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Unusual Electronic State of Tin Dopant Atoms in Surface Layers of $NiTiO_3$

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Abstract—The ^{119}Sn Mössbauer spectra of polycrystalline $NiTiO_3$ samples impregnated with a solution containing 0.3 at % Sn^{4+} are evidence that annealing in H_2 converts tin into the state with the electron density $|\Psi(0)|^2$ on ^{119}Sn nuclei corresponding to “Sn^{3+}” ions. The stabilization of tin atoms in such an untypical formal oxidation state occurs at a depth of no more than 2–3 nm from the surface of titanate crystallites. It was revealed that the Sn^{3+} ions are not subjected to spin polarization even at temperatures considerably lower than the Néel temperature of $NiTiO_3$, which can be explained by their location in the Ni^{2+} positions. The formation of Sn^{3+} prevents the further reduction of tin to the divalent state and, hence, precludes localization of ^{119}Sn probe cations in positions at the interface.

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Recent ^{119}Sn Mössbauer study [1] has shown that the synthesis of $MgTiO_3$ through annealing coprecipitated titanium and magnesium hydroxides with Sn^{4+} additions in H_2 results in stabilization of tin ions in the oxidation state +2 on the crystallite surface. Thus, this double oxide with an ilmenite structure turned out to be suitable for studying chemical reactions of ^{119}Sn probe atoms at the solid–gas interface, in addition to simple oxides previously used for this purpose [2]. As compared with isostructural 3*d*-metal titanates, an advantage of $MgTiO_3$ is the extremely high stability of Mg^{2+} cations under both oxidative and reductive conditions, which makes it possible to vary in a wide range the type of reaction involving ^{119}Sn. The stability of $MgTiO_3$ is especially important in annealing in H_2. This annealing is necessary to convert Sn^{4+} cation into the divalent state suitable for completing the solid–gas interface. This specific feature is caused by the fact that Sn^{2+} has a sterically active lone electron pair, which allows these cations to occupy positions with a low coordination number energetically unfavorable for major (structure-forming) cations [2, 3].

Study of ^{119}Sn Mössbauer spectra recorded in situ in an H_2 atmosphere revealed two interesting effects, which were not observed for simple oxides:

(i) The Sn^{2+} that appeared on the surface of $MgTiO_3$ crystallites in the course of annealing in H_2 at 600°C immediately converted into the tetravalent state on contact with air. However, after further annealing in H_2 at 900°C, the Sn^{2+} ions ceased to be oxidized even on long-term exposure to air. Such passivation of Sn^{2+} ions was in sharp contrast with their behavior on the surface of MgO crystallites, for which an increase in annealing temperature did not affect the kinetics of Sn^{2+} oxidation.

(ii) In addition to passivation of Sn^{2+}, annealing in H_2 at 900°C led to the appearance of a new spectral component with the isomer shift $\delta_{295\,K}$ 1. 6 mm/s. The δ value, intermediate between the typical values for tetra- and divalent tin oxides ($\delta \sim 0$ and ~ 3 mm/s, respectively), can be assigned neither to β-Sn (δ = 2.56 mm/s) nor to a tin compound capable of forming as clusters on annealing $MgTiO_3$ in H_2.

To explain these features, it was suggested in [1] that Ti^{4+} ions are partially reduced, which leads to the appearance of delocalized electron density in their t_{2g} orbitals. As a result of interaction of electrons transferred from hydrogen with adsorbed O_2 molecules, the latter lose the ability to oxidize neighboring Sn^{2+} cations at room temperature. The subsequent appearance of the spectral component with an intermediate isomer shift value (and, hence, intermediate electron density $|\Psi(0)|^2$ on ^{119}Sn nuclei) corresponding to tin atoms in the oxidation state +3 was explained by an increase in the number of electrons transferred to the titanate with an increase in annealing temperature and by partial localization of their charge density on Ti^{4+} ions in the vicinity of Sn^{4+} ions.

Additional information on the Sn^{3+} dopant centers, as well as on the local environment of Sn^{2+} ions on the crystallite surface, could be provided by studying isostructural titanates containing magnetically active cations of one of the 3*d* metals rather than diamagnetic Mg^{2+} cations. This is caused by the fact that spin polarization of the electronic shell of tin leads to the appearance of magnetic hyperfine splitting in the ^{119}Sn spectrum; parameters of this splitting are specifically sensitive to the cationic environment of the probe atom. In the present paper, we report the results of studying the Mössbauer spectra of $NiTiO_3$ doped with ^{119}Sn. For this titanate, an antiferromagnet with the Néel temperature T_N = 23 K [4], Mössbauer parameters of $^{119}Sn^{4+}$ in the titanium substitution positions in the crystallite bulk are known [5]. This fact facilitates the interpretation of the ^{119}Sn Mössbauer spectra of samples with a more complicated distribution of probe cations with respect to the interface. In addition, nickel titanate is active in many catalytic reactions, in particular, in the CO oxidation by oxygen [6]. This allows using this reaction in future for elucidating the modifying action of different tin forms identified by Mössbauer spectroscopy.

EXPERIMENTAL

Nickel titanate samples free of tin were obtained by coprecipitation of equimolar amounts of Ni^{2+} and Ti^{4+} ions from aqueous hydrochloric acid solutions. A hot 2 M NaOH solution was used for precipitation, which ensured quantitative deposition of both cations [5]. The resulting hydroxide precursor was dried in air and annealed in a nitrogen flow at 1000°C for 2 h. X-ray powder diffraction analysis of the samples thus synthesized showed that they were single-phase and represented rhombohedral $NiTiO_3$ (space group $R\bar{3}$ [7]).

Synthesis of samples of $NiTiO_3$ doped with Sn^{4+} ions (0.3 at %, 92% enrichment in ^{119}Sn) located in the bulk of the crystallites (reference) has also involved the preparation of the hydroxide precursor. However, it turned out impossible to simultaneously introduce Sn^{4+} cations into the precursor because of the formation of soluble sodium stannate at high pH values. Therefore, an acidified $^{119}SnCl_4$ solution was poured dropwise onto the preliminarily coprecipitated nickel and titanium hydroxides washed with distilled water and dried in air at 100°C. Before impregnation, the precursor was moistened with a 10% ammonia solution for neutralization of the impregnation solution to form $SnO_2 \cdot nH_2O$. The resulting solid was heat treated under the same conditions as those used in synthesis of $NiTiO_3$ free of tin additions.

The $NiTiO_3$ samples with tin additives in the surface layers were obtained by the following procedure. A required amount of tin(IV) chloride, corresponding as in the above case to the overall tin concentration of 0.3 at %, was poured dropwise onto a powder of crystalline $NiTiO_3$ preliminarily moistened with an ammonia solution, The resulting solid was dried in air, and annealed first in an N_2 flow for 2 h at 450 or 900°C and then in an H_2 flow for 2 h at 350°C.

X-ray powder diffraction analysis showed that the presence of tin did not affect the X-ray powder diffraction patterns of the samples.

Table 1. Ratios of atomic concentrations $\frac{[Sn]}{[Ni]+[Ti]}$ in samples I and II as determined by XPS

Sample (annealing conditions)	$\frac{[Sn]}{[Ni]+[Ti]}$
I (N_2, 450°C, 2 h + H_2, 350°C, 2 h)	0.18
II (N_2, 900°C, 2 h + H_2, 350°C, 2 h)	0.07

Note: X-ray photoelectron spectra revealed that the particle surface in both samples was contaminated with products of hydrolysis of sodium silicate. Their formation is caused by the interaction of a concentrated alkali solution with the walls of glassware. These contaminations are not detected by X-ray powder diffraction and they cannot be removed by additional washing of the samples. Therefore, in the synthesis of samples intended for catalytic tests, hydroxide coprecipitation should be carried out by less alkaline solutions stored in Teflon bottles.

The Mössbauer spectra were recorded on a constant-acceleration spectrometer. The source was $Ca^{119m}SnO_3$ at 295 K. Isomer shifts were referenced to the $Ca^{119}SnO_3$ absorber at 295 K. The spectra were processed using routine software.

X-ray photoelectron spectra were recorded on an ESCALAB VG 220i-XL spectrometer. Samples were pressed into indium foil. Atomic concentrations were calculated from the integrated intensities of the $Sn3d_{5/2}$ (E_b = 486.6 eV), $Ti2p_{3/2}$ (E_b = 458.8 eV), and $Ni2p_{3/2}$ (E_b = 854.6 eV) peaks with inclusion of effective photoionization cross-sections and electron absorption in a matrix [8]. The excitation source was nonmonochromated MgK_α line ($h\nu$ = 1253.6 eV). High-resolution spectra were processed with the AVANTAGE program package supplied by the ThermoFischer Scientific Company.

RESULTS AND DISCUSSION

Our first experiments showed that the procedure analogous to that used for localization of tin on the surface of $MgTiO_3$ crystallites turned out to be inefficient in the case of $NiTiO_3$. In particular, we demonstrated that annealing a sample containing Sn^{4+} ions in the bulk of $NiTiO_3$ crystallites in H_2 for 2 h at 350°C did not lead to a change in ^{119}Sn Mössbauer spectra. The spectrum at 4.2 K was as previously dominated by the system of magnetic hyperfine splitting lines due to $^{119}Sn^{4+}$ ions in the Ti^{4+} substitution position [5]. This is evidence that the diffusion of Sn^{4+} ions in the titanate lattice at 350°C is too slow for a noticeable enrichment of the particle surface with probe cations. According to X-ray diffraction data, increasing temperature of annealing in H_2 to 600°C resulted in partial decomposition of $NiTiO_3$ yielding nickel metal and titanium

Table 2. ^{119}Sn Mössbauer parameters of two $NiTiO_3$ samples obtained under different conditions of introduction of tin dopant atoms (0.3 at %)

Sample (annealing conditions)	T_{rec}, K	δ, ±0.05 mm/s	Δ or 2ε, ±0.07 mm/s	H, kOe	Γ, ±0.1 mm/s	A, ±9%
I (N_2, 450°C, 2 h + H_2, 350°C, 2 h)	4.2	(1) 0.13	0.4*	–	1.2*	20
		(2) 1.7	–	–	1.5	80
	295	(1) 0.03	0.4	–	1.2*	31
		(2) 1.63	–	–	1.5	69
II (N_2, 900°C, 2 h + H_2, 350°C, 2 h)	4.2	(1) 0.25	+0.23	50 ± 2	1.0	32
		(2) 3.02	2.03	–	1.0	30
		(3) 0.11	0.46	–	1.0	38
	295	(1) 0.06	0.53	–	1.0	83
		(2) 2.84	1.8	–	1.1	17

* Values fixed upon fitting.

dioxide. It is noteworthy that the Mössbauer spectrum of this sample at 295 K showed as previously only the peak with the isomer shift δ = 0.08 mm/s, which was evidence of the persistence of tin atoms in the oxidation state +4.

For this reason, we tried another method to stabilize Sn^{2+} ions in surface positions, which was based on impregnation of polycrystalline $NiTiO_3$ with a tin(IV) chloride solution. The aim was to obtain samples containing Sn^{4+} ions at a rather small distance from the surface (owing to the use of relatively mild annealing conditions in N_2) so that these ions could return to it at moderate annealing temperature in H_2 (at which the titanate is still not decomposed). Two samples were prepared at different temperatures of annealing in N_2 (T_{anneal} = 450 and 900°C for sample I and II, respectively, τ = 2 h). Thus, Sn^{4+} ions in II could migrate to a larger depth from the surface than in I. Further annealing of I and II in H_2 were carried out under the same conditions (T_{anneal} = 350°C; τ = 2 h).

XPS analysis (Table 1) indicates that in both samples, the atomic concentration of tin in surface layers about 2–3 nm thick considerably exceeds the average value corresponding to the amounts of tin, nickel, and titanium $\left(\frac{[Sn]}{[Ni]+[Ti]} = 0.003\right)$, used in the synthesis. It is worth noting that the enrichment of the surface layer in I with tin turned out to be higher than in sample II, which is consistent with the lower temperature of the preliminary annealing of I in an N_2 atmosphere. However, XPS did not reveal differences in the electronic state of tin in two samples under consideration.

The ^{119}Sn Mössbauer spectra in Figs. 1 and 2 show that the hyperfine coupling parameters of ^{119}Sn in I and II are not equivalent (Table 2).

In the spectrum of I at 4.2 K (Fig. 1a), the strong peak with the isomer shift δ_1 = 1.7 mm/s close to that observed for ^{119}Sn in $MgTiO_3$ is worth noting. However, in the case of $NiTiO_3$, the appearance of this peak could be a priori caused by the reduction in H_2 of some surface nickel and tin cations to the metals yielding the alloy (which cannot be detected by X-ray powder diffraction). Moreover, ^{119}Sn atoms in nickel have a close isomer shift value (at 295 K, δ = 1.5 mm/s [9], which corresponds, with taking into account the second-order Doppler shift, to δ ~ 1.6 mm/s at 4.2 K). Therefore, to unambiguously interpret the spectrum of I, it is important that, below the Curie point T_C = 631 K of the nickel metal, the tin atoms should be subjected to spin polarization (according to [10], for the Ni–0.5% Sn alloy at T = 78 K, H = 19 kOe), which is not the case. In addition, the very low temperature of recording the spectrum shown in Fig. 1a does not allow one to explain the lack of the magnetic splitting structure by superparamagnetic relaxation of Ni moments. All these facts mean that the appearance of the compo-

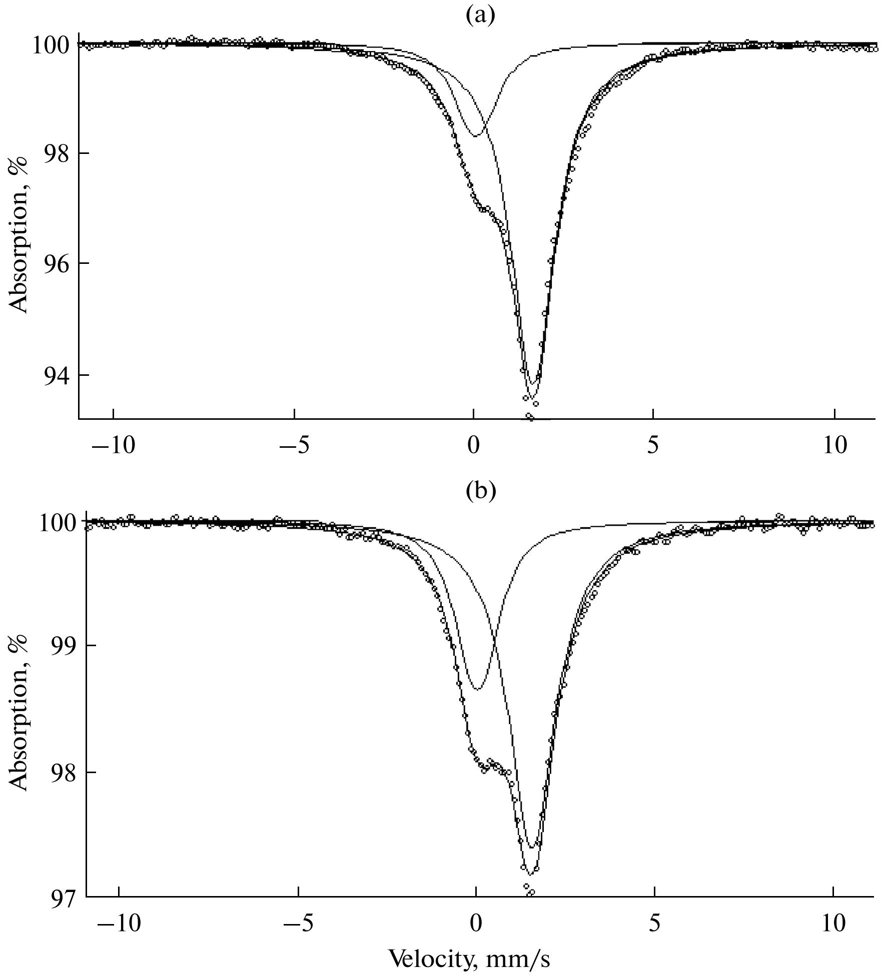

Fig. 1. ^{119}Sn Mössbauer spectra of sample I (annealing conditions: 2 h at 450°C in N_2 + 2 h at 350°C in H_2). T_{rec} is (a) 4.2 and (b) 295 K.

nent with $\delta_1 = 1.7$ mm/s in the spectrum of sample I is not related to the formation of the alloy;[1] rather, this is evidence of the stabilization of tin atoms in the untypical Sn^{3+} state, as was observed in $MgTiO_3$.

The spectrum in Fig. 1a also shows the resonance absorption at $\delta_2 = 0.13$ mm/s caused by tin atoms retaining the oxidation state +4. Analysis of this spectral component shows that it can be assigned to Sn^{4+} ions involved in quadrupole interactions of different strength corresponding to the mean quadrupole splitting $\langle\Delta_2\rangle = 0.4$ mm/s. This is also supported by the considerably larger width at half maximum of the components of the "averaged doublet" ($\Gamma_2 = 1.2$ mm/s) as compared with the Γ values for the spectrum of a thin reference sample of $CaSnO_3$ ($\Gamma_{ref} = 0.88$ mm/s).

With allowance for the high tin content in the near-surface layers of crystallites (Table 1), the distribution of electric field gradients corresponding to the distribution of Δ_2 values can be caused by fluctuations of interatomic distances for some Sn^{4+} ions with a different number of dopant cations in their local environment.

Measurements at 295 K showed (Fig. 1b) that the disappearance of magnetic order of Ni^{2+} moments upon the transition of $NiTiO_3$ into the paramagnetic state was not accompanied by narrowing of the Sn^{3+} peak. This means that its broadening at 4.2 K as compared with the spectrum of the reference absorber was of nonmagnetic origin and, hence, was caused by weak quadrupole interactions. Noteworthy is also a rather weak decrease in the spectral contribution of Sn^{3+} with an increase in temperature, which is comparable with

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[1] This conclusion was confirmed in studying a NiO sample containing 0.3 at % Sn^{4+} in the bulk of crystallites [11] after annealing in H_2. Indeed, according to X-ray powder diffraction evidence, this treatment at 600°C led to almost complete reduction of nickel oxide to the metal. Nevertheless, the ^{119}Sn Mössbauer spectra pointed to the persistence of tin atoms in the oxidation state +4 ($\delta \sim 0$ mm/s), most likely, as $NiSnO_3$ clusters [12]. Thus, this experiment demonstrated that the tin–nickel alloy did not form even under more favorable conditions than the annealing conditions for $NiTiO_3$.

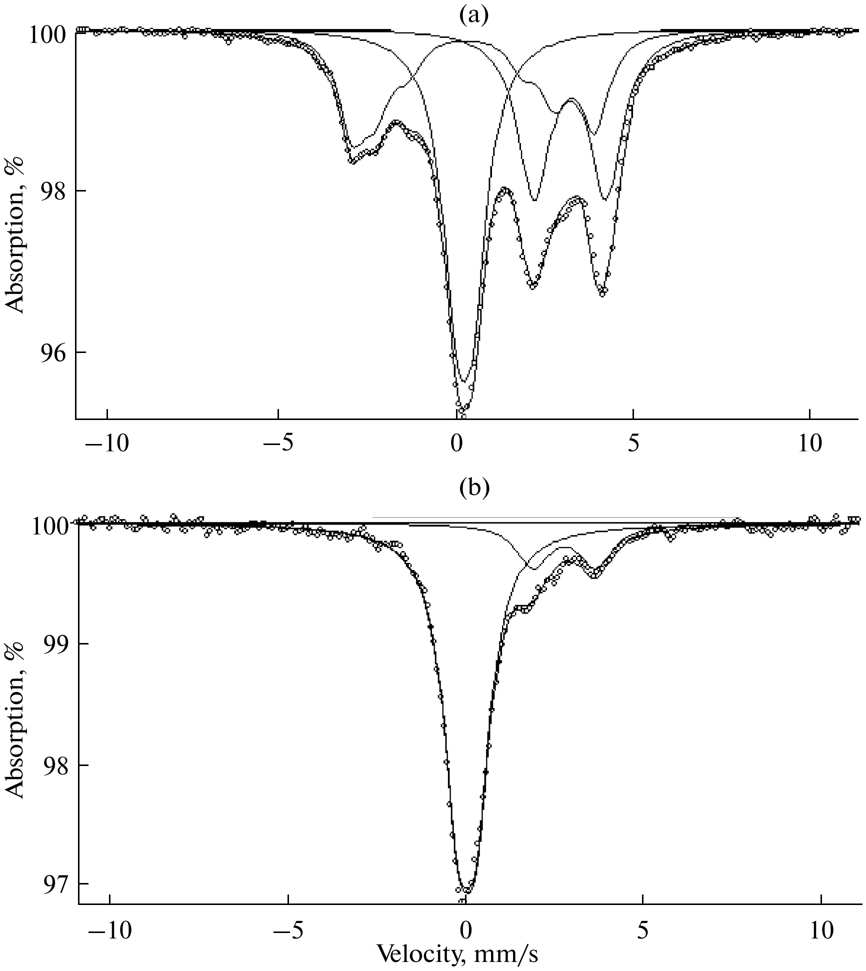

Fig. 2. ^{119}Sn Mössbauer spectra of sample II (annealing conditions: 2 h at 900°C in N_2 + 2 h at 350°C in H_2). T_{rec} is (a) 4.2 and (b) 295 K.

that observed for Sn^{4+} ions in Ti^{4+} substitution positions [5]. This result, indicative of the similarity of the coordination polyhedra of Sn^{3+} and Sn^{4+}, is another argument in favor of the existence of Sn^{3+} ions in the $NiTiO_3$ lattice, in spite of the δ_1 value untypical of the oxide matrix. Taking into account that the Ti^{4+} positions have a magnetically active cationic environment [5], the lack of magnetic hyperfine splitting in the spectrum at 4.2 K allows us to assume that the Sn^{3+} ions are located in Ni^{2+} positions. In this case, the completely occupied t_{2g} orbitals of Ni^{2+} are not able to induce spin polarization of the electronic shell of a neighboring coplanar tin cation, whereas 90-degree superexchange interactions involving the half-filled e_g orbitals are negligible. The idea that sample I contains Sn^{3+} ions (and corresponding Sn^{4+} parent cations) in the Ni^{2+} layer allows us to elucidate the reason for the increased electron density on Ni^{2+} cations in the vicinity of tin cations. Indeed, this effect can be explained by partial local compensation of the excess positive charge of Sn^{4+}.

To determine the conditions of formation of Sn^{3+} dopant centers, it is expedient to consider the ^{119}Sn Mössbauer parameters for sample II annealed in N_2 at a higher temperature (Table 2). The main specific feature of its spectrum at 4.2 K (Fig. 2a) is that it lacks the component corresponding to Sn^{3+} ions. Instead of this component, the spectrum shows the sextet of magnetic hyperfine splitting corresponding to Sn^{4+} ions in Ti^{4+} substitution positions in the bulk of crystallites ($H = 52.5$ kOe) [5], which was absent in the spectrum of I. In addition, the spectrum shows a quadrupole doublet with hyperfine splitting parameters ($\delta = 3.02$ mm/s, $\Delta = 2.03$ mm/s) typical of Sn^{2+} ions located on positions on the interface [1, 13]. Finally, the spectrum also shows a peak due to Sn^{4+} ions with nonpolarized spins ($\delta = 0.12$ mm/s, $H = 0$ kOe).

An increase in the recording temperature to 295 K led to the following changes (Fig. 2b):

(i) the disappearance of the magnetically split component caused by the $NiTiO_3$ transition into the paramagnetic state, which is quite expected;

(ii) the sharper decrease in the spectral contribution for Sn^{2+} than for Sn^{4+}, which is consistent with the sharper temperature dependence of the probability of recoilless transitions $f(T)$ for divalent tin.

Thus, comparison of information provided by the ^{119}Sn Mössbauer spectra of samples I and II allows us to draw the following conclusions.

(i) The fact that the $^{119}Sn^{3+}$ component is absent in the spectrum of II, although the layers of I and II examined by XPS contained comparable tin amounts, means that the formation of Sn^{3+} occurs at a very small distance from the interface. This result also points to a sharp difference in the tin concentration profiles in the near-surface layers of samples I and II.

(ii) The formation of Sn^{3+} prevents the further reduction of tin to the Sn^{2+} state (and, correspondingly, the distribution of doped tin over the positions on the interface).

(iii) The Sn^{2+} ions formed in sample II are not subjected to spin polarization at 4.2 K. This means that they should be located either in the first surface layer (111) of nickel cations or above the first surface layer (111) of Ti^{4+} cations. In this context, it is pertinent to recall that, in the case of $MnTiO_3$, the ^{119}Sn Mössbauer spectrum of surface $^{119}Sn^{2+}$ cations at $T \ll T_N$ was also represented by "nonmagnetic" (quadrupole) doublet [13].

(iv) Our additional experiments with sample II showed that Sn^{2+} ions almost does not interact with oxygen at room temperature, exactly as it was observed for $MgTiO_3$ [1] and $MnTiO_3$ [13]. This allows us to suggest that annealing these compounds in hydrogen leads to passivation of O_2 molecules adsorbed on them by a common mechanism.

Analysis of the Mössbauer spectra of ^{119}Sn in $NiTiO_3$ revealed the stabilization of tin dopant atoms in the oxidation state +3. XPS showed that Sn^{3+} ions are formed at a distance of no more than 2–3 nm from the surface of particles. The spectra of ^{119}Sn in antiferromagnetic $NiTiO_3$ revealed the absence of spin polarization of Sn^{3+} ions, which excludes their location in the Ti^{4+} substitution positions. Comparison of two samples obtained under different conditions for migration of Sn^{4+} ions into the near-surface layers showed that the formation of Sn^{3+} prevents the transition of tin into the divalent state and, hence, precludes the location of ^{119}Sn probe cations in positions at the interface.

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