X-ray diffraction and magnetic properties of vanadium dioxide VO$_{2\pm X}$ solid solutions V$_{1-X}$Fe$_X$O$_2$

Y V Kuznetsova$^1$, Vad I Surikov$^2$, N A Semenyuk$^2$, Val I Surikov$^2$, S V Yanchij$^2$ and S V Danilov$^2$

$^1$Surgut State University, Surgut, Russia
$^2$Omsk State Technical University, 11, Mira Ave., 644050, Russia

Abstract. The article considers the results of vanadium dioxide VO$_{2\pm X}$ study (within the homogeneity range) and solid solutions V$_{1-X}$Fe$_X$O$_2$, obtained by X-ray diffraction and the Faraday method. The temperature dependences of the magnetic susceptibility samples are presented, and it follows that dependence $\chi$ ($T$) character in the temperature range from 100 K up to 250 K is close to Curie law for paramagnetic in the area of the phase transition at temperature $T_{mp}$ ~ 340 K, and there is an abrupt change in $\chi$. It is considered that the magnetic properties of vanadium dioxide vary both with the change in the oxygen content in the samples and with the doping of vanadium dioxide with iron. It was established that vanadium dioxide VO$_{2\pm X}$ and solid solutions V$_{1-X}$Fe$_X$O$_2$ are paramagnetic both in the semiconductor and metallic states.

1. Introduction

Vanadium dioxide is characterized by a metal-semiconductor phase transition (MSPT), without changing the aggregate state, at temperature $T_{ms}$ ~ 340 K. The sample has a discontinuous change in physical properties (heat capacity, electrical resistivity, magnetic susceptibility) [1]. Due to this property vanadium dioxide is used in automation systems, including geophysical instruments to log oil wells exploration and production. However, it has recently been established that thermal destruction leads to mechanical destruction of VO$_2$ samples and change in the sample composition (towards oxygen deficiency) [2]. The electrical resistivities, heat capacity, X-ray diffraction features of VO$_{2\pm X}$ compounds are studied in detail [3]; they have MSPT at practically the same temperature as for the stoichiometric composition. Magnetic properties were studied for a stoichiometric composition compound [4]. As the authors noted, the magnetic susceptibility, $\chi$, VO$_2$ at low temperatures is well described by the Curie law. This circumstance, as well as the magnetic susceptibility, indicate that vanadium dioxide of stoichiometric composition at low temperatures is a paramagnetic substance. Starting from temperature ~ 250 K the sample $\chi$ increases several times to temperature ~ 360 K; the sample is established to remain paramagnetic in this case.

It should be noted that vanadium dioxide is metastable in air so it oxidizes with time to vanadium pentoxide [5]. To stabilize the phase, the dioxide is alloyed with iron mostly.

All of the foregoing proves that the study of the magnetic properties of VO$_{2\pm X}$ and iron-doped dioxide is quite an urgent task.

2. Theory

To obtain the initial sample (VO$_2$) vanadium pentoxide was dissociated at temperature 1300 K in vacuum. VO$_{2-X}$ compounds were prepared by subsequent dissociation of the starting sample in a deeper vacuum with a variation in the process temperature. VO$_{2-X}$ compounds were obtained by oxidizing the starting material in air at temperature 620 K, changing the oxidation time.

Samples of V$_{1-X}$Fe$_X$O$_2$ system were prepared by sintering vanadium pentoxide, vanadium trioxide (prepared by reduction of pentoxide in a stream of hydrogen) and, Fe$_2$O$_3$. The synthesis was carried out according to the equation:
All components of Fe₂O₃, V₂O₃ and V₂O₅ were weighed, thoroughly mixed, and pressed into tablets 5 mm in height and 10 mm in diameter under pressure 20*10⁷ Pa. Samples were placed in tungsten cups, the latter were placed into quartz evacuated tubes. The tubes were placed into an oven. The thermal treatment was carried out in three stages: the initial heating at temperature 873 K was carried out for 24 hours, and then the samples were held for 24 hours at temperature 1023 K and for 72 часов at temperature 1373 K.

The oxygen content in all synthesized samples was determined by the thermo gravimetric method, by oxidizing the preparations in a platinum dish to vanadium pentoxide at temperature Т=950 K in oxygen stream at atmospheric pressure. It should be noted that with changing in stoichiometric composition, there impurities appear in the preparations as phases VₙO₂ₙ₋₁ (3<n<9) in case “-x”, as V₂O₅ “+x”. This circumstance, in our opinion, should lead to some error in the study of physical properties.

The attestation of the samples synthesized in the area of homogeneity was also carried out by X-ray diffraction Shimadzu Maxima_X XRD-7000, aligned according to the Bregg-Brentano scheme with a curved quartz monochromator. Radiographs were obtained at temperature 293 K with radiation of copper CuKα (λ = 1.54056 Å) in a range of angles (2θ) 0-80°.

The magnetic susceptibility was measured in the temperature range 80 ÷ 400 K by the Faraday method, pure platinum was used as the standard. The measurement error does not exceed 6%. The error in the relative measurements was an order smaller.

3. Experimental results
The bar-diagrams shown in Figure 1 were developed according to the obtained X-ray patterns of the investigated samples. The tested samples are single-phase and belong to the structure of the vanadium dioxide, since they contain only VO₂ lines.

The results of magnetic susceptibility are presented in Table 1.

Table 1. Magnetic susceptibility of compounds

| Sample        | χ₀, 10⁻⁶ sm³/g at T=100K | χ₀, 10⁻⁶ sm³/g at T=250K | χₘᵢₜ, 10⁻⁶ sm³/g | Tₘᵢₜ, K | Δχ, 10⁻⁶ sm³/g | ΔТχ, K |
|---------------|--------------------------|--------------------------|-------------------|----------|----------------|--------|
| VO₂           | 6.5                      | 2.6                      | 1.1               | 320      | 7.0            | 20     |
| VO₁.₉₉₈       | 8.0                      | 3.2                      | 1.1               | 305      | 9.2            | 35     |
| VO₁.₉₉₅       | 8.6                      | 3.4                      | 1.2               | 305      | 9.2            | 35     |
| VO₂.₀₁       | 5.8                      | 2.3                      | 1.5               | 310      | 5.9            | 50     |
| V₀.₉₀Fe₀.₀₁O₂ | 6.0                      | 2.4                      | 2.0               | 315      | 6.3            | 30     |
| V₀.₉₇Fe₀.₀₃O₂ | 7.5                      | 3.0                      | 2.5               | 310      | 5.7            | 40     |

Where χₘᵢₜ is the minimum magnetic susceptibility for the compound at temperature Тₘᵢₜ.

The magnetic susceptibility of the samples VO₂, VO₂.₀₁, VO₁.₉₉₈ and VO₁.₉₉₅ on temperature in the range from 100 K up to 250 K is presented in Figure 2.

According to the obtained results, χ(T) varies close to the Curie-Weiss law in this temperature range:
\[ \chi(T) = \frac{C}{(T - \Theta)}, \] (2)

And it is for VO\(_2\) \(\Theta = 0\), for VO\(_{2.01}\) \(\Theta > 0\), but for VO\(_{1.998}\) and VO\(_{1.995}\) \(\Theta < 0\).

This, as well as the magnetic susceptibility for the samples studied and the nature of the field dependences make possible to state that these are paramagnetic samples. The results obtained for the sample of the stoichiometric composition match with the results of [4].

VO\(_{2.00}\) compound synthesized by us was used as a starting point for the synthesis of other VO\(_{2+\Delta}\) samples. The synthesis conditions of this sample facilitated the production of a homogeneous preparation. As a consequence, there is a rather sharp, temperature-diffuse jump of susceptibility, \(\Delta\chi\) (Figure 3). The temperature jump is \(\sim 20\) K. The minimum value of the magnetic susceptibility for this sample is \(\sim 1\times10^{-6}\) sm\(^3\)/g at temperature 320 K. If the temperature is 340 K \(\chi = 8\times10^{-6}\) sm\(^3\)/g, i.e. close to MSPT, the change in the magnetic susceptibility is \(7\times10^{-6}\) sm\(^3\)/g.

![Figure 1. The bar diagrams of vanadium dioxide VO\(_{2+\Delta}\) and solid solutions V\(_{1-X}\)Fe\(_X\)O\(_2\)](image-url)
Figure 2. Dependence of magnetic susceptibility on temperature VO_{2±X}

Figure 3. Dependence of magnetic susceptibility on temperature in the area of phase transition
4. Discussion
As the oxygen content in the sample decreases (compound VO1.998) the nature of the dependence does not change mainly. However, the temperature jump $\Delta \chi$ increases noticeably with MSPT. For this sample, the minimum value of the magnetic susceptibility, as well as for stoichiometric vanadium dioxide, is also $\sim 1 \times 10^{-6}$ sm$^3$/g at temperature 305 K. If the temperature is 340 K the magnetic susceptibility is $\sim 10.2 \times 10^{-6}$ sm$^3$/g. Thus, the magnitude of the magnetic susceptibility jump is $9.2 \times 10^{-6}$ sm$^3$/g, and the temperature variation $\chi$ close to MSPT for VO1.998 sample is at least 35 K. The values of the temperature jump increase in the magnetic susceptibility close to each other during the phase transition are observed for the sample VO1.995. It is $\sim 35$ K (from 305 K up to 340 K). The magnetic susceptibility changes from $\sim 1 \times 10^{-6}$ sm$^3$/g at temperature 305 K up to the magnetic susceptibility $\sim 10.2 \times 10^{-6}$ sm$^3$/g at temperature 340 K. Thus, the jump in the magnetic susceptibility is $9.2 \times 10^{-6}$ sm$^3$/g, the same as it is for VO1.998.
For the sample with excess oxygen content (VO2.02) the jump in the magnetic susceptibility is 50 K, and the value of the jump $\Delta \chi$ is $5.9 \times 10^{-6}$ sm$^3$/g.
In our opinion, an increase in the temperature increase in the temperature value of the phase transition, which records the temperature dependence of the magnetic susceptibility, due to the shift of minimum $\chi$ to the lower temperature area in samples with lower oxygen content than for the stoichiometric compound, is associated with the synthesis of the preparations. As indicated above, VO2-X compounds were prepared by dissociating the starting sample in a deeper vacuum. Despite our efforts to homogenize the samples by repeatedly rubbing them in an agate mortar during the synthesis, the upper layers of the sample grains are depleted in oxygen compared to the deep layers. The difference in MSPT temperature for these layers fixes the shift of the minimum of the magnetic susceptibility to the area of lower temperatures in comparison with stoichiometric vanadium dioxide. This assumption is confirmed by the fact of increasing the temperature jump $\chi$ for samples VO2-X.
For samples containing iron, the form $\chi(T)$ does not change. After MSPT from sample to sample, the magnetic susceptibility dependence on temperature is increasingly noticeable. The jump value $\Delta \chi$ in the phase transition with increasing iron content in the sample decreases from $6.3 \times 10^{-6}$ sm$^3$/g for V$_{0.99}$Fe$_{0.01}$O$_2$ up to $5 \times 10^{-6}$ sm$^3$/g for V$_{0.97}$Fe$_{0.03}$O$_2$. The absolute value of the magnetic susceptibility (at appropriate temperatures) increases noticeably with increasing iron content. In this case, the temperature $\Delta T\chi$ of jump $\Delta \chi$ is close to that for VO2-X samples ($\Delta T\chi$ was determined as the difference between the temperatures of the start and the end of the jump in the magnetic susceptibility). The latter circumstance may possibly serve as an indication of an increase in the inhomogeneity of the sample (from the core of the grain to the periphery) with the growth of iron in the sample.

5. Conclusion
In the course of experimental studies, powdered vanadium dioxide samples were synthesized within the homogeneity range and solid solutions V$_{1-X}$Fe$_X$O$_2$. The temperature dependences of the magnetic susceptibility are investigated. The investigated samples are paramagnetic, both in the semiconductor and metal states. In the phase transition area, the magnetic susceptibility increases abruptly with increasing temperature, and it is associated with an additional contribution to the total susceptibility due to the 3-d band of vanadium conduction electrons (free electrons).
The absence of a temperature dependence of the magnetic susceptibility at temperature above the phase transition temperature can be due to both a low degeneracy temperature and a narrow d-band and high density of electronic states near the Fermi level characteristic for vanadium compounds [6].
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