Low-temperature heat capacity VO₂±δ and solid solutions V₁-XFeXO₂

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Abstract. The article reports the study results of the heat capacity of vanadium dioxide compounds (VO₂) (within the homogeneity range) and stoichiometric solid solutions V₁-XFeXO₂ at temperature range from 5 K to 100 K. Separation of various constituents of heat capacity with its additivity assumption has been conducted: crystal lattice heat capacity and defects heat capacity. It is shown that a considerable contribution to the heat capacity is produced by the crystal lattice defects (till ~ 25 K) at low temperatures, and at higher temperatures the heat capacity is determined mainly with the crystal lattice. Using the Debye function table for the heat capacity for all compounds, the characteristic Debye temperatures Θ_D were determined.

1. Introduction
Some compounds 3d-, 4d- and 5f- elements had phase transition metal – dielectric (PTMD) caused with temperature change. These compounds - vanadium dioxide (VO₂) - properties both as in practical as in purely scientific aspects are widely reported [1, 2]. Phase transition temperature of the compound Т_M_D considering hysteresis effects is (340±5) K.

2. Problem statement
However, a number of works noted that naturally, vanadium dioxide is metastable and subject to spontaneous oxidation under the influence of atmospheric oxygen [3]. Certain phase stabilization is achieved with doping the vanadium dioxide (VO₂) by iron [3, 4]. The study of low-temperature heat capacity (when temperature is below 20 K) [5], as well as X-ray diffraction analysis with pycnometric density measurement showed that there is a considerable number of defects both in pure vanadium dioxide and in solid solutions V₁-XFeXO₂ [5]. Obviously, these defects influence various properties including thermophysical properties of these compounds.

3. Theory
The article reported the results of studies of the heat capacity at constant pressure C_p, a number of compounds VO₂±δ and solid solutions V₁-XFeXO₂ in the temperature range from 5 K to 100 K. Heat capacity value at constant volume C_V is noted to be used while discussing theoretical positions. It was shown in [6], that at low temperatures the difference between C_p and C_V is not large and at 100 K is no more than 3%. The heat capacity was measured by the method of a vacuum adiabatic calorimeter of the Strelkov type on an installation made in the Khabarovsk VNIIFTRI branch. Measurement of the reference materials heat capacity (in this capacity, benzoic acid and electrolytic copper of Kyshtym copper electrolytic plant were used) showed that the error in determining the heat capacity in the entire investigated temperature range does not exceed 1 %. Liquid helium and liquid hydrogen were used as refrigerants (with evacuation of vapors if necessary). The temperature was registered with a
The samples element composition was refined on an electronic scanning microscope that attested by VNIIFTRI. The initial sample VO₂ for the studies was prepared from the powdered material of vanadium pentoxide grade HSC by dissociation in vacuum at pressure 7 Pa, at temperature 1300 K. Samples VO₂+: were obtained from VO₂ with further dissociation in vacuum 0.15 Pa at different temperatures. Samples VO₂, were obtained by oxidation at atmospheric pressure at temperature 620 K changing the oxidation time.

To prepare samples containing iron V₁₋ₓFeₓO₂, there were mixed necessary amounts of oxides V₂O₃ and V₂O₅ with Fe₂O₃:

\[(1-2x)V₂O₃ + V₂O₅ + 2xFe₂O₃ \xrightarrow{900°C} 4FeₓV₁₋ₓO₂\]

The samples were tested using a diffractometer Shimadzu Maxima X XRD-7000, studies have shown that all samples are single-phase and belong to the structure VO₂.

The samples element composition was refined on an electronic scanning microscope JEOL JCM – 5700 at voltage 15.0 kV.

4. Experimental results

The results of the studies are shown in Fig. 1-3 and in Tables 1–2.

### Table 1. Values of heat capacities and characteristic Debye temperatures for VO₂

| Temperature, K | VO₁,995 | VO₁,995 | VO₁,998 | VO₂ | VO₂,01 |
|---------------|---------|---------|---------|-----|--------|
| 5             | 0.0027  | 0.0032  | 0.0033  | 0.0035 | 0.0060 |
| 10            | 1.16    | 0.0127  | 0.0141  | 0.0154 | 0.0176 |
| 20            | 0.0334  | 0.0413  | 0.0468  | 0.0577 | 0.0453 |
| 25            | 0.0562  | 0.0682  | 0.0782  | 0.102  | 0.0694 |
| 50            | 0.16    | 0.18    | 0.17    | 0.24  | 0.16   |
| 60            | 0.20    | 0.26    | 0.29    | 0.40  | 0.23   |
| 70            | 0.31    | 0.40    | 0.46    | 0.63  | 0.36   |
| 80            | 0.48    | 0.59    | 0.68    | 0.91  | 0.53   |
| 90            | 0.65    | 0.84    | 0.93    | 1.24  | 0.75   |
| 100           | 0.87    | 1.08    | 1.22    | 1.59  | 0.98   |
| Θₒ, K         | 890     | 840     | 780     | 700   | 850    |

### Table 2. Values of heat capacities and characteristic Debye temperatures for V₁₋ₓFeₓO₂

| Temperature, K | V₀,99Fe₀,01O₂ | V₀,97Fe₀,03O₂ | V₀,95Fe₀,05O₂ | V₀,91Fe₀,07O₂ |
|---------------|--------------|--------------|--------------|--------------|
| 5             | 0.0035       | 0.0027       | 0.0025       | 0.0025       |
| 10            | 0.0149       | 0.0130       | 0.0116       | 0.0101       |
| 20            | 0.0547       | 0.0492       | 0.0419       | 0.0396       |
| 25            | 0.0943       | 0.0840       | 0.0707       | 0.0661       |
| 50            | 0.27         | 0.19         | 0.21         | 0.16         |
| 60            | 0.37         | 0.33         | 0.27         | 0.26         |
| 70            | 0.58         | 0.52         | 0.43         | 0.40         |
| 80            | 0.84         | 0.76         | 0.63         | 0.59         |
| 90            | 1.15         | 1.04         | 0.87         | 0.84         |
| 100           | 1.49         | 1.35         | 1.15         | 1.08         |
| Θₒ, K         | 720          | 750          | 800          | 820          |
Having information on the heat capacity at temperatures above 50 K, characteristic Debye temperatures $\Theta_D$ for all samples in the temperature range from 50 K to 100 K are possible to be determined using Debye function tables for heat capacity. Their values are indicated in Tables 1 and 2. At temperatures $T \sim \Theta_D/12$, within the framework of the Debye model, the lattice heat capacity $C_{LET}$ is related with Debye temperature [7]:

$$C_{LET} = \beta T^3$$

(1)

$$\beta = \frac{12\pi^4 V N k n}{(5\Theta_D^3)}$$

(2)

where $V$ is the volume of the unit lattice,

$N$ is the number of cells in the volume under consideration,

$k$ is Boltzmann's constant,

$n$ is the number of atoms in the cell.

Extrapolating certain values of the Debye temperatures to the low-temperature area, the heat capacity of the defects can be determined:

$$C_{DEF} = C_P - C_{LET}$$

(3)

Dependences of the heat capacity $C_P$ on temperatures for three samples are presented in Fig.1: VO$_2$, V$_{0.97}$Fe$_{0.03}$O$_2$ and VO$_{1.990}$. A gradual increase in the heat capacity is observed for all samples with increasing temperature. Heat capacity dependences on temperature, both the total and its components are presented in Fig. 2 and Fig. 3: the heat capacity of the crystal lattice and the heat capacity of the defects for two samples (Fig. 1 is for the sample VO$_2$; Fig. 2 is for the sample V$_{0.97}$Fe$_{0.03}$O$_2$). As presented, the heat capacity of crystal lattice defects first increases with increasing temperature (up to $T_K \sim 14$ K), and then with further increasing temperature $C_{DEF}$ does not depend on the temperature. It suggests that the defects in the crystal are as quantum particles, and $T_K$ is degeneracy removal temperature.

![Figure 1. Dependency of heat capacity $C_P$ on temperature.](image-url)
5. Discussion
As the obtained results prove, at low temperatures the heat capacity of pure vanadium dioxide “VO₂” is minimal for VO_{1.990} (0.0027 J/mol K at 5 K) and it is maximum for VO_{2.03} (0.0060 J/(mol K)). The low-temperature heat capacity of other samples “VO₂” varies within these limits. With temperatures close to 100 K (high temperature part of the heat capacity) for the samples “VO₂” minimum values of heat capacity are for VO_{1.990} (0.87 J/(mol K), and maximum are for VO_{2} (1.59 J/(mol K)).
At low temperatures, the heat capacity of solid solutions based on vanadium dioxide containing iron $V_{1-x}Fe_xO_2$ is minimal for the samples containing iron 5% ($V_{0.95}Fe_{0.05}O_2$) and 7% ($V_{0.93}Fe_{0.07}O_2$) (0.0025 J/mol K at 5K). The heat capacity of a sample containing iron 3% ($V_{0.97}Fe_{0.03}O_2$) differs a little. The heat capacity $V_{0.99}Fe_{0.01}O_2$ (0.0035 J/mol K) is much larger if to compare. At temperatures close to 100 K, $V_{0.99}Fe_{0.01}O_2$ has the highest values of heat capacity, and the least values are for the heat capacity $V_{0.93}Fe_{0.07}O_2$. In whole, alloying with iron leads to leveling heat capacity samples.

6. Conclusion
Thus, the article reports the results of a study of the heat capacity VO$_{2+\delta}$ and solid solutions $V_{1-x}Fe_xO_2$. The heat capacity is established to depend strongly on the composition of the sample. Analysis of the measurement results made possible to isolate the heat capacity of the defects and its dependence on temperature. According to the nature of $C_{\text{DEF}}(T)$ the quantum nature of defects is concluded.

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