Magnetic phase transition in yttrium orthovanadite

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It is established that a magnetic phase transition of the type $G_xF_x \rightarrow C_yF_x$ exists in YVO_3 near 80 °K, on the basis of magnetic, neutron-diffraction, and thermophysical studies. It is shown that deviation from stoichiometry in the YVO_3 leads to an increase of T_N and of the absolute value of the spontaneous ferromagnetic moment, but does not influence the temperature of the considered phase transition.

Yttrium orthovanadite (YVO_3) has the crystal structure of orthorhombically distorted perovskite[1,2] and possesses a number of interesting magnetic properties. According to the data of[1], YVO_3 at T = 1.3°K is a weak ferromagnet with $n_B = 0.5\ \mu_B$. However, according to[2] only the presence of antiferromagnetism below 110°K was established in this compound, and it is indicated that there is no spontaneous ferromagnetic moment. To be sure, the possibility of a certain deviation from stoichiometry in the composition of the YVO_3 single crystals used for the measurements is not excluded in[2]. Attention is also called to a remark made by Goodenough in a discussion of a communication[3] concerning an anomaly on the differential thermal analysis curve near T = 73°K, which points to the possible existence of a phase transition.

In connection with the foregoing, and also with an aim at determining more accurately the presence and the causes of the anomalous behavior of the properties of the orthovanadite of yttrium, we have undertaken a comprehensive investigation of this compound using magnetic, neutron-diffraction, and thermophysical methods.

The YVO_3 was produced, in accordance with the procedure of[4], by reducing yttrium orthovanadate YVO_4 in a stream of purified hydrogen at 1000°C. The YVO_4 was obtained by the usual ceramic technology from the oxides V_2O_5 of grade "os.ch." (specially purified) and Y_2O_3 of classification "00000." X-ray diffraction investigations (Cr, K_α radiation, VRS-3 camera) have shown that the end product is single-phase and has the structure of orthorhombically distorted perovskite with parameters a = 5.278 ± 0.003 Å, b = 5.605 ± 0.003 Å, c = 7.574 ± 0.003 Å (space group Pbnm), which agrees with[2]. A chemical analysis has shown that the compound has the stoichiometric composition of YVO_3.

The magnetic measurements were performed with a Dominicali-type magnetic balance in the temperature interval from 60 to 300°K. The sensitivity of the apparatus was no worse then 10^{-8} emu/g. Use of a VRT-2 regulator together with a copper-constantan thermocouple made it possible to maintain the sample temperature accurate to ±0.5°. These investigations have established that yttrium orthovanadite obtained in accordance with the technology described above is antiferromagnetic at temperatures lower than 110°K and has a spontaneous ferromagnetic moment with a complicated temperature dependence (Fig. 1). Our results agree with the conclusions of[1] and contradict to some extent the communication[2]. It was shown earlier[5] that the spontaneous magnetization of the vanadites $NdVO_3$ and $EuVO_3$, obtained by the same technology, increases following additional annealing in vacuum at 1300–1400°C. For this reason, the YVO_3 sample was further annealed in vacuum at 1300° for 24 hours, followed by chemical and x-ray analyses. It was established that the additional annealing caused a certain transition to the chemical composition $YVO_{3.012\pm0.003}$, without a significant change in the crystal-lattice parameters. At the same time, newly performed magnetic measurements yielded somewhat different information on the properties of the compound with this composition. In particular, it turned out that the spontaneous magnetic moment (absolute value) and the Neel temperature of the annealed sample increased (Fig. 1). However, the behavior of the polytherm of the spontaneous magnetic moment n_B, with a pronounced minimum near 80°K, remains the same. The magnetic characteristics in the paramganetic region likewise remain practically constant. Thus, the anomaly of $\sigma(T)$ near 80°K that was observed in the stoichiometric YVO_3 sample also occurs in the second nonstoichiometric sample.

Neutron-diffraction investigations were performed by us to determine the causes of this behavior of n_B in YVO_3. They were performed in the temperature region from 4.2 to 300°K at a neutron wavelength λ = 1.07 Å using a lead monochromator. The contribution from λ/2 did not exceed 0.5%. In the interval from 60 to 300°K, the neutron-diffraction patterns were obtained by placing an ampule with the sample in a nitrogen

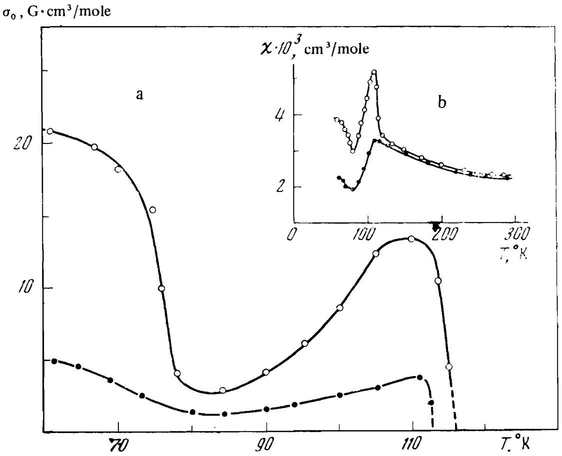

FIG. 1. a) Temperature dependence of the spontaneous ferromagnetic moment of YVO_3; b) polytherms of the magnetic susceptibility for a sample annealed at T = 1300°C (○) and for a non-annealed sample (●).

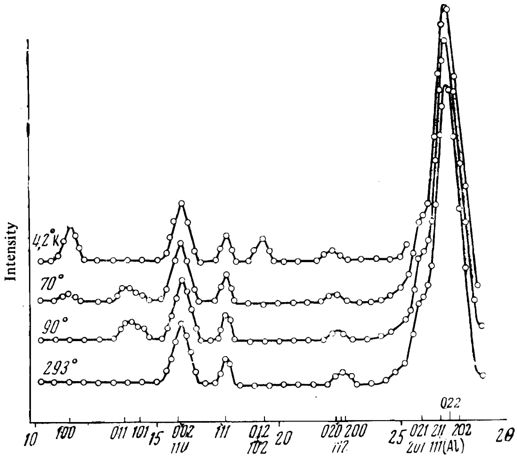

FIG. 2. Neutron diffraction patterns of YVO$_3$.

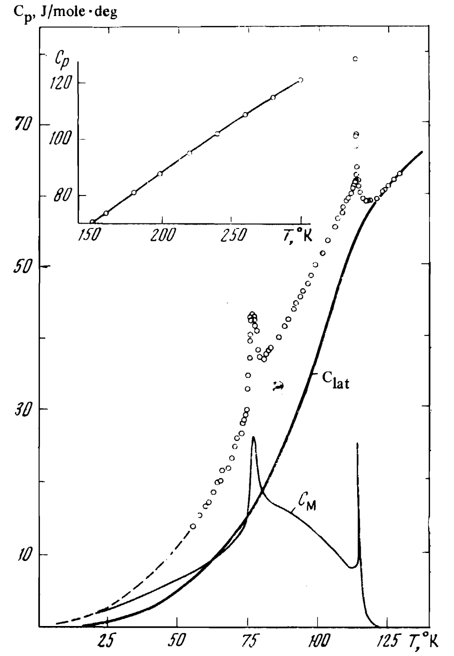

FIG. 3. Temperature dependence of heat capacity of YVO$_3$.

cryostat. The gradient along the sample was ~3°. All the neutron diffraction patterns were taken point by point in steps of 0.2°. The results of these investigations are shown in Fig. 2. It follows from them that at 90°K the neutron-diffraction pattern contains the reflections (011) and (101), which are typical of G-type magnetic order $(h + k = 2n + 1, l = 2n + 1)$. The ratio of these two lines indicates that we are dealing here with G_XF_Z-type magnetic order. With this type of order, an antiferromagnetic interaction is observed between the vanadium ions in the planes, and an antiferromagnetic interaction between neighboring planes along the axis. At 70°K, an additional reflection (100) appears on the neutron diffraction pattern, and the integrated intensity of the reflections (011) and (101) begins to decrease. The only reflections present at 4.2°K are (100), (012), and (102), corresponding to C_YF_X-type magnetic order $(h + k = 2n + 1, l = 2n)$. In C-type order, the trivalent-vanadium ions interact antiferromagnetically in the planes and ferromagnetically between neighboring planes. Thus, the observed anomalous behavior of the $\sigma(T)$ dependence in the compound YVO$_3$ can be due to a magnetic phase transition wherein the magnetic subsystem undergoes a transformation from type G_XF_Z to type C_YF_X.

A thermodynamic analysis of the observed anomalies was carried out by calorimetry. The temperature dependence of the specific heat of the annealed sample with composition YVO$_{3.012}$ was investigated in the region $0.48 \leq T/T_N \leq 2.6$ by the method employing an adiabatic calorimeter on the universal thermophysical apparatus designed by the Chemical Branch of the All-Union Scientific Research Institute of Physicotechnical and Radiotechnical Measurements. A TSPN-2A platinum resistance thermometer was used to measure the calorimeter temperature. The temperature regimes of the adiabatic screens were maintained automatically. The absolute measurement error did not exceed 0.3%. The results obtained in these measurements are shown in Fig. 3. It follows from them that two singularities appear on the $C_p(T)$ plot. The temperature $T_1 = 114.60°K$ is a λ point and is the Neel point of YVO$_3$, while the transformation occurring in the region of $T_2 = 77.7°K$ spans a temperature interval of ~6.5° and is characterized by the following excess parameters: anomalous transition heat $\Delta Q = (29.9 \pm 0.1)$ J/mole and excess transition entropy $\Delta S = (0.38 \pm 0.01)$ J/mole-deg. Since, in accord with the foregoing, the transition in the vicinity of the temperature T_2 may be the result of a rearrangement of the magnetic structure of YVO$_3$, the above excess parameters should characterize a transition from a magnetic order of the C_YF_X type to an order of the G_XF_Z type.

The solid curve of Fig. 3 shows the magnetic component of the heat capacity of YVO$_3$. The resolution of the measured heat capacity into magnetic and lattice components was carried out by the method described in[6]. The obtained parameters, the magnetic energy and entropy of the yttrium orthovanadite, are equal to $\Delta H_M = (927 \pm 7)$ J/mole and $\Delta S_M = (14.2 \pm 0.1)$ J/mole-deg, constituting respectively 5.5 and 13.4% of the enthalpy and entropy of the YVO$_3$ under standard conditions.

Thus, the diagram of the magnetic state of YVO$_3$ can be regarded as consisting of two magnetic phases, high-temperature G_XF_Z and low-temperature C_YF_X. In each phase, the absolute values of the spontaneous ferromagnetic moment are different.

We note also that our investigations cannot as yet identify unequivocally the type of the phase transition observed at 77.7°K. On the one hand, the magnetic measurements reveal no temperature hysteresis on the $\chi(T)$ plot within the limits of the experimental scatter of the points (~2–3%), and point to a smooth change in the degree of the magnetic order. On the other hand, the measurements of the heat capacity in the vicinity of this temperature point to an integral character of the transition. Unlike the temperature T_N, where the heat capacity experiences a discontinuity $\Delta C_p = 0.5$ J/mole-deg, no such discontinuity is observed here. It appears that further magnetic investigations of single-crystal YVO$_3$ samples will help provide a less ambiguous answer to this question.

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