dioxide [12–19]. The point is that the study of doped samples can help to understand the MIT mechanism in  $VO_2$ .

### 2. Experiment

Thin polycrystalline films of vanadium dioxide  $V_{(1-x)}In_xO_2$  were synthesized by simultaneous laser evaporation of targets from metallic V(99.9%) and metallic In(99.7%) in a controlled oxygen atmosphere at a temperature of 750–900 K. The degree of doping ( $x$ ) was judged from the relative evaporation time of each of the

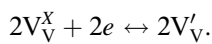
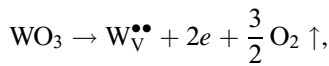
targets.  $\text{Al}_2\text{O}_3$  (1000) were used as substrates. The film thickness was 100 nm.

The phase transition in the samples under study was monitored by the change in reflectivity at the wavelength  $\lambda = 1.54 \mu\text{m}$  and by the change in the electrical conductivity of the films measured by the standard four-probe technique. In the latter case, prior to film synthesis, electrodes made of metallic Pt with a thickness of  $\sim 100$  nm were deposited on a sapphire substrate by laser deposition in vacuum.

### 3. Results and discussion

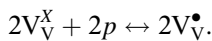
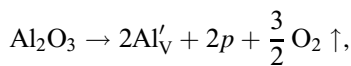
The temperature dependences of the electrical conductivity of thin films of pure and indium-doped vanadium dioxide are shown in Fig. 1. It can be seen that the introduction of indium lowers the phase transition temperature, despite the fact that  $\text{In}^{3+}$  is also an acceptor, like  $\text{Al}^{3+}$  or  $\text{Cr}^{3+}$ .

Let us consider in more detail the elastic stresses resulting from the introduction of classical donors and acceptors into vanadium dioxide. Let's start with hexavalent tungsten. In the Kroeger-Wink symbols, the reaction of the introduction of hexavalent tungsten into the crystal lattice of vanadium dioxide can be written as



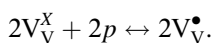
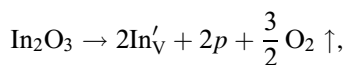
Replacement of the  $\text{V}^{4+}$  ion by the  $\text{W}^{6+}$  ion leads to the formation of two  $\text{V}^{3+}$  ions in the crystal lattice of vanadium dioxide. Let us use the values of effective ionic radii in oxides with a coordination number of 6 [20]. The ionic radius  $\text{W}^{6+}$  is only slightly larger than the ionic radius  $\text{V}^{4+}$  it replaces. These values are 0.060 and 0.058 nm, respectively. At the same time, the two  $\text{V}^{3+}$  ions that appeared upon the introduction of the tungsten cation have a noticeably larger size, namely, 0.064 nm. It is obvious that the total effect is the occurrence of elastic expansion stresses.

Introduction of trivalent Al can be written in Kroeger-Wink symbols

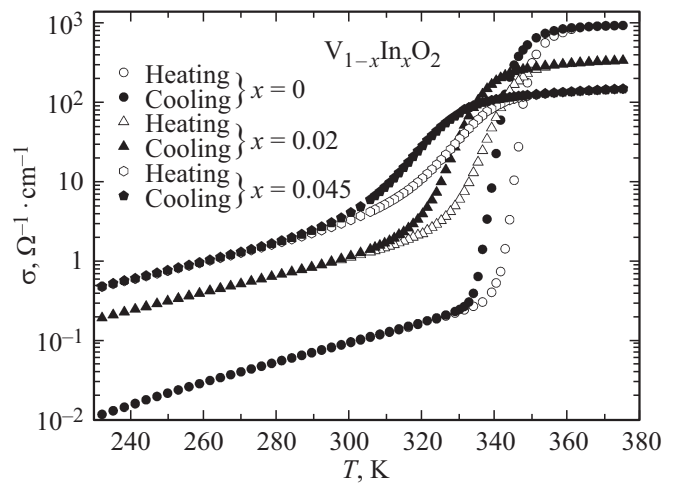


Introduction of each  $\text{Al}^{3+}$  ion in this case is accompanied by the appearance of a  $\text{V}^{5+}$  ion in the lattice instead of the  $\text{V}^{4+}$  ion.

The same equation is valid for the case of incorporation of indium



Let us compare the stresses arising in the crystal structure of vanadium dioxide upon the introduction of aluminum and

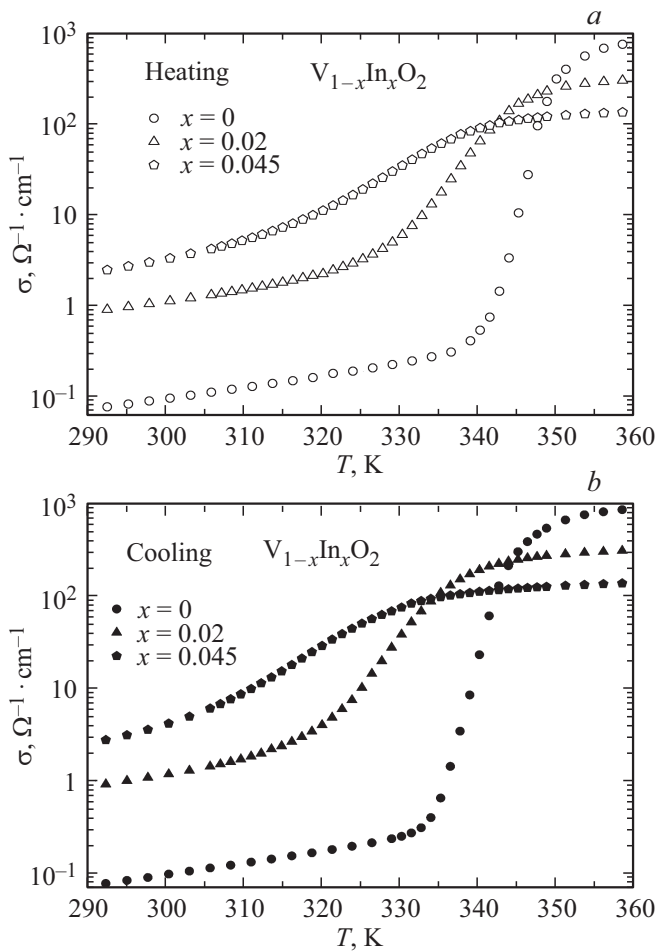


**Figure 1.** Temperature dependences of the electrical conductivity of  $\text{V}_{(1-x)}\text{In}_x\text{O}_2$  films with varying indium concentration.

indium. In both cases, states  $\text{V}^{5+}$  arise. The ionic radii  $\text{V}^{4+}$  and  $\text{V}^{5+}$  are equal to 0.0580 nm and 0.0540 nm [20], respectively, i.e. the mentioned replacement is accompanied by compressive stress. Now let's compare the ionic radii of  $\text{Al}^{3+}$  and  $\text{In}^{3+}$  with the ionic radius  $\text{V}^{4+}$ , which they replace. They are equal to 0.0535 and 0.0800 nm, respectively [20]. It can be seen that the radius of the  $\text{Al}^{3+}$  ion is slightly smaller than the radius of the  $\text{V}^{4+}$  ion, i.e. there is still an additional compression of the crystal structure. On the contrary, the ionic radius of trivalent indium is much larger than the radius of tetravalent vanadium, which leads to the fact that the total effect of indium introduction is significant expansion stresses. This leads to a decrease in  $T_c$ .

Simultaneously with an increase in the degree of doping, the electrical conductivity  $\sigma$  of the oxide insulator phase also increases, while the magnitude of the electrical conductivity jump decreases. In this case, the jump  $\sigma$  decreases not only due to an increase in the electrical conductivity of the insulator phase, but also due to a monotonic decrease in the electrical conductivity of the metallic phase as the dopant concentration increases. The electrical conductivity of the metallic phase of pure  $\text{VO}_2$  is  $\sigma_m \sim 10^3 \Omega^{-1} \cdot \text{cm}^{-1}$ , which is close to the Mott limit for the minimum metallic conductivity [21], but the  $\sigma(T)$  character is not metallic. This is apparently due to Anderson localization at defects and grain boundaries (polycrystalline films). In single crystals  $\sigma_m \sim 10^4 \Omega^{-1} \cdot \text{cm}^{-1}$  and the conductivity has a metallic character [1]. As  $\text{VO}_2$  is doped with indium, the electrical conductivity of the metallic phase gradually decreases to  $\sigma_m \sim 10^2 \Omega^{-1} \cdot \text{cm}^{-1}$ . We have previously observed a similar decrease in the electrical conductivity of the metallic phase in thin films of vanadium dioxide when alloyed with hydrogen [19] and nickel [22], which are not substitutional impurities.

Figure 2, *a, b* shows the  $\sigma(T)$  dependences in the MIT region during heating and cooling of thin films of pure  $\text{VO}_2$  and  $\text{V}_{(1-x)}\text{In}_x\text{O}_2$  ( $x = 0.02, 0.045$ ), respectively. The



**Figure 2.** Temperature dependences of the electrical conductivity of pure and indium-doped VO<sub>2</sub> films in the phase transition region. *a* are obtained by heating, *b* are obtained by cooling.

temperature range of MIT in doped thin films broadens with increasing indium concentration against the background of a decreasing jump in electrical conductivity  $\Delta\sigma$ . Broadening of the temperature region of phases coexistence can be caused by the gradual transformation of the first-order phase transition into a second-order transition due to diffusion of the metal-insulator phase boundary.

The results of measuring the electrical conductivity of pure and indium-doped VO<sub>2</sub> upon cooling to a temperature of  $T = 230$  K are shown in Fig. 1. It can be seen that the dependence of  $\sigma(T)$  in the insulator phase is linear in the coordinates  $\lg(\sigma)$  on  $T$ . Previously, we studied the electrical conductivity of vanadium dioxide and showed that its conductivity is described by small-radius polaron hops, which are affected by thermal vibrations of the lattice [1]. Since the mechanism of charge transfer in the insulator phase should not change when vanadium dioxide is doped, it is appropriate to consider the electrical conductivity  $V_{(1-x)}In_xO_2$  within the framework of the Bryskin model [23]. This model takes into account the effect of thermal displacement of lattice atoms on the probability

of interstitial jumps of small polarons. Displacements of atoms lead to changes in the overlap of the wave functions of states on the neighboring sites. This overlap defines the resonance integral ( $I$ ). In a first approximation  $I$  changes with the distance ( $R$ ) at which the jump occurs, as  $\exp(-\alpha R)$ , where  $\alpha^{-1}$  is the effective localization radius. In turn, the hopping mobility of the charge carrier, which determines the electrical conductivity of vanadium dioxide, is proportional to  $I^2$ . For small values  $\alpha^{-1}$ , on the order of the lattice oscillation amplitude ( $\rho$ ), it can be assumed that  $I^2$  should depend linearly on  $\rho$ . Therefore, if  $I^2$  depends on  $\rho$ , it is permissible to replace  $I^2$  by  $\langle I^2 \rangle$ , where the angle brackets denote phonon averaging in terms of the renormalization of the Debye–Waller factor.

$$\langle I^2 \rangle = I^2 \exp(2\alpha^2 \langle \rho^2 \rangle), \quad (1)$$

where  $\langle \rho^2 \rangle$  is the root-mean-square thermal displacement of atoms at lattice sites. The calculation of the hopping conductivity in the model of small-radius polarons, taking into account the effect of thermal vibrations of the lattice on the resonance integral, leads to the following dependence of the electrical conductivity on temperature

$$\sigma = en \frac{ea^2}{2h} \frac{\pi^{1/2} I^2}{E_a^{1/2} (k_B T)^{3/2}} \exp\{-E_a/k_B T + k_B T/\varepsilon\}, \quad (2)$$

where  $a$  is lattice parameter,  $E_a$  is energy required for electron hopping,  $n$  is concentration of charge carriers,  $e$  is electron charge,  $h$  is Planck constant,  $\varepsilon$  is a quantity having the dimension of energy and taking into account the effect of thermal vibrations of the lattice on the resonant integral. At high temperatures, when  $2k_B T > \hbar\omega_q$  (where  $\hbar = h/2\pi$ ,  $\omega_q$  is optical phonon frequency),  $\varepsilon$  is related to the root-mean-square thermal displacement  $\langle \rho^2 \rangle$  by the relation

$$\varepsilon = k_B T / 2\alpha^2 \langle \rho^2 \rangle. \quad (3)$$

An analysis of expression (2) shows that at low temperatures the second term under the exponent becomes negligibly small compared to the first one, while at high temperatures the second term already dominates. Therefore, in the low-temperature limit, expression (2) can be represented as

$$\ln(\sigma T^{3/2}) = A - E_a/k_B T, \quad (4)$$

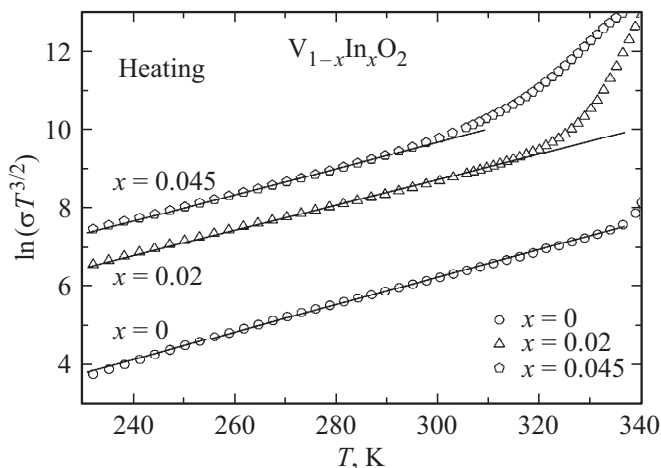
where  $A$  and  $E_a$  do not depend on temperature.

On the contrary, in the high-temperature limit, expression (2) can be represented as

$$\ln(\sigma T^{3/2}) = A + k_B T/\varepsilon, \quad (5)$$

where  $A$  and  $E_a$  do not depend on temperature.

In [1] we showed that  $\sigma(T)$  VO<sub>2</sub> at temperatures above  $T \sim 240$  K can be described by the dependence (5). These dependencies for pure VO<sub>2</sub> and  $V_{(1-x)}In_xO_2$  ( $x = 0.02, 0.045$ ) shown in Fig. 3. Comparison of pure VO<sub>2</sub> and doped  $V_{(1-x)}In_xO_2$  shows that the slope of the



**Figure 3.** Dependence  $\ln(\sigma T^{3/2}) = A + k_B T / \varepsilon$  of  $V_{(1-x)}In_xO_2$  films with different concentrations of indium.

straight line equal to  $\varepsilon^{-1}$ , slightly different from the slope in pure  $VO_2$ . The value  $\varepsilon$  for pure  $VO_2$  is  $\varepsilon = 2.5 \cdot 10^{-3}$  eV, and for doped samples  $V_{(1-x)}In_xO_2$  ( $x = 0.02, 0.045$ ) it is  $\varepsilon = 2.71 \cdot 10^{-3}$  eV. It follows from (1) and (3) that the value  $\varepsilon$  is proportional to the time of small polaron tunneling through the barrier between neighboring nodes. In other words, the greater the mobility of the polaron, the smaller the  $\varepsilon$  value. It follows from our data that when vanadium dioxide is doped with indium,  $\varepsilon$  increases, and this can be interpreted as an increase in the charge carrier localization on a site.

#### 4. Conclusion

It is shown that vanadium dioxide doping with indium leads to a significant change in the temperature dependence of the electrical conductivity of  $V_{(1-x)}In_xO_2$  compared to that of pure  $VO_2$ . It has been suggested that additional diffusion of the MIT region with an increase in the degree of doping of thin films  $VO_2$  may be a consequence of diffusion of the R– $M_1$  phase boundary. The electrical conductivity of the insulator phase  $V_{(1-x)}In_xO_2$  is well described by the small polaron model, which takes into account the effect of lattice atoms thermal vibrations on the resonance integral. The characteristic parameter of the model  $\varepsilon$  is determined for pure and indium-doped  $VO_2$ . It is shown that the energy  $\varepsilon$  increases with doping compared to pure  $VO_2$ . This is apparently due to an increase in the lattice parameters when vanadium dioxide is doped with indium.

#### Conflict of interest

The authors declare that they have no conflict of interest.

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