LOW-DIMENSIONAL SYSTEMS

Influence of Particle Size, Stoichiometry, and Degree of Long-Range Order on Magnetic Susceptibility of Titanium Monoxide

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Abstract—In situ measurements of the magnetic susceptibility of ordered and disordered titanium monoxides TiO_y in the temperature range from 300 to 1200 K have revealed that it depends on the size of crystals, their stoichiometry, and long-range order parameters. Analysis of the data for both the ordered and disordered TiO_y has demonstrated that the dependence of the Van Vleck paramagnetism on the nanocrystal size is inversely proportional due to the breaking of symmetry of the local environment of titanium and oxygen atoms near the surface of nanocrystals. It has been found that the Van Vleck contribution from the atomic vacancy disorder in monoxide nanocrystals of superstoichiometric composition, as well as in the crystalline stoichiometric monoxide, is proportional to the deviation of the degree of long-range order from the maximum value.

1. INTRODUCTION

Interest in the study of nanocrystals, both from the fundamental and practical points of view, is associated with the fact that a decrease in their size below a certain threshold value leads to a radical change in their structure and physicochemical properties [1]. The atomic structure of the surface in nanocrystals differs from the atomic structure in the bulk of the material. Owing to this feature, nanocrystals exhibit unusual magnetic phenomena and properties: the magnetic quantum size effect, hard and soft magnetic properties, colossal magnetoresistance, superparamagnetism, etc. [2–8].

Moreover, in recent years, investigation of the influence of the size of titanium oxide nanocrystals on their stoichiometry has become an important issue, because titanium oxides are promising materials for use in photocatalysts active under sunlight or under ordinary artificial light [9–11]. Nanocrystals of titanium monoxide are candidates for use in nanoelectronics [12] as single-electron transistors. The use of single-electron transistors based on quantum tunneling effects can significantly miniaturize computer processors.

Therefore, in this work, we have thoroughly investigated the nonstoichiometric titanium monoxide containing a large amount of structural vacancies in two sublattices simultaneously [13–17]. The purpose of this study was to reveal the influence of the particle size, stoichiometry, and long-range order parameter on the magnetic susceptibility of titanium monoxide and to analyze the Van Vleck contribution due to the breaking of the symmetry of the local environment of atoms both with a decrease in the nanocrystal size and upon atomic vacancy ordering.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Microcrystals of titanium monoxide TiO_y with an average size of approximately 25 μm were synthesized by solid-phase sintering from a mixture of metallic titanium and titanium dioxide TiO_2 powders in a vacuum at a pressure of 10^{-3} Pa and at a temperature of 1770 K. In order to achieve the disordered state of titanium monoxide, evacuated (to a pressure of 10^{-3} Pa) quartz ampoules with samples were annealed for 3 h at a temperature of 1330 K, after which the ampoules with samples were dropped into water. The quenching rate was approximately 200 K/s. The ordered state of TiO_y was achieved using two annealing regimes: stoichiometric powders were annealed at 673 K in evacuated (to a pressure of 10^{-3} Pa) quartz ampoules for 4 h and then slowly cooled to 300 K at a rate of 10 K/h. Superstoichiometric powders were annealed at 1330 K for 3 h and then slowly cooled to 300 K at 10 K/h. The multiparameter characterization of the samples was

carried out using chemical, spectral, pycnometric, X-ray powder diffraction, and X-ray diffraction analyses. Details of the heat treatment for the preparation of disordered and ordered states and the results of the characterization of the synthesized samples can be found in [18].

Titanium monoxide nanocrystals were prepared using high-energy fragmentation in a PM-200 Retsch planetary ball mill. In order to prevent contamination of the samples during the fragmentation, zirconium dioxide ZrO_2 stabilized with yttrium oxide Y_2O_3 was chosen as the material for milling balls and bowls. The smallest size of nanocrystals was obtained with the $10 : 1$ weight ratio of the milling balls and titanium monoxide powders. The milling liquid was isopropyl alcohol. The speed of rotation of the supporting disk for milling bowls was 500 rpm at a fragmentation duration of 480 min.

The X-ray powder diffraction analysis of the initial samples and samples after measurements of the magnetic susceptibility χ was performed in the $CuK_{\alpha1}$ radiation on a STOE STADI-P automatic diffractometer (Germany) and in the $CuK_{\alpha1, 2}$ radiation on a Shimadzu XRD-7000 automatic diffractometer in the Bragg−Brentano geometry using step-by-step scanning within the range of 2θ angles from $10°$ to $120°$ with a scan step $\Delta(2\theta) = 0.02°$.

A completely ordered state of titanium monoxide is achieved when all the long-range order parameters are equal to unity, i.e., $\eta_1 = \eta_4 = \eta_{10} = 1$. In this case, as follows from distribution functions (1) and (2) presented below for titanium and oxygen atoms, respectively, the relative concentration of titanium atoms in the metal sublattice is $x = 5/6$, the relative concentration of oxygen atoms in the nonmetal sublattice is $z = 5/6$, and the stoichiometric composition of the ideal monoclinic superstructure can be represented as $Ti_{5/6}O_{5/6}$ or Ti_5O_5 ($Ti_5\blacksquare O_5\square$).

The distribution function of titanium atoms in the monoclinic (space group $C2/m$) superstructure of the titanium monoxide Ti_xO_z has the form [18]

$$n_{Ti}(x_I, y_I, z_I) = x - (\eta_{10}/6)\cos 2\pi z_I$$
$$- (\eta_4/3)\cos[4\pi(x_I + z_I)/3] \qquad (1)$$
$$- (\eta_I/3)\cos[2\pi(2x_I - z_I)/3]$$

with the parameters $\gamma_{10} = 1/6$, $\varphi_{10}^{(1)} = \pi$; $\gamma_4 = 1/6$, $\varphi_4^{(1)} = \pi$, $\varphi_4^{(2)} = -\pi$; and $\gamma_1 = 1/6$, $\varphi_1^{(1)} = \pi$, $\varphi_1^{(2)} = -\pi$. The parameter $\gamma(\mathbf{k}_s^{(j)}) = \gamma_s \exp(i\varphi_s^{(j)})$ is a coefficient that takes into account the symmetry of the crystal and is chosen so that the long-range order parameters equal to unity correspond to a completely ordered crystal; $\mathbf{k}_s^{(j)}$ is the jth arm of the star with number s; and $\varphi_s^{(j)}$ is the phase shift of the concentration wave.

The distribution of oxygen atoms in the monoclinic (space group $C2/m$) superstructure of the titanium monoxide Ti_xO_z is described by the function

$$n_O(x_I, y_I, z_I) = z + (\eta_{10}/6)\cos 2\pi z_I$$
$$- (\eta_4/3)\cos[4\pi(x_I + z_I)/3] \qquad (2)$$
$$+ (\eta_I/3)\cos[2\pi(2x_I - z_I)/3]$$

with the parameters $\gamma_{10} = 1/6$, $\varphi_{10}^{(1)} = 0$; $\gamma_4 = 1/6$, $\varphi_4^{(1)} = \pi$, $\varphi_4^{(2)} = -\pi$; and $\gamma_1 = 1/6$, $\varphi_1^{(1)} = 0$, $\varphi_1^{(2)} = 2\pi$.

The long-range order parameters η of titanium monoxide were calculated from the intensity ratio of the X-ray diffraction structure and superstructure reflections before and after the measurement of the magnetic susceptibility. In the calculation of the intensity of superstructure reflections of the Ti_5O_5 phase, it is necessary to take into account that the sublattices of superstructure reflections for the arms of the stars $\{\mathbf{k}_{10}\}$, $\{\mathbf{k}_4\}$, and $\{\mathbf{k}_1\}$ from the metal and nonmetal sublattices coincide pairwise with each other. In this respect, the intensity of superstructure reflections depends on the difference in the phase shifts of concentration waves of the metal and nonmetal atoms, as well as on the indices (hkl) of the structure site $\mathbf{H}$ near which the superstructure reflection is formed. Taking into account the particular values of γ_s and φ_s corresponding to the stars $\{\mathbf{k}_s\}$, on the one hand, and to the titanium and oxygen sublattices, on the other hand, the intensity of superstructure reflections in the X-ray diffraction pattern of the ordered monoclinic phase Ti_5O_5 (space group $C2/m$) is described by the formula [19]

$$I_{sup}(q) = N^2$$

$$\times \sum_{\mathbf{H}} \{[(f_{(Ti)}\eta_{10}^{(Ti)} - (-1)^{(h+k+l)}f_0\eta_{10}^{(0)})^2/36]$$

$$\times P(q = |\mathbf{H} + k_{10}^{(j)}|)$$
$$+ [(f_{(Ti)}\eta_4^{(Ti)} + (-1)^{(h+k+l)}f_0\eta_4^{(0)})^2/18] \qquad (3)$$
$$\times P(q = |\mathbf{H} + k_4^{(j)}|)$$
$$+ [(f_{(Ti)}\eta_1^{(Ti)} - (-1)^{(h+k+l)}f_0\eta_1^{(0)})^2/18]$$
$$\times P(q = |\mathbf{H} + k_1^{(j)}|)\},$$

where N is the number of sites in the crystal lattice, f_{Ti} and f_0 is the atomic scattering factors, q is the length of the reduced diffraction vector, and P are the multiplicity factors of the structure and superstructure reflections from the polycrystal. From this formula, it follows that the intensity of superstructure reflections is proportional to the square of the degree of long-range order and decreases rapidly with a decrease in the degree of long-range order in the crystal.

The diameter of nanocrystals D was determined from the broadening of X-ray diffraction reflections by the Williamson−Hall method [20, 21]. The average

diameters of nanocrystals or the coherent scattering regions determined by extrapolating the dependence of the reduced broadening β^* on the scattering vector s to the value of s equal to zero, depending on the milling time, are found to be approximately equal to 30 nm. The techniques used for the preparation of nanocrystals by means of fragmentation, analysis of X-ray diffraction patterns, and calculation of coherent scattering region sizes were described in detail in [22].

The magnetic susceptibility χ was investigated on titanium monoxide microcrystals of the stoichiometric composition, as well as on microcrystals and nanocrystals of superstoichiometric titanium monoxide with different degrees of long-range order. The magnetic susceptibility χ of titanium monoxide was measured in the temperature range from 300 to 1200 K in magnetic fields with a strength from 7.2 to 8.8 kOe. The measurements were performed by the Faraday method on a Domenicali pendulum balance in a vacuum at a pressure of 10^{-3} Pa. The rates of heating and cooling of the samples in measurements of the magnetic susceptibility were approximately equal to 1 K/min. The weight of the powder and the crystal structure of titanium monoxide were controlled before and after the measurement of the magnetic susceptibility. The accuracy in the measurement of the magnetic susceptibility was approximately equal to $\pm 0.05 \times 10^{-6}$ emu/g.

Fig. 1. In situ temperature dependences of the magnetic susceptibility for microcrystals of the disordered (closed circles) and ordered (open circles) stoichiometric titanium monoxides TiO_y. The left−right arrows indicate reversible changes in the magnetic susceptibility. The circles are the magnetic susceptibilities at room temperature in different states: (*1*) initial quenched state, (*2*) final state of the initially quenched sample after heating to 1200 K and cooling to room temperature during the measurement of the magnetic susceptibility, (*3*) initial annealed state, and (*4*) finite state of the initially annealed sample after heating to 1200 K and cooling to room temperature during the measurement of the magnetic susceptibility. The vertical arrows indicate nonequilibrium irreversible transitions from the nonequilibrium partially ordered state to the equilibrium ordered state.

3. EXPERIMENTAL RESULTS

In situ measurements of the magnetic susceptibility of titanium monoxide with different stoichiometries in the temperature range from 300 to 1200 K demonstrated that microcrystals and nanocrystals of titanium monoxide are weak paramagnets, and the magnetic susceptibility in the entire temperature range under investigation varies from 0.90×10^{-6} to 3.05×10^{-6} emu/g depending on the stoichiometry, the structural state, and the size of the crystals.

Figure 1 shows in situ temperature dependences of the magnetic susceptibility for microcrystals of disordered (closed circles) and ordered (open circles) stoichiometric titanium monoxides. During heating of the disordered sample from the initial state (state *1* in Fig. 1) to 1000 K, the magnetic susceptibility exhibits a reversible behavior. A further increase in the temperature to 1073 K leads to the diffusion of atoms and vacancies of titanium and oxygen. As a result, the sample is transformed from the nonequilibrium partially ordered state to the equilibrium ordered state. Upon annealing for 3 h at a temperature of 1073 K and quenching (state *2* in Fig. 1) from the temperature of 1073 K, it can be seen that the transition to the equilibrium ordered state is accompanied by a decrease in the Van Vleck contribution. This equilibrium ordered state is stable, and the temperature dependence of the magnetic susceptibility during heating from 300 to
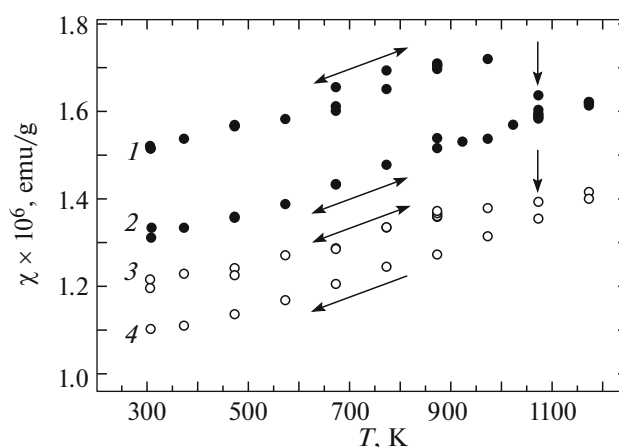
1173 K and cooling from 1173 to 300 K has a reversible character. The analysis of the X-ray diffraction pattern of the initial disordered sample (spectrum *1* in Fig. 2) revealed that, in addition to the cubic phase TiO_y (space group $Fm\overline{3}m$), the sample in the initial state contains the ordered phase Ti_5O_5 (space group $C2/m$), and the long-range order parameter has the value of $\eta = 0.21$. After the measurements of the magnetic susceptibility, the X-ray diffraction pattern (spectrum *2* in Fig. 2) demonstrates an increase in the intensity of reflections from the ordered phase Ti_5O_5. The analysis of changes in the intensity of the structure and superstructure reflections showed that the long-range order parameter reaches the value of $\eta = 0.54$. Thus, the slow annealing to high temperatures and slow cooling to room temperature made it possible to increase the degree of long-range order in the disordered titanium monoxide.

During heating of the ordered sample (open circles) from the initial state (Fig. 1, state *3*) to 1073 K, the magnetic susceptibility exhibits a reversible behavior. At a temperature of 1073 K, the sample is transformed into a more ordered state. A further heating to 1200 K and cooling to 300 K (Fig. 1, state *4*) already do not lead to the repetition of the temperature behavior of the magnetic susceptibility upon heating. The analysis of the X-ray diffraction pattern of the initial
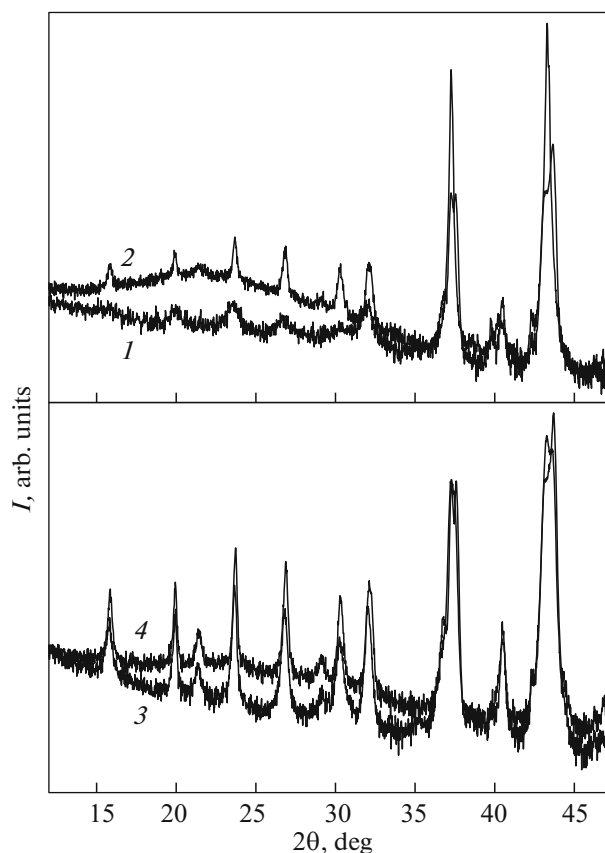
Fig. 2. X-ray diffraction patterns of the stoichiometric titanium monoxide. Numerals correspond to the states of the samples at room temperature (see Fig. 1): (*1*) initial quenched (disordered) state, (*2*) final state of the initially quenched sample after heating to 1200 K and cooling to room temperature during the measurement of the magnetic susceptibility, (*3*) initial annealed (ordered) state, and (*4*) final state of the initially annealed sample after heating to 1200 K and cooling to room temperature during the measurement of the magnetic susceptibility.

Fig. 3. In situ temperature dependences of the magnetic susceptibility for microcrystals of the disordered (closed symbols) and ordered (open symbols) superstoichiometric titanium monoxides TiO_y: (I) region of the reversible behavior of the magnetic susceptibility with increasing and decreasing temperature and (II) region of the irreversible behavior of the magnetic susceptibility with increasing temperature. Squares with arrows show the magnetic susceptibilities of the annealed (open square) and quenched (closed square) samples after in situ quenching from the temperature of 1200 K.

ordered titanium monoxide (spectrum *3* in Fig. 2) revealed that, after the annealing performed at a low temperature of 673 K in evacuated (10^{-3} Pa) quartz ampoules for 4 h, the titanium monoxide did not reach the complete ordering, and the long-range order parameter had the value of $\eta = 0.62$. After a series of measurements of the magnetic susceptibility, the structure of the sample, according to the analysis of the X-ray diffraction pattern (spectrum *4* in Fig. 2), remained monoclinic (space group $C2/m$), but the degree of ordering increased. Thus, the slow annealing of the sample to 1200 K and slow cooling to room temperature led to the complete ordering, and the long-range order parameter increased and reached a maximum value close to unity.

A different situation occurs with in situ temperature dependences of the magnetic susceptibility for microcrystals and nanocrystals of the ordered and dis-
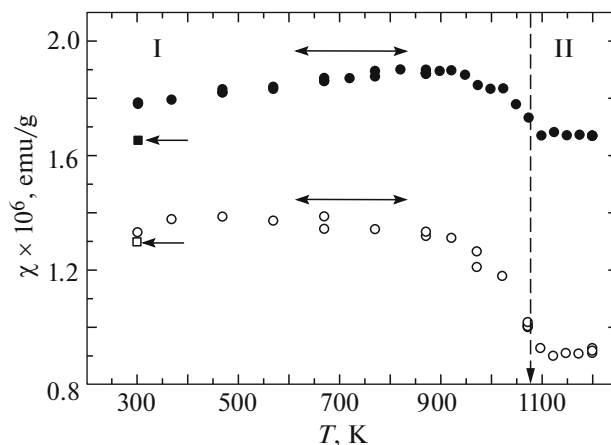
ordered titanium monoxides of the superstoichiometric composition.

In situ temperature dependences of the magnetic susceptibility for microcrystals of the disordered (closed symbols) and ordered (open symbols) titanium monoxides of the superstoichiometric composition are shown in Fig. 3. An increase in the temperature from 300 to 1073 K and cooling from 1073 to 300 K lead to a reversible behavior of the magnetic susceptibility for both the disordered and ordered microcrystals of the titanium monoxide TiO_y. An increase in the temperature above 1073 K up to 1200 K results in the diffusion of atoms and vacancies of titanium and oxygen in the disordered titanium monoxide. The diffusion leads to a transition of the sample to the equilibrium ordered state with increased values of the long-range order parameter, which is accompanied by a decrease in the Van Vleck paramagnetic contribution. The analysis of the X-ray diffraction patterns of the initial microcrystals of the disordered monoxide revealed that the sample in the initial state contains only the cubic phase TiO_y (space group $Fm\overline{3}m$) with the long-range order parameter $\eta = 0$. After a series of measurements of the magnetic susceptibility, the X-ray diffraction pattern contained reflections from only one ordered monoclinic phase, namely, Ti_5O_5 (space group $C2/m$). The analysis of changes in the intensity of the structure and superstructure reflections showed that the long-range order parameter increased to $\eta = 0.55$. Thus, the slow annealing to high temperatures and slow cooling to room temperature
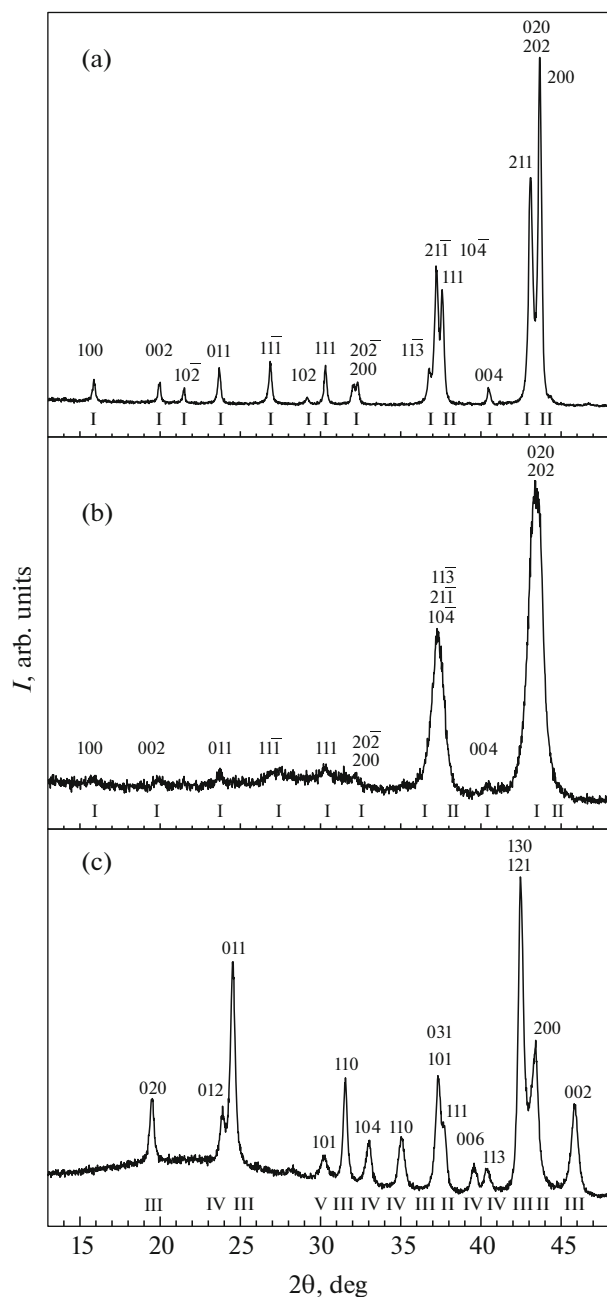
Fig. 4. X-ray diffraction patterns of titanium monoxide powders of the superstoichiometric composition: (a) initial ordered nanocrystals and (b) initial ordered microcrystals, Roman numerals indicate phases (I) Ti_5O_5 and (II) TiO_y; (c) after the measurement of the magnetic susceptibility of the ordered nanocrystal powder, Roman numerals indicate phases (II) TiO_y, (III) $Ti_{4.5}O_5$, (IV) Ti_2O_3, and (V) $ZrO_2-Y_2O_3$. The indices of the reflections of the corresponding phases are shown near the peaks.

resulted in a partial ordering of the sample. The ordered titanium monoxide in the initial state, according to the analysis of the X-ray diffraction pattern (Fig. 4a), contained two phases: cubic TiO_y (space group $Fm\bar{3}m$) and monoclinic Ti_5O_5 (space
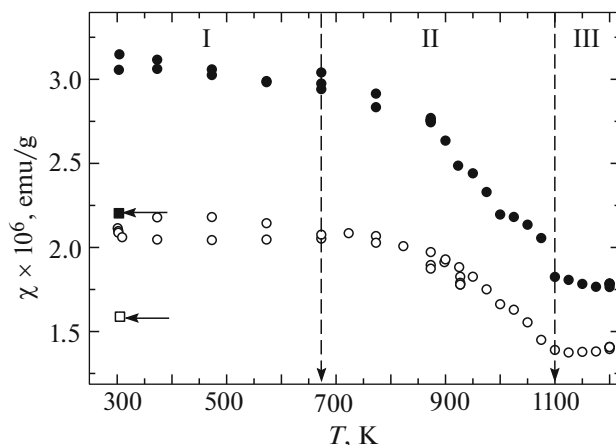

Fig. 5. In situ temperature dependences of the magnetic susceptibility for nanocrystals of the disordered (closed symbols) and ordered (open symbols) superstoichiometric titanium monoxides TiO_y: (I, III) regions of the reversible behavior of the magnetic susceptibility with increasing and decreasing temperature and (II) region of the irreversible behavior of the magnetic susceptibility with increasing temperature. Squares with arrows have the same meaning as in Fig. 3.

$C2/m$). After a series of measurements of the magnetic susceptibility, the structure of the microcrystals, according to the X-ray diffraction pattern, remained monoclinic, and the long-range order parameter decreased from the maximum value to 0.79.

In contrast to the microcrystals, the nanocrystals of the ordered and disordered titanium monoxides exhibit other effects. Figure 5 shows in situ temperature dependences of the magnetic susceptibility for nanocrystals of the disordered (closed symbols) and ordered (open symbols) titanium monoxides. In the temperature range from 300 to 673 K (region I in Fig. 5), the magnetic susceptibility exhibits a reversible behavior. This indicates that the state of the nanocrystals at these temperatures is stable. At temperatures above 673 K (region II in Fig. 5), there is a nonequilibrium decrease in the magnetic susceptibility due to the change in the phase composition of the system and growth of nanocrystals. The X-ray diffraction analysis revealed that, in this region, the initial nanocrystal, which contained the cubic phase TiO_y (disordered sample) or a mixture of the cubic TiO_y and monoclinic Ti_5O_5 phases (ordered sample, Fig. 4b), is transform into the ordered phase $Ti_{4.5}O_5$ (space group $Immm$) and the stoichiometric phase Ti_2O_3 (space group $R\bar{3}2/c$) (Fig. 4c). Thus, it can be argued that, in region II, the state of the system changes significantly. Since the system is not restored to the initial state with an increase in the temperature, we can assume that the state of the system becomes more stable.

At a temperature of approximately 1100 K and higher (region III in Fig. 5), the magnetic susceptibil-
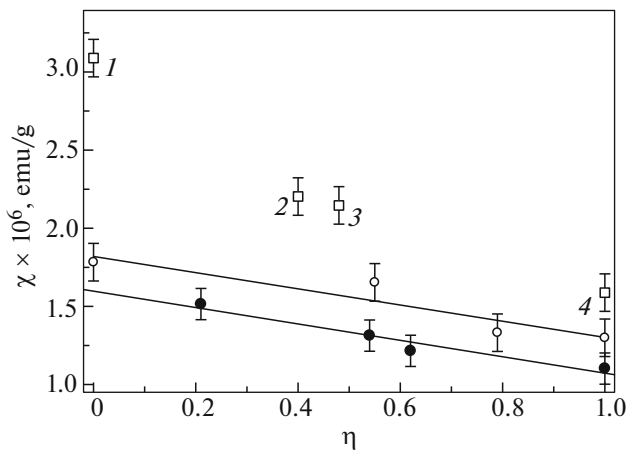
Fig. 6. Dependences of the magnetic susceptibility for microcrystals and nanocrystals of titanium monoxide TiO$_y$ of different compositions on the degree of long-range order. Solid lines represent the results of the linear approximation using the least-squares method for microcrystals of the stoichiometric composition [23] (closed circles) and superstoichiometric composition according to the data of this work (open circles). Open squares show the magnetic susceptibilities for nanocrystals of the superstoichiometric composition (data of this work). The experimental points correspond to particle sizes of (*1*) 30, (*2*) 60, (*3*) 80, and (*4*) 205 nm.

ity ceases to decrease. In region III between the temperatures of 1100 and 1200 K, the reversible behavior of the magnetic susceptibility is observed during heating and cooling. This indicates that the system reached a stable equilibrium state. In situ rapid cooling of the samples from 1200 K to room temperature (squares in Fig. 5) results in the quenching of the high-temperature state corresponding to region III.

The analysis of the experimental data obtained in this study demonstrates that the magnetic susceptibility is the greater, the higher is the degree of disorder, which agrees the conclusions drawn in [23, 24]. Moreover, the results obtained in this study allow the important conclusion that the smaller is the size of nanocrystals, the greater is the magnetic susceptibility.

This behavior is explained by a significant additional contribution from the Van Vleck paramagnetism to the magnetic susceptibility

$$\chi_{VV} = \frac{2N_V \left| \langle s | \mu_z | 0 \rangle \right|^2}{\Delta}, \qquad (4)$$

where χ_{VV} is the Van Vleck paramagnetic contribution, N_V is the number of atoms per unit volume, μ_z is the operator of the z-component of the total orbital and spin moments of all electrons of the system, and the square of the absolute value $2N_V \left| \langle s | \mu_z | 0 \rangle \right|^2$) of the off-diagonal matrix elements of the operator M_z determined the probability of quantum transitions described by the operator (HM_z). The nature of the

Van Vleck contribution is associated with the breaking of local symmetry of atoms in the disordered state and on the surface of the nanocrystals.

The dependence of the magnetic susceptibility on the degree of long-range order for stoichiometric (dark circles) and superstoichiometric (open symbols) microcrystals (Fig. 6) is approximated using the least-squares method by the linear function

$$\chi = \chi_{cryst} + k_{disorder}(1 - \eta), \qquad (5)$$

where $\chi_{cryst} = 1.1 \times 10^{-6}$ emu/g for the stoichiometric composition and $\chi_{cryst} = 1.30 \times 10^{-6}$ emu/g for the superstoichiometric composition. The magnetic susceptibility for the superstoichiometric composition is higher than that for the stoichiometric composition. As can be seen from Fig. 6, the slopes of the two straight lines within the error are identical and equal to $k_{disorder} = 0.52 \times 10^{-6}$ emu/g, which indicates the universality of this relationship for microcrystals with different chemical compositions.

Thus, according to the experimental data, in the case of atomic ordering in the microcrystals, the dependence of the magnetic susceptibility on the degree of long-range order is linear, which agrees with the conclusions drawn in [23]. The known (for ordering systems) quadratic dependence of the magnetization on the long-range order parameter, which is based on symmetry considerations, holds true only for second-order phase transitions. Moreover, this dependence is expected only in a small vicinity near the phase transition point. In the case of titanium monoxide, the atomic vacancy ordering occurs through the mechanism of the first-order phase transition. Therefore, the Landau theory for second-order phase transitions in this case does not work. Indeed, the symmetry analysis shows that the Ti$_5$O$_5$ superstructure is formed through the order–disorder TiO$_y$–Ti$_5$O$_5$ transition channel including five nonequivalent vectors: one arm $\mathbf{k}_{10}^{(1)} = (\mathbf{b}_1 + \mathbf{b}_2)/2 = (0\ 0\ 1)$ of the Lifshitz star $\{\mathbf{k}_{10}\}$, two arms $\mathbf{k}_4^{(5)} = \mu_4(\mathbf{b}_1 + 2\mathbf{b}_2 + \mathbf{b}_3) = (2/3\ 0\ 2/3)$ and $\mathbf{k}_4^{(6)} = -\mathbf{k}_4^{(5)}$ of the non-Lifshitz star $\{\mathbf{k}_4\}$ with the current parameter $\mu_4 = 1/3$, and two arms $\mathbf{k}_1^{(7)} = \mu_1^{(1)}(\mathbf{b}_2 + \mathbf{b}_3) - \mu_1^{(2)}(\mathbf{b}_1 + \mathbf{b}_2) = (2/3\ 0\ -1/3)$ and $\mathbf{k}_1^{(8)} = -\mathbf{k}_1^{(7)}$ of the non-Lifshitz star $\{\mathbf{k}_1\}$ with the current parameters $\mu_1^{(1)} = 1/3$ and $\mu_1^{(2)} = 1/6$ [14, 24]. The presence of the vectors of two non-Lifshitz stars $\{\mathbf{k}_4\}$ and $\{\mathbf{k}_1\}$ in the order–disorder TiO$_y$–Ti$_5$O$_5$ transition channel means that the Lifshitz criterion for second-order phase transitions does not hold, and the formation of the monoclinic superstructure Ti$_5$O$_5$ in titanium monoxide TiO$_y$ should occur through the mechanism of the first-order phase transition.
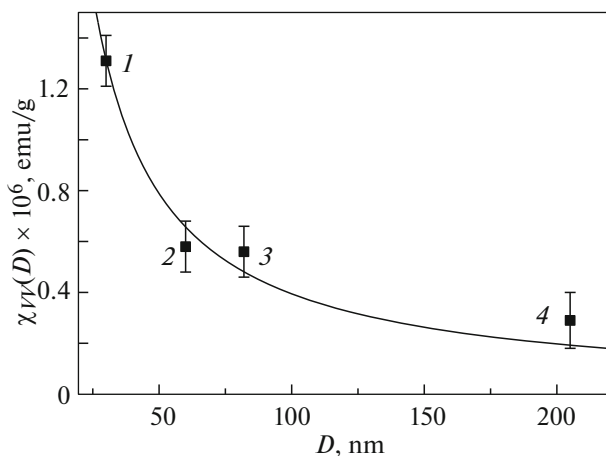
Fig. 7. Van Vleck contribution to the magnetic susceptibility for nanocrystals of the superstoichiometric titanium monoxide TiO$_y$. Experimental points *1–4* correspond to the same particle sizes as in Fig. 6. The solid line represents the result of the least-squares approximation by the hyperbolic function.

In addition to the data for microcrystals, Fig. 6 shows the magnetic susceptibility for nanocrystals (open squares) of titanium monoxide TiO$_y$ of the superstoichiometric composition as a function of the degree of long-range order. The experimental dependences in the figure correspond to the nanocrystal sizes of 30 (squares *1*), 60 (squares *2*), 80 (squares *3*), and 205 nm (squares *4*). The significantly higher magnetic susceptibility for small nanocrystals and the monotonic dependence of the magnetic susceptibility on the degree of long-range order suggest that the magnetic susceptibility of nanocrystals depends to a greater extent on the nanocrystal size than on the degree of long-range order.

The analysis of all the results of this work leads to the conclusion that the magnetic susceptibility for nanocrystals is the sum of three components, namely, the contribution to the magnetic susceptibility from the crystal with the maximum degree of order χ_{cryst}, the Van Vleck contribution from the degree of disorder $\chi_{VV}(1 - \eta)$, and the Van Vleck contribution from atoms on the surface of nanocrystals $\chi_{VV}(D)$:

$$\chi = \chi_{cryst} + \chi_{VV}(1 - \eta) + \chi_{VV}(D). \qquad (6)$$

The dependence of the Van Vleck contribution to the magnetic susceptibility (at room temperature) for nanocrystals of the superstoichiometric titanium monoxide on their size is shown in Fig. 7. Since the Van Vleck contribution $\chi_{VV}(1 - \eta)$ from the degree of disorder in the nanocrystals has the same nature as in the microcrystals and the influence of the surface of the nanocrystals on this contribution, within the experimental error, can be ignored, this contribution is subtracted from the magnetic susceptibility of the

nanocrystals. The approximation of the magnetic susceptibility by the hyperbolic function $\chi_{VV}(D) = 39.44/D$ [10^{-6} emu/g] shows that the Van Vleck contribution $\chi_{VV}(D)$ is proportional to the specific surface area $S = 6/(\rho D)$ of the nanocrystals

$$\chi_{VV}(D) = k_{surface} \frac{6}{\rho D}, \qquad (7)$$

where ρ is the density of the nanocrystals and D is the diameter of the nanocrystals. The contribution to the magnetic susceptibility, which is proportional to the specific surface area, is associated with the breaking of symmetry of the local environment of atoms near the surface of the nanocrystals.

4. CONCLUSIONS

In this work, it was found that the magnetic susceptibility of titanium monoxide TiO$_y$ in the temperature range from 300 to 1200 K depends not only on the degree of long-range order but also on the size of nanocrystals and the stoichiometry. It was revealed that there is an inversely proportional dependence of the Van Vleck paramagnetism on the size of titanium monoxide nanocrystals of the superstoichiometric composition. It was also found that the contribution from the Van Vleck paramagnetism to the magnetic susceptibility of the smallest nanocrystals is of the order of 1.00×10^{-6} emu/g, while all the samples are weak paramagnets, and the magnetic susceptibility varies from 0.90×10^{-6} to 3.05×10^{-6} emu/g with a change in the temperature depending on the stoichiometry, the structural state, and the size of particles. It was established that the magnetic susceptibility for ordered titanium monoxide nanocrystals consists of three contributions: the contribution to the magnetic susceptibility from the crystal with a maximum degree of order, the Van Vleck contribution from the degree of disorder, and the Van Vleck contribution proportional to the number of atoms located on the surface of the nanocrystals. It was assumed that the observed size effect is typical not only for titanium monoxide over the entire homogeneity region of this compound but also for paramagnetic nanocrystals of other compounds.

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