

Physico-chemical properties of $V_{1-x}Fe_xO_2$ and FeV_2O_6

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Abstract. The article presents the results of a study of the heat capacity of $V_{1-x}Fe_xO_2$, temperatures of phase transformations in the semiconductor phase have been determined. The phase transition diagram of the $V_{1-x}Fe_xO_2$ system is presented. Values of the change in the entropy of phase transformations for $V_{1-x}Fe_xO_2$ materials are determined. It was determined that the values of the change in the entropy of the metal-semiconductor phase transition decrease with iron concentration increasing. The results of differential thermal analysis, temperature dependences of electrical resistivity, magnetic susceptibility, and thermoelectric coefficient are presented for the FeV_2O_6 compound. It was determined that the FeV_2O_6 compound is a semiconductor in the temperature range from 100 K up to 400 K.

1. Introduction

According to the isothermal section of the phase diagram of the Fe- V-O ternary system, when the iron content being increased, the formation of solid solutions of $V_{1-x}Fe_xO_2$ and the chemical compound FeV_2O_6 is possible [1]. The latter is widely used in the chemical industry as a catalyst and as an additive in powder metallurgy [2]. The $V_{1-x}Fe_xO_2$ solid solutions have a metal-semiconductor phase transition (MSPT) at temperature of ~ 340 K [3, 4] and are used as thermal relays, thermistors, and temperature sensors. The X-ray structural, electrical, and magnetic properties of $V_{1-x}Fe_xO_2$ solid solutions were studied in detail in [4, 5]. For the FeV_2O_6 compound, the information available in different references mainly characterizes the synthesis conditions and its structure and, in part, its physical properties [6]. However, there is practically no information in references on the thermophysical properties and the presence of phase transitions in the semiconductor phase of $V_{1-x}Fe_xO_2$ solid solutions, and the physicochemical properties of the FeV_2O_6 compound in a wide temperature range have not been adequately studied.

2. Problem statement

The study subject of the article is to study the thermophysical properties in the field of MSCPT for $V_{1-x}Fe_xO_2$ solid solutions, as well as in the semiconductor state; to study physico-chemical properties for the FeV_2O_6 compound.

3. Theory

$V_{1-x}Fe_xO_2$ solid solutions were obtained by solid phase sintering of the starting reagents using V_2O_5 , V_2O_3 and Fe_2O_3 grades in three stages with the corresponding temperature mode of 900 K,



1000 K and 1400 K in an evacuated quartz ampoule [7]. Compounds $V_{0.99}Fe_{0.01}O_2$; $V_{0.97}Fe_{0.03}O_2$; $V_{0.93}Fe_{0.07}O_2$; $V_{0.87}Fe_{0.13}O_2$ were obtained which were finely divided black polycrystalline powder.

Vanadium tetraoxide was prepared from V_2O_3 and V_2O_5 charge by roasting in vacuum quartz ampoules, V_2O_3 was obtained by reducing V_2O_5 in a hydrogen stream at 870 – 1270 K, and FeV_2O_6 was prepared by roasting a mixture of oxides in vacuum quartz ampoules. Samples were annealed at 870 K for 10 hours. After intermediate grinding, annealing was performed at 970 K for 20 hours. Another (second) series of samples was synthesized. It was obtained from the first one by annealing at 1100 K for 20 hours.

Material certification was carried out by X-ray diffraction analysis on a Shimadzu XRD - 7000 diffractometer. X-ray phase analysis confirmed that the material obtained was single-phase.

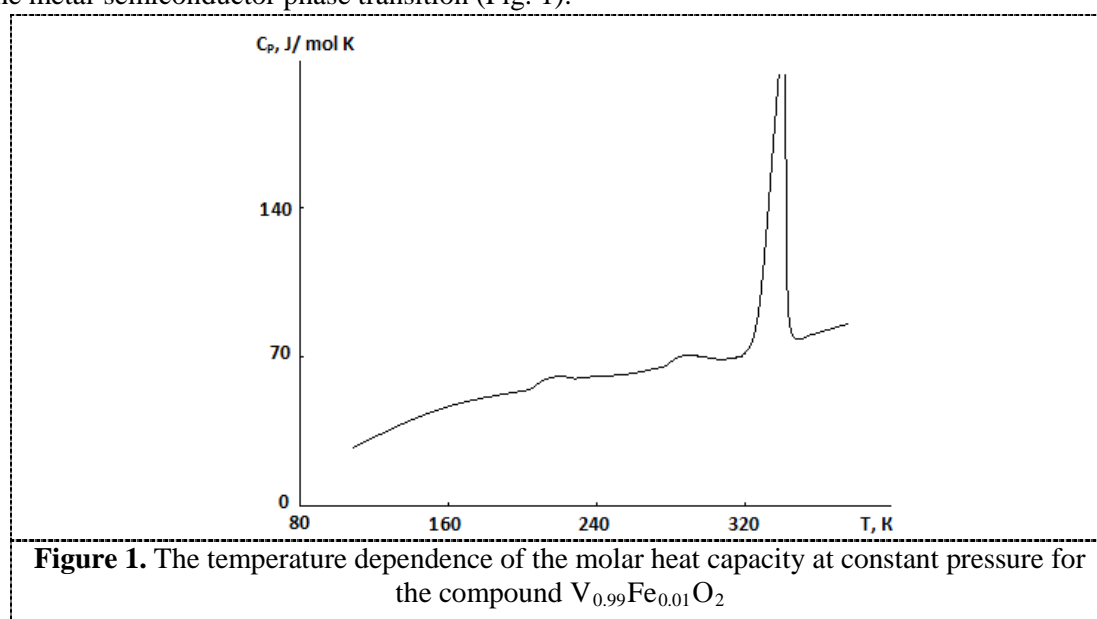
The temperature dependences of the molar heat capacity at constant pressure $C_p(T)$ for $V_{1-x}Fe_xO_2$ materials were recorded in the heating mode from 100 K up to 400 K with the vacuum adiabatic calorimeter method. The error in the measurement of heat capacity was no more than 1 %.

Differential thermal analysis (DTA) was carried out on a MOM derivatograph. Chrome-dropping thermocouples graduated at VNIIFTRI as temperature sensors for the derivatograph were used. The electrical resistance was determined with the standard two-contact method, with a relative error of not more than 10%.

The temperature dependences of the electrical resistivity, ρ , thermoelectric coefficient, α , and magnetic susceptibility, χ , were studied on the same sample pressed from a finely divided powder into a tablet measuring $5 \times 5 \times 5 \text{ mm}^3$. Thermoelectric coefficient effect was studied in the temperature range from 80 K up to 300 K. The temperature difference between the ends of the sample was measured using copper-constantan thermocouples and did not exceed 6 K. The temperature of the sample was determined as the arithmetic mean. The error in determining α in the entire studied temperature range did not exceed 5 %.

4. Experimental results

As a result of studying the temperature dependence of the molar heat capacity at constant pressure, it was determined that two bursts of heat capacity are observed at $T_3 = 295 \text{ K}$ and $T_4 = 230 \text{ K}$ at a low iron concentration in vanadium dioxide ($x=0.01$) along with the main peak ($T = 340 \text{ K}$), corresponding to the metal-semiconductor phase transition (Fig. 1).



The heat capacities of other $V_{1-x}Fe_xO_2$ compounds are of a similar nature. The critical temperatures for them are shown in Table 1. The magnitude of the additional peak is much smaller than the main one and its maximum shifts to low temperatures with increasing x .

The experimental results prove that, for the compound $x = 0.03$, in addition to the peaks corresponding to T_1 and T_2 , there is another peak in heat capacity at $T_3=330$ K. Obviously, these anomalies in the heat capacity are connected with phase transformations in the samples.

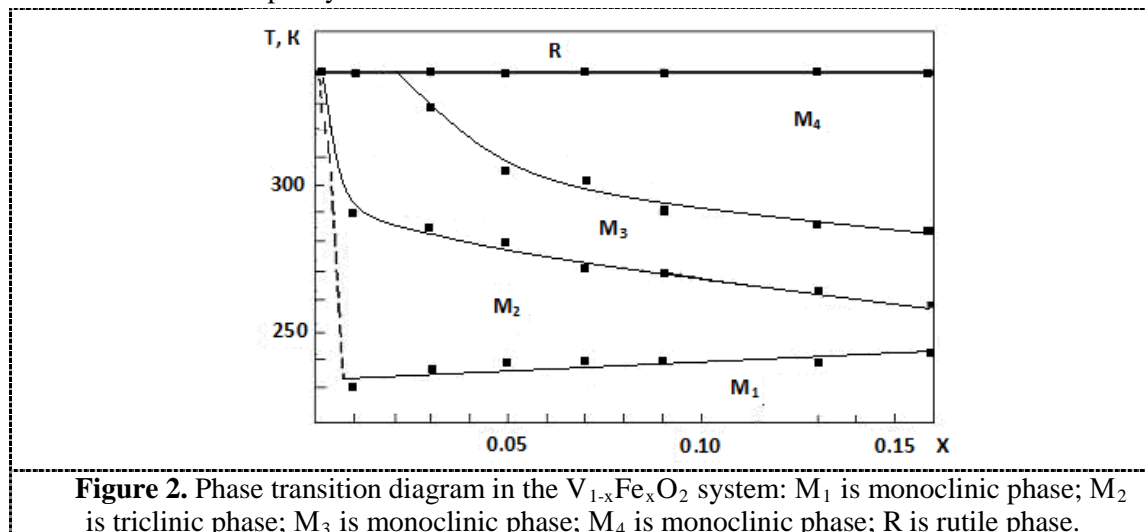
Four peaks in the temperature dependences of the specific heat were recorded for the remaining samples (Table 1). It can be noted that, the position of the heat capacity peak corresponding to the MSCPT has the same T_{MSC} for all samples, temperature, and the position of other anomalies depends on the iron content in the sample.

Table 1. Phase transition temperatures for $V_{1-x}Fe_xO_2$ samples					
Sample	T_1, K	T_2, K	T_3, K	T_{MSC}, K	θ_D, K
VO_2				340	700
$V_{0.99}Fe_{0.01}O_2$	230	295		340	650
$V_{0.97}Fe_{0.03}O_2$	235	280	330	340	750
$V_{0.93}Fe_{0.07}O_2$	238	270	305	340	750
$V_{0.87}Fe_{0.13}O_2$	235	260	285	340	840

It is worth paying attention to the fact that the temperatures of the anomalies and peaks in the dependences $C_p(T)$ are matching with the kinks in the dependences $\ln(R/R_0) = f(T^{-1})$ and with the anomalies in the dependences $\chi(T)$ given in [2]. The Debye temperatures (θ_D) determined at temperature of 150 K are shown in Table 1. As the obtained results show, θ_D increases with increasing iron content in the sample, which may indicate an ever increasing number of point defects in the samples with increasing iron concentration.

Comparing the phase transition temperatures obtained from the results of electrical resistance and heat capacity studies, a phase transition diagram for iron doped vanadium dioxide was developed. The results of developing a diagram (when constructing a diagram, the results of [1, 2] were also used) are shown in Fig.2.

It should be noted that the determining the temperatures of phase transformations according to electrical resistance is carried out with a sufficiently large error (at least 5%). Therefore, the diagram shows the experimental results for samples with $x = 0.00; 0.01; 0.03; 0.07$ and 0.13 , obtained from measurements of heat capacity.



Our results correspond with the results of [1, 2]. The phases M_1 , M_2 , M_3 and M_4 are semiconductor, and above 340 K the samples are in the metallic state R.

A study of the temperature dependences of the specific heat allowed calculating the change in the entropy ΔS for various phase transformations of the preparations. In this case, the temperature of the phase transition $M_1 \rightarrow M_2$ is denoted as T_1 , the transition $M_2 \rightarrow M_3$ is denoted as T_2 , the transition $M_3 \rightarrow M_4$ is denoted as T_3 . The metal-semiconductor transition temperature, as before, is denoted as T_{MSC} . The change in the entropy ΔS , was determined from the classical ratio

$$\Delta S = \Sigma \Delta C_p \Delta T / T. \quad (1)$$

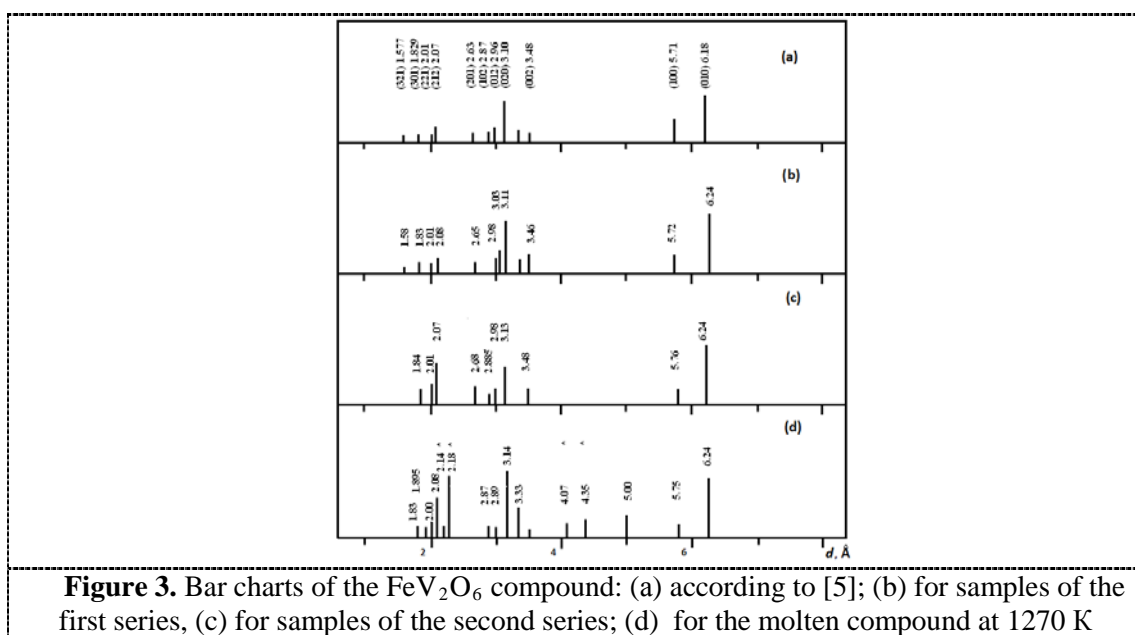
Here ΔC_p is the difference between the experimentally determined heat capacity and the heat capacity determined with extrapolation of the regular branch C_p from the area below the phase transition temperature for a given value of T ; ΔT is step width, taken equal to 0.2 K; T is the temperature corresponding to the middle of the temperature step.

The results of the corresponding calculations are presented in Table 2.

Table 2. Change in the entropy of phase transitions ΔS of materials of the $V_{1-x}Fe_xO$ system				
Sample	Entropy of phase transitions ΔS , J/(mol*K)			
	T_1 , K	T_2 , K	T_3 , K	T_{MSC} , K
VO_2				16.5
$V_{0.99}Fe_{0.01}O_2$	0.9	2.5		15.0
$V_{0.97}Fe_{0.03}O_2$	0.8	2.0	5.0	11.5
$V_{0.93}Fe_{0.07}O_2$	0.7	1.2	6.5	10.5
$V_{0.87}Fe_{0.13}O_2$	0.4	0.3	3.2	10.5

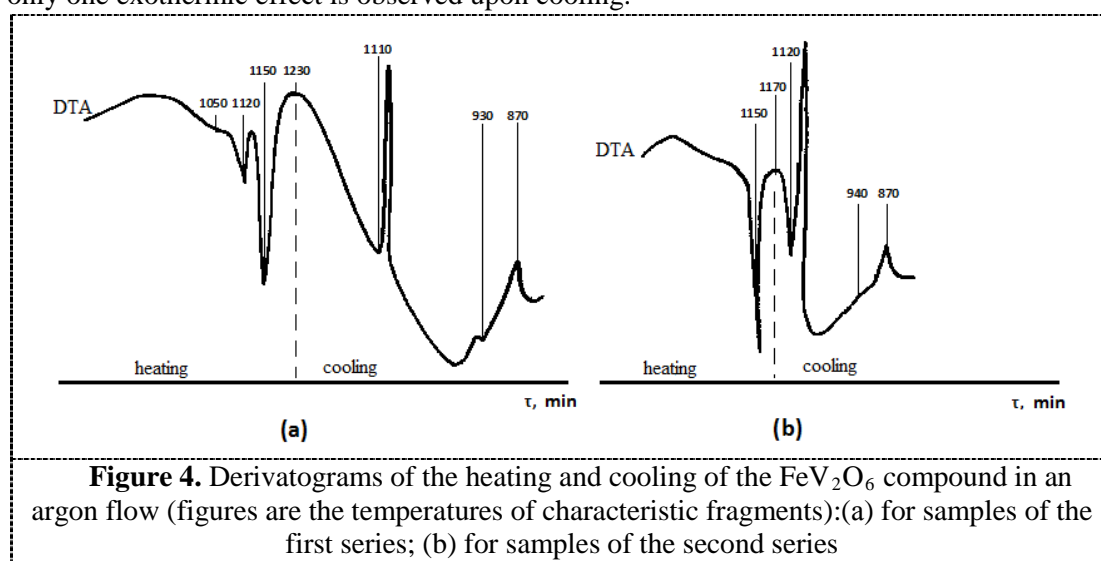
According to the results obtained the change in the entropy of phase transitions for all samples at the corresponding temperatures decreases with iron content increasing. They increase with increasing transition temperature for each sample. The highest values of ΔS have metal-insulator in the phase transition.

Based on the analysis of X-ray diffraction studies of FeV_2O_6 (bar charts are shown in Fig.3) it was determined that the FeV_2O_6 compound has a rhombic structure.



The unit cell parameters calculated in X-ray data (in rhombic syngony) were $a = 5.72 \text{ \AA}$, $b = 6.24 \text{ \AA}$, $c = 6.92 \text{ \AA}$, which corresponds with the results [5]. The methodology for processing the results is presented in [4]. When comparing the bar diagrams of powder samples of the first and second series (Fig.3, b, c) an increase in the intensity of 3 lines (010), (020), (212) and a weakening of the intensity of the remaining lines (Fig.3 c) are noticeable. According to the X-ray diffraction pattern of FeV_2O_6 argon melted in the flow (Fig. 3, d) V_2O_5 , is observed among the decomposition products, their reflexes are indicated with an asterisk in the bar diagram. This conclusion is also indirectly confirmed with effects on the differential thermal curve in the temperature range 910 – 940 K, corresponding to the melting of eutectic mixtures of the $\text{Fe}_2\text{O}_3 - \text{V}_2\text{O}_5$ system (Fig.4).

The thermal analysis derivatograms (DTA) of heating and cooling in an argon flow are shown in Fig.4. Two endothermic effects are observed upon heating in the temperature range 1020 K – 1230 K; and only one exothermic effect is observed upon cooling.



The derivatograms of heating and cooling in an argon flow differ for samples of the first and second series (Fig. 4 a, b). Only one endothermic effect is observed upon heating for samples of the second series; the differential - thermal curves of heating and cooling are more symmetrical than for samples of the first series. The step on the thermal curve corresponds to the melting point of FeV_2O_6 (1150 K). According to the state diagram of Fe-V-O [7] the compound $\text{Fe}_2\text{V}_4\text{O}_{13}$ should be formed under equilibrium conditions. Due to the fact that the rate of formation of $\text{Fe}_2\text{V}_4\text{O}_{13}$ at low temperatures is insignificant, the oxidation products under nonequilibrium conditions are additionally V_2O_5 and FeVO_4 . The group of endothermic effects at temperatures of 940 – 970 K on the differential thermal curve characterizes the melting of the eutectic mixture $\text{Fe}_2\text{V}_4\text{O}_{13} - \text{V}_2\text{O}_5$ and then incongruent melting of $\text{Fe}_2\text{V}_4\text{O}_{13}$ with the formation of iron orthovanadate and the melt. The endothermic effect at temperatures of 1140 – 1150 K is connected with the incongruent melting of iron orthovanadate. The peritectic crystallization reaction proceeds exothermically at 1110 – 1120 K. Crystallization processes end completely in the range 940 – 820 K.

The results of studies of electrical resistance, magnetic susceptibility and thermoelectric coefficient are presented in Fig. 5.

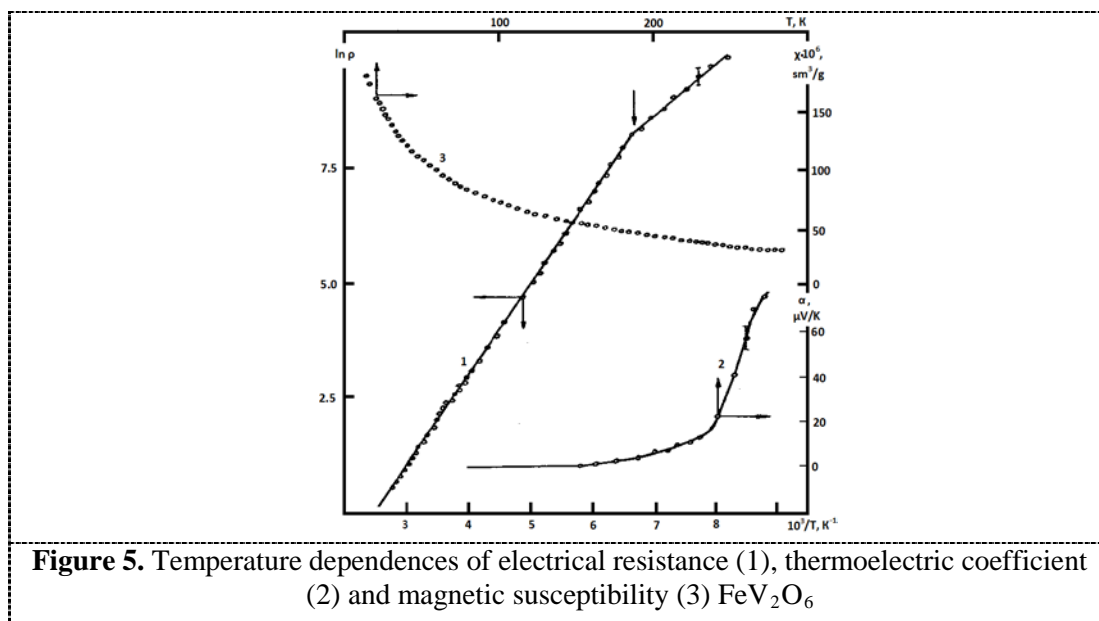


Figure 5. Temperature dependences of electrical resistance (1), thermoelectric coefficient (2) and magnetic susceptibility (3) FeV_2O_6

According to the dependence of electrical resistance on temperature, the compound is a semiconductor in the temperature range from 100 K up to 400 K. A small kink is observed in the dependence $\ln \rho = f(1/T)$ at a temperature of about 150 K which indicates a change in the band gap from 0.12 eV at low temperatures to 0.17 eV at high temperatures. Non-zero thermoelectric coefficient signal appears at temperature corresponding to a kink in the dependence $\ln \rho = f(1/T)$. When increasing temperature to 300 K, α increases reaching about to 70 $\mu\text{V/K}$ at room temperature.

An analysis of the dependence of magnetic susceptibility on temperature in the coordinates $1/\chi = f(T)$ showed that above 11 K the magnetic susceptibility follows the Curie-Weiss law. It should be noted that the magnetic properties of the FeV_2O_6 compound are similar to the properties of FeVO_4 iron orthovanadate [7]; the lower Néel temperature of the FeV_2O_6 compound ($T_N = 11$ K) as compared with FeVO_6 ($T_N = 22$ K), is probably due to a decrease in the indirect exchange due to structural-forming polyhedra. For FeV_2O_6 the effective magnetic moment equal to $5.49 \cdot 10^{-23}$ J/T as well as for orthovanadate, approximately corresponds to the number of unpaired electrons and slightly differs from $(n(n-1))^{1/2}$ (n is the number of partially unpaired electrons, equal to (5), which partially testifies to a rather high degree of localization of 3d electrons near the nuclei of transition elements in this compound.

5. Conclusion

According to the results of studying the molar heat capacity at constant pressure for $\text{V}_{1-x}\text{Fe}_x\text{O}_2$ it was determined that these materials in addition to the MSCPT at 340 K experience phase transitions in the semiconductor state, followed by a change in entropy. The change in entropy during the MSCPT is connected both with the rearrangement of the crystal lattice (ΔS_{LAT}), and the contribution of the electronic energy spectrum (ΔS_{EL}), connected with the appearance of conduction electrons (free electrons) in the vanadium 3d zone. The minimum Debye temperature of 650 K corresponds to vanadium dioxide containing 1% iron.

The FeV_2O_6 compound, subjected to various annealings, has insignificant differences in thermal and structural properties; moreover, after annealing at 970 K, it apparently has internal ordering.

6. References

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