Complex research of vanadium dioxide in the homogeneity field

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Abstract. The complex research results of vanadium dioxide VO₂±X obtained with X-ray analysis method, a method of vacuum adiabatic calorimeter and Faraday method are discussed. The samples temperature dependences of electrical resistivity, heat capacity, and also magnetic susceptibility are presented and they prove that these characteristics jump abruptly in the phase transition area. Thermophysical, electrical, magnetic properties of vanadium dioxide are established to vary with the oxygen content in the samples. Values of Debye characteristic temperatures θ_D for samples VO₂±X determined at temperature 150 K are presented. Values of entropy change as an amount of electronic and phonon components at phase transition were calculated. The results obtained allow to consider the phase transition of a metal semiconductor as a Mott-Peierls transition, and also to use vanadium dioxide in temperature sensors manufacture.

1. Introduction
Vanadium dioxide (VO₂±X) and solid solutions based on it were tested in about 340 K structural phase transition [1, 2] (without changing the aggregation state) accompanied with a change of electrical (electrical resistivity jump may be up to 10 orders), optical, magnetic and other properties. It is widely used while manufacturing temperature sensors in automatic control systems of various technological processes.

2. Statement of the problem
The substances VO₂±X within the homogeneity field have been synthesized and electrical resistivity, heat capacity and magnetic susceptibility as well as their temperature dependence in about temperatures of the phase transition metal-semiconductor (PTMS) have been studied on these samples (~340 K).

3. Theory
Samples for the study were prepared by dissociation of vanadium pentoxide at temperature 1300 K in vacuum. The obtained samples, and X-ray diffraction analysis shows it, are close in composition to stoichiometric analysis. Compounds VO₂-X were obtained with initial sample dissociation in high vacuum, and VO₂+X samples were obtained with oxidation of the sample in air at 600 K.

The samples obtained were subjected to x-ray analysis on ray diffractometer Shimadzu Maxima X XRD-7000, it showed that samples VO₁.₉₉₀, VO₁.₉₉₅, VO₁.₉₉₈, VO₂₀₀, VO₂₀₁₀, VO₂₀₃₀, selected for the studies are single-phase fine powders of black color. The analysis performed on an electron, scanning microscope JEOLJCM-5700 made possible to clarify the elemental composition of each sample.

The samples electrical resistivity was measured on the compressed tablets using a standard two-contact method with a relative error less than 10%. The heat capacity was studied with a vacuum adiabatic calorimeter method of Strelkov type. The sample temperature was controlled with a platinum resistance thermometer, the error in determining the heat capacity did not exceed 1%. The magnetic
susceptibility was determined with the Faraday method. The error in determining the susceptibility was about 5% and is mainly related to the sample weight determination.

4. The results of the experiment

The heat capacity temperature dependence of vanadium dioxide near the phase transition is presented in Fig.1. The obtained results show that a sharp increase in the heat capacity is observed at 338 K, and it confirms the presence of a phase transition at given temperature. Analogous temperature dependences are also observed for other samples studied.

The electrical resistivity temperature dependence of the sample VO$_{2.00}$ is shown at Fig. 2 obtained in the sample heating and cooling mode. A jump in the electrical resistivity is clearly observed in PTMS, as well as hysteresis in the phase transition.

Similar results were obtained for other samples. PTMS temperatures determined from the data on the heat capacity (temperatures corresponding to the peak $C_p$), and determined from data on research $\rho(T)$ while heating the sample correspond with each other.

Vanadium dioxide is well known to be observed with the temperature hysteresis of PTMS phase transition [3]. For the samples, it can be established from the results of electrical resistivity temperature dependences study.
Hysteresis for the samples under study does not exceed 8 K, it has a minimum value for the sample VO$_{2.00}$ (4.0 K), and it changes little and irregularly with changes in the oxygen composition. It should be noted that the hysteresis appreciably depends on the sample heating temperature: the higher (near $T_{\text{MP}}$) heated sample, the lower the hysteresis. In this article all the samples, when determining the hysteresis of the phase transition, were heated to temperature 370 K. The values of the phase transition temperature determined according to electrical resistivity ($T_{\text{MP}}$) and heat capacity ($T_{\text{MC}}$) as well as temperature hysteresis transition ($\Delta T_{\text{MD}}$) are shown in Table 1.

Estimates of the entropy changes during metal-insulator phase transitions are presented for all the samples studied in the same Table 1 [4]. The entropy change at the phase transition was determined from the experimental values $C_p(T)$:

$$\Delta S = \sum (\Delta C \Delta T/T)$$  \hspace{1cm} \hspace{1cm} (1)

where $\Delta C$ is difference between the set of the heat capacity and the heat capacity value determined with extrapolation of regular branch $C_p$ from the area below the phase transition temperature for a given $T$, step width $\Delta T$ was assumed equal to 1K. Temperature $T$ corresponds to the middle of the value $\Delta T$, the values of the Debye characteristic temperatures $\theta_D$ are given for these samples determined at 150 K.

**Table 1.** Values of the phase transition temperature $T_{\text{MD,p}}$, $T_{\text{MD,c}}$, hysteresis $\Delta T_{\text{MD}}$, entropy phase transition $\Delta S$ and debue temperature characteristic $\theta_D$.

| Compounds  | $T_{\text{MD,p}}$, K | $T_{\text{MD,c}}$, K | $\Delta T_{\text{MD}}$, K | $\Delta S$, J/K | $\theta_D$, K |
|-----------|----------------------|----------------------|---------------------------|----------------|-------------|
| VO$_{1.990}$ | 338                  | 338.0                | 4                         | 25.2           | 1040        |
| VO$_{1.995}$ | 339                  | 338.4                | 8                         | 25.2           | 950         |
| VO$_{1.998}$ | 339                  | 339.6                | 6                         | 25.8           | 890         |
| VO$_{2.00}$ | 340                  | 340.0                | 4                         | 16.5           | 700         |
| VO$_{2.010}$ | 342                  | 340.5                | 6                         | 16.0           | 1090        |
| VO$_{2.030}$ | 343                  | 341.0                | 4                         | 20.2           | 1190        |

From the magnetic susceptibility measurement completed the density of electronic states near the Fermi level $g(E_F)$ [1] can be estimated, if to assume that the discontinuity of the magnetic susceptibility ($\Delta \chi$) at PTMS relates primarily to the contribution to susceptibility appeared in the 3d-zone of vanadium conduction electrons $g(E_F)$:

$$N(E_F) = \Delta \chi / 2 \mu_B^2$$  \hspace{1cm} \hspace{1cm} (2)

Where $\mu_B$ is Bohr magneton.

Electronic heat capacity coefficient ($\gamma$) also allows to evaluate $g(E_F)$:

$$\gamma = (2/3)(\pi \kappa)^2 N(E_F)$$  \hspace{1cm} \hspace{1cm} (3)

Value $\gamma$ can be estimated from the change in the entropy electronic component in the phase transition ($\Delta S_{\text{el}}$):

$$\Delta S_{\text{el}} = \gamma T_{\text{MD}}$$  \hspace{1cm} \hspace{1cm} (4)

where $\kappa$ is the Boltzmann constant in equation (3).

The joint solution of equations (2)–(4) allowed determining the entropy electronic component of the phase transition, $\Delta S_{\text{el}}$.

The experimentally determined values $\Delta \chi$ and the calculated values $\gamma$ are presented in Table 2. The values $\Delta S_{\text{el}}$ and lattice contribution $\Delta S_{\text{lat}}$ to the entropy are changed when PTMS.
Table 2. Values of experimentally determined $\Delta \chi$, calculated $g$ and values $\Delta S_{el}$ and $\Delta S_{lat}$ at PTMS.

| Compounds  | $\Delta \chi \times 10^2$, g/sm$^3$ | $\gamma \times 10^4$, J/(mol*K$^2$) | $\Delta S_{el}$, J/K | $\Delta S_{lat}$, J/K |
|------------|------------------------------------|-------------------------------------|---------------------|---------------------|
| VO$_{1.990}$ | 5.3                                | 51                                  | 3.4                 | 21.8                |
| VO$_{1.995}$ | 9.2                                | 88                                  | 6.0                 | 19.5                |
| VO$_{1.998}$ | 9.2                                | 88                                  | 6.0                 | 19.5                |
| VO$_{2.000}$ | 7.0                                | 67                                  | 4.6                 | 11.9                |
| VO$_{2.010}$ | 5.9                                | 56                                  | 3.8                 | 12.2                |
| VO$_{2.030}$ | 6.1                                | 58                                  | 4.0                 | 16.2                |

The lattice contribution was estimated under the assumption of entropy additivity in the phase transition.

$$\Delta S = \Delta S_{el} + \Delta S_{lat}. \quad (5)$$

The dependences $\Delta S_{el}$ and $\Delta S_{lat}$ on phase transition temperatures $T_{PTMS}$ (phase transition temperature have been determined from the data on the heat capacity) and they are presented in Fig. 4 and 5.

![Figure 4. The entropy electronic component PTMS](image)

![Figure 5. The entropy lattice component PTMS](image)

5. The discussion of results

Analyzing the results obtained, first of all it should be noted that the samples obtained are powdery. Due to our method of synthesis, each particle is inhomogeneous in volume. It leads to a non-simultaneous temperature transition in different micro-regions of each vanadium dioxide separate particle. Depending on the oxygen content in the sample, the peripheral layer of a single powder is either depleted (in the reduction reaction case) or enriched (in the oxidation reaction case) with oxygen. When moving from the periphery to the center of the powder, the oxygen concentration most likely varies nonlinearly, but in any case it changes. It leads to the fact that when studying the heat capacity and magnetic susceptibility, such heterogeneity of the composition over each sample individual powder volume changes the temperature width $T_{PTMS}$: it is the smallest for the initial sample and increases for the remaining samples, regardless of the oxygen composition. The electric current, with the method of study, flows along the surfaces of the powders and in this case it is not an integral characteristic. In determining the characteristic temperatures as in [3], $C_p$ is assumed to be approximately equal to $C_v$.

From the results obtained it is evident that $\Delta S_{el}$ and $\Delta S_{lat}$ well correlated with $T_{PTMS}$. In our opinion, it suggests that both the Mott electronic mechanism and the Peierls mechanism determine $PTMS$ in vanadium dioxide.
Entropy change of phase transitions $\Delta S$ at PTMS for samples $\text{VO}_{2x}$ does not differ and significantly exceeds $\Delta S$ (more than 20%) for samples $\text{VO}_{2-x}$.

As the results show, the Debye temperatures within the homogeneity field extremely changed having a minimum value for $\text{VO}_{2.00}$. One can assume that in the samples of oxygen as deficient as excess the crystal lattice undergoes distortion. These distortions are due to crystal lattice defects such as Schottky defects that can cause a change in the boundary Debye frequencies, and, consequently, the Debye temperatures.

6. Conclusions

From the obtained experimental results it can be concluded that the reduced samples are more inhomogeneous in their composition (they have more temperature range of the phase transition) than the oxidized ones. So, the dissociation $\text{VO}_{2}$ proceeds at a much slower rate than the oxidation in an oxygen stream.

Measurement results processing allowed to estimate the electronic $\Delta S_{\text{El}}$ and phonon $\Delta S_{\text{lat}}$ entropy components PTMS. Correlations $\Delta S_{\text{El}}$ and $\Delta S_{\text{lat}}$ with $T_{\text{MD}}$ allow to consider PTMS and, accordingly, the mechanism of the transition as Mott-Peierls transition.

References

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