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Magnetic behavior of $MnCo_2O_{4+\delta}$ spinel obtained by thermal decomposition of binary oxalates

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ABSTRACT

Manganese cobaltites $MnCo_2O_{4.62}$ and $MnCo_2O_{4.275}$ having a spinel structure were studied by measuring magnetization, AC susceptibility and by XANES spectroscopy. These compounds were synthesized by decomposition of the binary oxalate $Mn_{1/3}Co_{2/3}C_2O_4 \cdot 2H_2O$ in air at 220 and 500 °C, respectively. It was found that the differences in magnetic characteristics of these cation-deficient spinels are due mainly to variations in the degree of oxidation of manganese. It was shown that the complex oxide $MnCo_2O_{4.62}$ formed right after decomposition of the binary oxalate contains about 5×10^{-4} mass% metallic cobalt, which determines the dependence of magnetic susceptibility χ on the magnetic field at 300 K. The magnetic transition peculiar to the stoichiometric spinel $MnCo_2O_4$ at 183 K decreases to 167.5 K for $MnCo_2O_{4.275}$ and 67.5 K for $MnCo_2O_{4.62}$.

1. Introduction

Transition metal cobaltites having a spinel structure ACo_2O_4 (A=Mn, Ni, Zn) possess various functional properties defining their application as materials for sensors, fuel cell electrodes, electrical catalysts, etc. [1–4]. Those compounds are currently synthesized by low-temperature techniques allowing to obtain the final products in the nanocrystalline or ultradisperse states. Spinels synthesized in this way have a very developed surface and electrocatalysts possess an extremely high specific surface energy. The low-temperature methods of synthesis are based on decomposition of precursors—preliminarily deposited hydroxides or salts of cobalt and other transition metals—at 400 °C or lower temperatures (Ref. [2] and references therein). Nitrates, oxalates, acetates of the corresponding metals, etc., are usually used as salts.

In the works [5,6] we studied the conditions of formation of cobaltites ACo_2O_4 (A=Mn, Zn) in the form of wire-like whiskers or spheroids by thermal decomposition of presynthesized binary oxalates of cobalt and manganese (zinc) $A_{1/3}Co_{2/3}C_2O_4 \cdot 2H_2O$ in air. The chemical composition and the microstructure of the decomposition products were examined. It was found in particular that spinel phases with different composition are formed depending on the temperature of decomposition of oxalates $A_{1/3}Co_{2/3}C_2O_4 \cdot 2H_2O$. The cubic spinel begins to form at about 200 °C. That phase has an extremely low crystallinity and an excessive content of oxygen: $ACo_2O_{4+\delta}$ ($\delta > 0$). Therefore cobalt or manganese (or a part of these elements) in this phase have a higher valence as compared with the stoichiometric spinel ACo_2O_4. As the temperature rises further, this phase gradually loses oxygen and turns to the ACo_2O_4 spinel. An increase of temperature to 700 °C results in improved crystallinity of the cubic phase and an enhanced parameter of the cubic cell. The increase of the unit cell parameter with temperature is due to variations in the chemical composition, i.e. reduction of some cobalt or manganese. These findings are in agreement with data (Ref. [2] and references therein), according to which the manganese cobaltite $MnCo_2O_{4+\delta}$ synthesized at low temperatures has the structure of the cation-deficient spinel with enhanced oxygen content.

The foregoing suggests that the magnetic characteristics of the spinel $MnCo_2O_{4+\delta}$ depend on the value of δ determined by the conditions of synthesis. The magnetic properties of $MnCo_2O_4$ were reported in a number of studies. The ferromagnetism of this spinel was first reported by Lotgering [7] who examined a specimen synthesized by decomposition of oxalates at 500 °C. Wickham and Croft [8] have investigated solid solutions $Co_{3-x}Mn_xO_4$ with a cubic spinel structure ($0 \leqslant x \leqslant 1.2$) obtained by solid-phase sintering of oxide mixtures in air at 1000 °C ($x > 0.5$) and 800 °C ($x \leqslant 0.5$). The following distribution of cations in the structural sites was

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deduced based on magnetic measurements: $Co^{2+}[Co^{3+}_{2-x}Mn^{3+}{}_x]O_4$. For $MnCo_2O_4$, the Neel temperature (T_N) is ~187 K. Using data Lotgering [7], Blasse [9] made another conclusion about the distribution of cations: $Co^{2+}[Co^{2+}Mn^{4+}]O_4$. Vainshtein et al. [10] also interred based on X-ray absorption spectra that the charge of manganese in $MnCo_2O_4$ is close to +4. Mixed oxidation states of cobalt (Co^{2+} and Co^{3+}) and manganese (Mn^{3+} and Mn^{4+}) in solid solutions $Co_{3-x}Mn_xO_4$ ($0 \leqslant x \leqslant 1$) obtained by thermal decomposition of nitrates at 400 °C were reported [1].

At present, the magnetic properties of the $Co_{3-x}Mn_xO_4$ system attract particular interest owing to unusual hysteresis phenomena and magnetization processes, as well as magnetic behavior of $MnCo_2O_4$ in the nanocrystalline and thin-film states [11–14]. The information on the influence of methods of synthesis and especially the temperature of synthesis on the magnetic properties of nonstoichiometric specimens $MnCo_2O_{4+\delta}$ is not available. At the same time, for spinels of other compositions, in particular, $NiMn_2O_{4\pm\delta}$ [15], oxygen stoichiometry was found to exert a certain effect on magnetic characteristics.

In this work, we studied the magnetic properties of two manganese cobaltites $MnCo_2O_{4+\delta}$ having different composition ($\delta = 0.275$ and 0.62). To evaluate the degrees of oxidation of Mn and Co, we examined the near-edge fine structure of X-ray absorption using XANES spectroscopy.

2. Experimental

The binary dihydrate of Mn and Co oxalate with the composition $Mn_{1/3}Co_{2/3}C_2O_4 \cdot 2H_2O$ was prepared from aqueous 0.2 M solutions of cobalt and manganese sulfates ASO_4 by deposition with oxalic acid $H_2C_2O_4$. Element analysis for the content of Mn and Co in the examined specimens was carried out employing atomic adsorption spectroscopy in "acetylene-air" flame on a Perkin-Elmer setup and atomic emission on an inductive-plasma spectrum analyzer JY-48. The oxygen content of the compounds was established with the use of thermogravimetric (TG) analysis based on the loss of mass in the process of reduction of compounds during calcination in air to 800 °C.

The microstructure and the sizes of particles of the $Mn_{1/3}Co_{2/3}C_2O_4 \cdot 2H_2O$ oxalate and manganese cobaltites $MnCo_2O_{4+\delta}$ were determined with a scanning electron microscope Tesla BS-301. Images were obtained by surveying in inversely mapped electrons by SEM with 1000 and 5000 power magnification.

Magnetic measurements were performed on a SQUID magnetometer MPMS-XL-5 produced by QUANTUM DESIGN. Temperature was varied from 2 to 300 K. Controlled magnetic field strength H was set to 50 kOe. Measurements were carried out when a specimen was cooled in zero (zero-field cooling (ZFC)) and measured (field cooling (FC)) magnetic field. A specimen was first cooled in zero field to 2 K, then magnetization M was measured when it was heated to 300 K (ZFC mode). After that magnetization was measured when the specimen was cooled from 300 to 2 K (FC mode). From these measurements we found the static magnetic susceptibility $\chi = M/H$, whereas the AC susceptibility measurement technique was used to determine the real χ' and imaginary χ'' components of dynamic susceptibility for the amplitude value of variable magnetic field 4 Oe.

XANES spectra of Co–K and Mn–K were measured in the Center of Synchrotron Radiation at the Institute of Nuclear Physics SB RAS (Novosibirsk). A monoblock cutting monocrystal Si(III) was used as a two-crystal X-ray monochromator, and an Ar/He ionization chamber served as a monitoring detector.

3. Results and discussion

3.1. Synthesis and characterization

As was noted in the Introduction, the content of oxygen in the manganese cobaltite $MnCo_2O_{4+\delta}$ depends essentially on the temperature, at which the specimens are synthesized. Three specimens of manganese cobaltite $MnCo_2O_{4+\delta}$ with different values of δ were prepared in this work. The first specimen was obtained by decomposition of $Mn_{1/3}Co_{2/3}C_2O_4 \cdot 2H_2O$ in air at 220 °C for 6 h, the second specimen—at 500 °C for 4 h, and the third—at 750 °C for 4 h. X-ray diffraction patterns of all these cobaltites are given in Fig. 1. It is seen that all the decomposition products are characterized by the cubic spinel structure and a different degree of crystallinity. The cubic cell parameter a of $MnCo_2O_4$ (750) was found to be 8.224(2) Å. It is difficult to determine precise parameters for specimens obtained at 220 and 500 °C. Considering that X-ray diffraction peaks of these compounds are shifted towards greater angles in comparison with $MnCo_2O_4$ (800), it may be asserted that the unit cell sizes of the spinel decrease when the temperature of synthesis lowers.

To determine the content of oxygen, TG studies of specimens obtained at 220 and 500 °C were carried out. Fig. 2 presents data of TG examination of the $MnCo_2O_4$ (220) specimen in air. The reduction in the mass of the specimen in the range 80–200 °C is indicative of isolation of H_2O absorbed during storage, and at 280–650 °C—of isolation of oxygen. Based on the variation of the

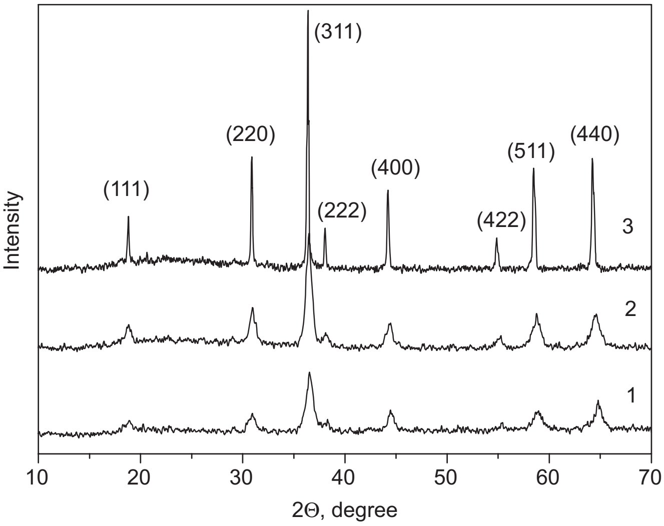

Fig. 1. X-ray diffraction patterns of $MnCo_2O_{4+\delta}$: (1) (220), (2) (500), (3) 750 °C. 3 is indexed as a cubic spinel Fd3m (227).

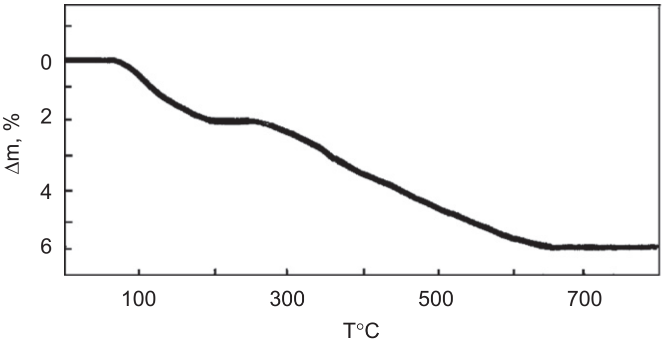

Fig. 2. TG curve of $MnCo_2O_4$ (220) in air at a heating rate of 10 °C min^{-1}.

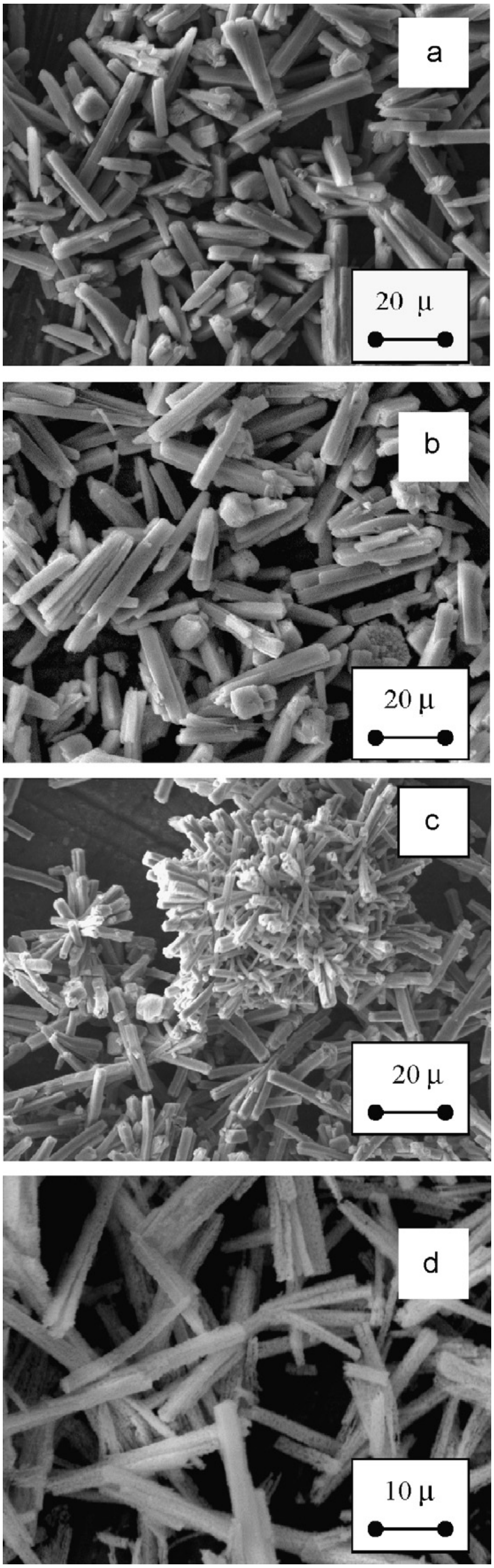

Fig. 3. SEM micrographs of (a) $Mn_{1/3}Co_{2/3}C_2O_4 \cdot 2H_2O$ and (b–d) $MnCo_2O_{4+\delta}$ whiskers; decomposition temperature of (b) 220, (c) 500 and (d) 800 °C.

specimen's mass in the interval 280–650 °C it was calculated that the composition of the cobaltite corresponds to the formula $MnCo_2O_{4.62}$. Excessive oxygen results in the formation of vacancies in the cationic subsystem and in enhanced mean degree of oxidation of Mn and Co (+3.07). The chemical composition of this spinel phase without allowance for the distribution of cations in structural sites may be expressed by the formula $Mn_{0.87}Co_{1.732}O_4$. According to an analogous study of the specimen synthesized at 500°C, the content of oxygen in it corresponds to the formula $MnCo_2O_{4.275}$ ($Mn_{0.936}Co_{1.871}O_4$) and the mean degree of oxidation of Mn and Co is +2.85.

The binary oxalate $Mn_{1/3}Co_{2/3}C_2O_4 \cdot 2H_2O$ prepared by deposition with oxalic acid under the described above technique has the form of fibers (whiskers). In conformity with SEM studies (Fig. 3), the products of decomposition of $Mn_{1/3}Co_{2/3}C_2O_4.2H_2O$ retain this microstructure during heating in air in spite of changes in the chemical composition:

$$Mn_{1/3}Co_{2/3}C_2O_{4.2}H_2O \rightarrow Mn_{1/3}Co_{2/3}C_2O_4$$
$$\rightarrow MnCo_2O_{4+\delta} \rightarrow MnCo_2O_4$$

These $MnCo_2O_4$ fibers are 2–4 μm in diameter, 15–40 μm in length and do not change considerably with temperature. The particles exhibit a porous structure reflecting the procss of isolation of H_2O, CO and CO_2 from the binary dihydrate of Mn–Co oxalate, which is well seen on the specimen upon sintering at 800 °C (Fig. 3d).

3.2. *Magnetic properties of $MnCo_2O_{4.275}$*

Temperature dependences of magnetic susceptibility χ for the $MnCo_2O_{4.275}$ spinel synthesized at 500 °C in ZFC and FC modes in magnetic field 0.5 kOe are depicted in Fig. 4. Below 180 K, χ rises abruptly and the $\chi(T)$ curves for the specimen cooled in zero field (ZFC mode) and measured field (FC mode) diverge at $T \leqslant 165$ K. Measurements in the zfc mode show that the $\chi(T)$ dependence exhibits a maximum at 157 K. The character of changes in susceptibility in the considered magnetic transition is analogous to that described in [12] for $MnCo_2O_4$ synthesized from oxides at 1000 °C. However the point of magnetic transformation for $MnCo_2O_{4.275}$ (167.5 K) is obtained from the plot of $d\chi/dT$ versus T (Inset on Fig. 4) is somewhat lower than T_N for the stoichiometric spinel $MnCo_2O_4$ (183 K [12]). In the region of low temperatures, the zfc and FC curves $\chi = f(T)$ exhibit a number of

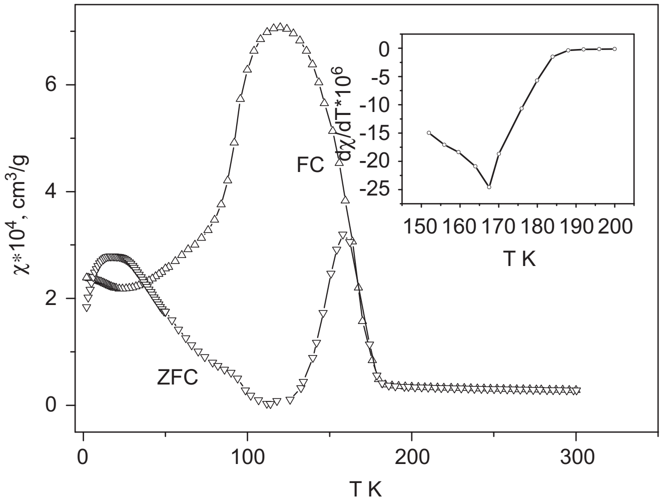

Fig. 4. Temperature dependence of χ for $MnCo_2O_4$ (500) in magnetic field 0.5 kOe. Inset: dependence of $d\chi/dT$ for $MnCo_2O_4$ (500).

peculiarities. So, the ZFC susceptibility increases below 120 K and there is a broad maximum at ~18 K on the curve in addition to that at 157 K. The FC dependence exhibits a maximum at 120 K and a minimum at ~15 K. We suppose that the observed anomalous behavior of the $MnCo_2O_{4.275}$ spinel at low temperatures may be due to the second magnetic phase formed on the first stage of decomposition of the precursor.

The inset in Fig. 5 displays magnetization measurement results for $MnCo_2O_{4.275}$ as a function of magnetic field at 2 and 14 K. The measurements were performed using specimens cooled in the ZFC mode when the magnetic field was decreased from 50 kOe. Both at 2 and 14 K the σ versus H curves are not linear, and magnetization does not reach saturation in the magnetic field 50 kOe. Residual magnetization is 1.25 cm^3/g at 2 K and approaches zero at 14 K.

The temperature dependence of inverse magnetic susceptibility $1/\chi$ (Fig. 5) for $MnCo_2O_{4.275}$ above 230 K obeys the Curie-Weiss law:

$$\chi = C/(T - \theta),$$

where χ is the molar susceptibility, C is the Curie constant ($C_{\mathrm{exp}} = 4.07\,\mathrm{cm^3\,K/mole}$), and θ is the Weiss temperature ($\theta = -329.5\,\mathrm{K}$). The molar magnetic susceptibility χ_{mol} and the Curie constant C_{exp} are related to the formula $Mn_{0.936}Co_{1.872}O_4$ reflecting the cation-deficient structure of the spinel formed at 500 °C.

In order to evaluate the valence state of Co and Mn and their distribution in tetrahedral and octahedral sites, we compared the experimental C_{exp} and calculated C_{calc} values of the Curie constant. The C_{calc} constant was found in accordance with the combination of Co and Mn cations described in [8]. According to [8], the tetrahedral sites of the $Co_{3-x}Mn_xO_4$ spinel are occupied by cobalt in the form of Co^{2+} cations, whereas in the octahedral site there are trivalent cations of cobalt and manganese: $Co^{2+}[Co_{2-x}{}^{III}Mn_x{}^{3+}]O_4$. With account for these data, we deduced the following formula for $MnCo_2O_{4.275}$: $Co^{2+}_{0.936}[Co^{III}_{0.936}Mn^{3+}_{0.421}Mn^{4+}_{0.515}]O_4$, where Co^{III} is a low-spin cobalt cation ($S = 0$), and Co^{2+} and Mn^{3+} are high-spin cations (spins S are 1.875 and 3 cm^3 K/mole, respectively). The calculated Curie constant C_{calc} for this composition is 3.984 cm^3 K/mole, which is close to the experimental value (4.07 cm^3 K/mole). This favors the inference that the $MnCo_2O_{4.275}$ phase is formed due to oxidation of manganese when the content of oxygen increases. The average degree of oxidation of cations in this phase is +2.85, i.e. it is higher than in the stoichiometric compound $MnCo_2O_4$ (+2.67). The appearance of Mn^{4+} cations in octahedral sites is the most probable reason for the decreased T_N of this cobaltite in comparison with the stoichiometric $MnCo_2O_4$. It is noteworthy that the absence of data on the composition and quantity of the impurity phase found in magnetic measurements at low temperatures may introduce certain corrections in the composition of the spinel.

3.3. Magnetic properties of $MnCo_2O_{4.62}$

Magnetic susceptibility measurement results for the $MnCo_2O_{4.62}$ spinel in the temperature interval 2–300 K in the FC and ZFC modes in magnetic field 0.5 kOe are given in Fig. 6. The inset in Fig. 6 presents dynamic magnetic susceptibility (χ') versus temperature.

According to the data obtained, the $MnCo_2O_{4.62}$ spinel, as distinct from $MnCo_2O_{4.275}$, contains one magnetic phase with a much lower transition temperature. The curves measured in ZFC and FC modes begin to diverge at 65 K (Fig. 5). In the ZFC measurements in magnetic field 0.5 kOe, susceptibility exhibits a maximum at 46 K. In measurements in magnetic field 10 kOe, the

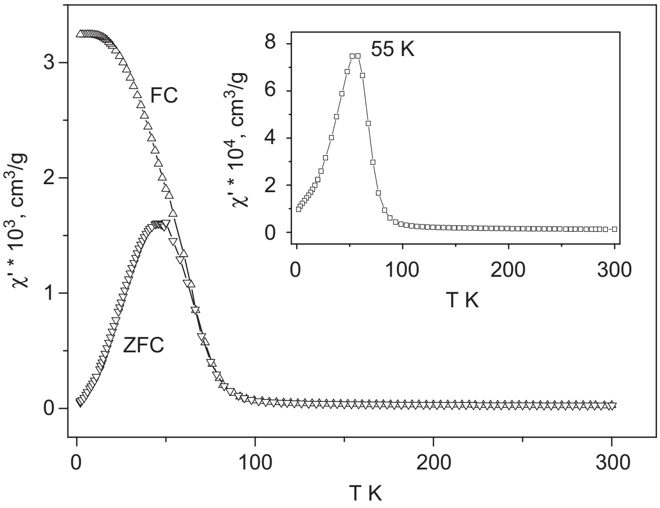

Fig. 6. Temperature dependence of field-cooled (FC) and zero field cooled (ZFC) susceptibility χ of $MnCo_2O_4$ (220). Inset: temperature dependence of χ' for $MnCo_2O_4$ (220).

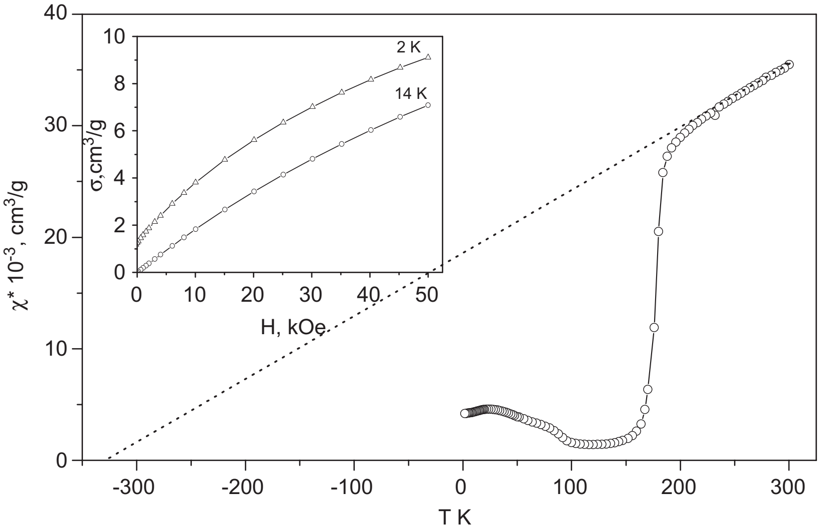

Fig. 5. Dependence of $1/\chi = f(T)$ for $MnCo_2O_4$ (500) in the magnetic field 0.5 kOe. Inset: dependence of magnetization σ on magnetic field for $MnCo_2O_4$ (500) at 2 and 14 K.

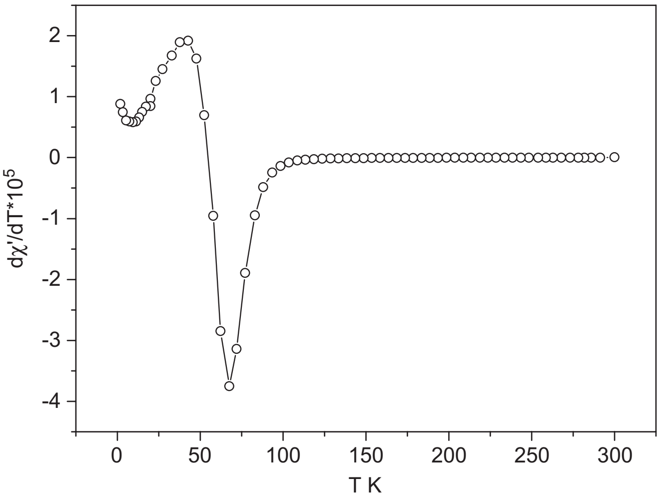

Fig. 7. Temperature dependence of $d\chi'/dT$ for $MnCo_2O_4$ (220).

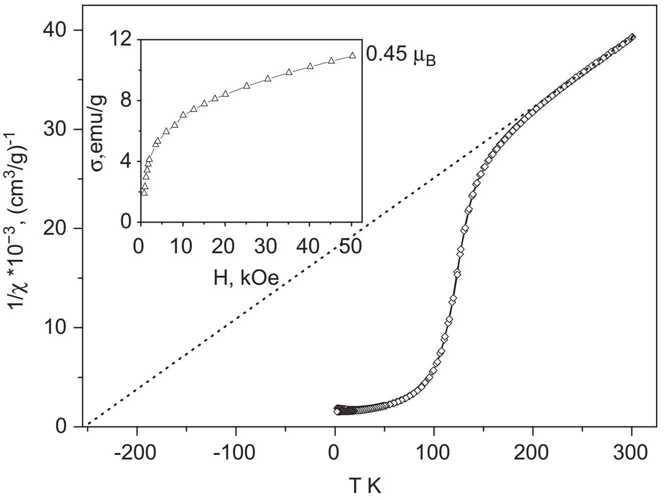

Fig. 8. Dependence of $1/\chi = f(T)$ in the magnetic field 10 kOe for $MnCo_2O_4$ (220). Inset: dependence of magnetization σ on magnetic field for $MnCo_2O_4$ (500) at 2 K.

maximum is displaced to 20 K (not shown). When temperature decreases, susceptibility measured during the FC procedure increases and below 20 K reaches a plateau. Attention is drawn to the large difference between field-cooled and zero-field-cooled magnetization for $MnCo_2O_{4.62}$, which is indicative of high magnetocrystalline anisotropy of this compound. The maximum on the temperature AC susceptibility χ' (inset in Fig. 6) corresponds to 55 K. The plot of $d\chi'/dT$ versus T exhibits sharp minimum at 67.5 K (Fig. 7). This temperature is assumed to be T_N of this cobaltite.

The dependence between magnetization M and applied magnetic field H at 2 K (inset in Fig. 8) does not reach saturation in the field 50 kOe (measurements were performed on a ZFC specimen when the field was decreased from 50 to 0 kOe).

Above 230 K, χ of $MnCo_2O_{4.62}$ follows the Curie-Weiss law with the Curie constant $C_{exp} = 3.04\,cm^3\,K/mole$ and the Weiss temperature $\theta = -250\,K$ (Fig. 8). Based on the chemical composition of $Mn_{0.866}Co_{1.732}O_4$, we derived the formula reflecting the oxidation states of cations and their distribution in the structural sites of the spinel: $Co^{2+}_{0.66}[Mn^{4+}_{0.866}Co^{III}_{1.072}]O_4$. The calculated Curie constant C_{calc} for this composition is $2.86\,cm^3\,K/mole$. A higher value of C_{exp} may be explained by incomplete freezing of the orbital component of the Co^{2+} cation, which leads to an enhanced effective magnetic moment as compared with the purely spin value. Thus, the cobaltite formed at 220 °C contains by about 10% more Co^{3+} cations and 100% Mn^{4+} cations as compared with $CoMn_2O_{4.275}$.

Compounds with a spinel structure belong to collinear ferrimagnetics. For such compounds it is possible to verify rather reliably presumed distribution of cations in structural sites by measuring spontaneous magnetization at temperatures close to 0 K. Provided that magnetic moments of tetrahedral high-spin Co^{2+} ($e_g^4t_{2g}^3$) cations interact antiferromagnetically with magnetic moments of octahedral $Mn^{4+}(t_{2g}^3e_g^0)$ cations, the $Co^{2+}_{0.66}[Mn^{4+}_{0.866}Co^{III}_{1.072}]O_4$ spinel should have a spontaneous moment 0.62 μ_B at 0 K. According to the data presented in the inset in Fig. 8, magnetization of $MnCo_2O_{4.62}$ at 2 K and 50 kOe is 0.45 μ_B. Taking into account that there is no saturation of magnetization in the measured interval of magnetic field, deviations from the calculated spontaneous moment may be considered reasonable.

The measurements performed showed that the $MnCo_2O_{4.62}$ spinel, as distinct from $MnCo_2O_{4.275}$, is characterized by a small dependence of magnetic susceptibility χ on applied magnetic field (Fig. 9) at 300 K in the region to ~10 kOe. Our version of appearance of the ferromagnetic component in $MnCo_2O_{4.62}$ at 300 K is based on possible presence of metallic cobalt in the specimen. The emergence of cobalt in the complex oxide $MnCo_2O_{4.62}$ may be attributed to the process of decomposition of the $Mn_{0.33}Co_{0.67}C_2O_4 \cdot 2H_2O$ oxalate in air, during which this element is partially reduced to the metallic state. This mechanism of destruction was established in the cause of thermal treatment of cobalt oxalate in argon [16] and nitrogen [17] flow. We found no available evidence in the literature for the reduction of cobalt to metal during decomposition of oxalate in air. Apparently, this is rather difficult to do with conventional methods since the content of metallic cobalt in the $MnCo_2O_{4.62}$ specimen found from spontaneous magnetization value at 300 °C is as small as 5.3×10^{-4} mass%. In view of a small content of metallic cobalt, it produces an insignificant effect on magnetic susceptibility in the measured temperature range and the Curie–Weiss equation parameters. As a result of calcination in air at higher temperatures, cobalt oxidizes and the ferromagnetic component in $MnCo_2O_{4.275}$ disappears.

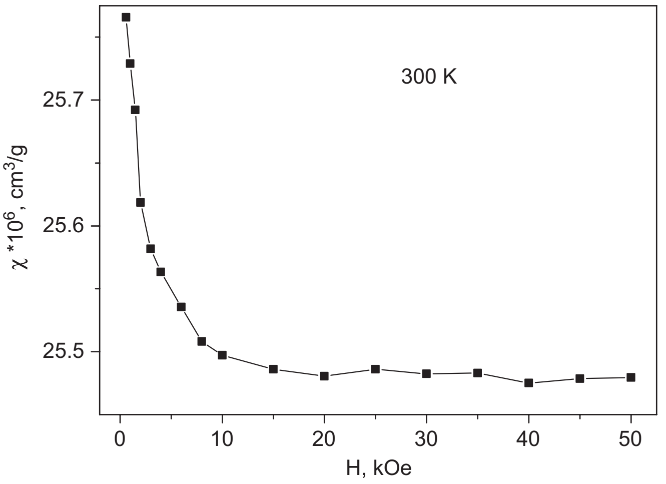

Fig. 9. Dependence of χ on magnetic field for $MnCo_2O_4$ (220) at 300 K.

3.4. XANES spectroscopy

In order to determine the degrees of oxidation of Co and Mn, we have carried out spectroscopic studies of the short-range fine structure of X-ray absorption (XANES spectroscopy) of the compounds $MnCo_2O_{4.275}$ and $MnCo_2O_{4.62}$. The fine near-threshold structure of absorption XANES spectra is very sensitive both to the electronic state of the absorbing atom and its local neighborhood. This method allows to examine in particular the topology of the atom environment and establish the degrees of oxidation of elements by comparison with reference compounds. To evaluate the oxidation state of cobalt and manganese in $MnCo_2O_4$, cobalt CoO and Co_3O_4 and manganese MnO, Mn_2O_3 and MnO_2 oxides were studied under the same conditions.

Figs. 10 and 11 display Co–K and Mn–K XANES spectra of $MnCo_2O_{4.275}$ and $MnCo_2O_{4.62}$ and reference compounds CoO, Co_3O_4 and MnO, Mn_2O_3, MnO_2, respectively. Absorption XANES spectra of these compounds are characterized by a sharp intensive peak and several peaks of smaller intensity. The electronic transitions from 1s to unoccupied nd states are related to the so-called pre-edge peaks located before the basic absorption peaks. Their intensity and location on the energy scale speak of the element's coordination and state of oxidation, respectively. If the coordination environment has a center of inversion, the electronic 1s→nd transitions turn out to be forbidden and the pre-edge peaks on the spectra are absent. Along with octahedral sites, there are positions with less symmetrical tetrahedral environment in the spinel structure. Therefore, 1s→3d transitions are partially permitted. An increase in the degree of oxidation of an element leads to a displacement of the pre-edge peak to the high-energy region. If the element has a mixed valence, the pre-edge peak widens or bifurcates.

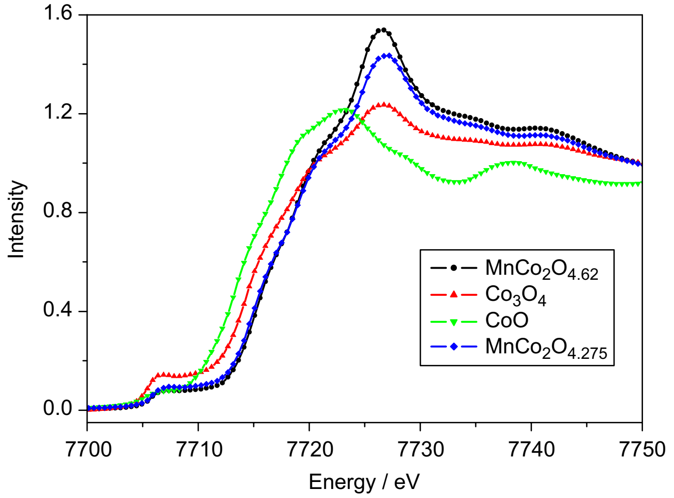

Fig. 10. Co–K XANES spectra of $MnCo_2O_{4.275}$ and $MnCo_2O_{4.62}$ and reference compounds CoO and Co_3O_4.

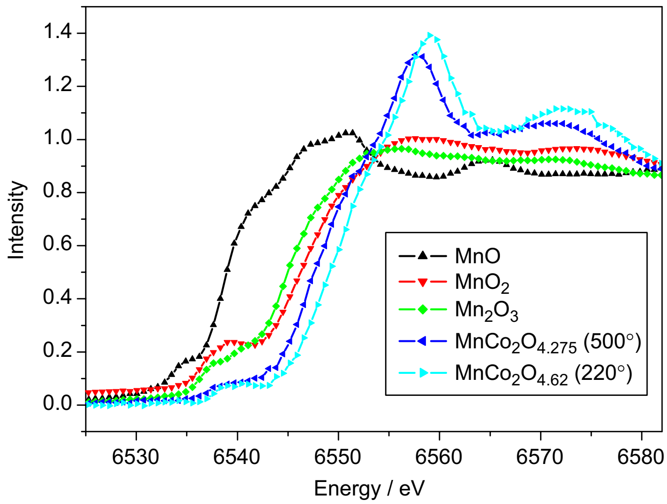

Fig. 11. Mn–K XANES spectra of $MnCo_2O_{4.275}$ and $MnCo_2O_{4.62}$ and reference compounds MnO, Mn_2O_3 and MnO_2.

Conclusions about the state of oxidation of cobalt in $MnCo_2O_{4.275}$ and $MnCo_2O_{4.62}$ were made from the pre-edge K-peak, whose location usually corresponds to the energy values about 7709–7712 eV [18]. According to Fig. 10, the pre-edge peak has the smallest intensity in the CoO spectrum. This is quite natural since this oxide has the NaCl structure and cobalt is in the symmetrical environment. The pre-edge peaks in the spectra of other transition-metal monoxides are also of inconsiderable intensity [19]. The greatest intensity of the pre-edge peak is observed in the Co_3O_4 spectrum (Fig. 10), which is attributed to the tetrahedral environment of Co^{2+}cations. The spectra of Fig. 10 show that the Co K-edge XANES in Co_3O_4, $MnCo_2O_{4.275}$ and $MnCo_2O_{4.62}$ have a larger width of pre-edge features as compared with CoO. The considered peaks are characterized by a complicated structure brought about by mixed valence of cobalt in all these compounds. It follows from Fig. 10 that Co–K XANES spectra in $MnCo_2O_{4.275}$ and $MnCo_2O_{4.62}$ are almost identical. Therefore the states of oxidation of cobalt in these compounds are close. Thus, the XANES spectra allow us to assert that cobalt in the two examined spinels is in a mixed (+2 and +3) state. A somewhat smaller intensity of the pre-edge peak for the specimen synthesized at 220 °C is likely to be due to a greater structure imperfection in the tetrahedral sites of the spinel.

Mn K-edges of XANES spectra of MnO, Mn_2O_3, MnO_2, $MnCo_2O_{4.275}$ and $MnCo_2O_{4.62}$ are depicted in Fig. 11. Attention is drawn to a smaller intensity of pre-edge peaks of complex oxides with a spinel structure as compared with simple manganese oxides. This indicates that manganese in the spinel has a higher-symmetry environment, and in particular that it occupies octahedral sites. Mn pre-edge peaks, K-edges and the basic absorption peak for $MnCo_2O_{4.62}$ are shifted in the high-energy region in comparison with $MnCo_2O_{4.275}$, which testifies to a higher degree of oxidation of manganese in the former compound. It is evident from comparison with Mn_2O_3 and MnO_2 spectra that the content of Mn^{4+} cations is higher in $MnCo_2O_{4.62}$ than in $MnCo_2O_{4.275}$. This inference supports the data obtained by interpreting magnetic properties measurements for these two compounds. It is also typical that a similar displacement of the basic peak in XANES spectra of $MnCo_2O_4$ was recorded for the specimens prepared by decomposition of nitrates and chlorides of Co and Mn [20].

4. Conclusions

In accordance with the above results, cobaltites $MnCo_2O_{4.275}$ and $MnCo_2O_{4.62}$ differ in the degrees of oxidation of manganese: in the former cobaltite the Mn^{4+}/Mn^{3+} ratio is ~5/4, whereas the latter compound contains manganese only as Mn^{4+}. The concentration of Co^{3+} cations with respect to Co^{2+} in the more oxidized phase $MnCo_2O_{4.62}$ increases by approximately 10%. These findings are crucial in analyzing the differences in the properties of these nonstoichiometric spinels and the stoichiometric spinel $MnCo_2O_4$. The considerable decrease in T_N of $MnCo_2O_{4.62}$ in comparison with $MnCo_2O_{4.275}$ and $MnCo_2O_4$ is associated with substantial structure imperfection in the cationic sublattice of this spinel and substitution of Mn^{4+} for Mn^{3+} cations. The imperfect spinel $MnCo_2O_{4.62}$ possesses ferrimagnetism caused by antiferromagnetic exchange between tetrahedral Co^{2+} cations and octahedral Mn^{4+} cations. The peculiarities on ZFC and FC dependences $\chi = f(T)$ for $MnCo_2O_{4.275}$ below 120 K may be due to variations in the composition of the magnetic phase in the process of heat-treatment temperature increase and the presence of impurities. The absence of the spontaneous moment for $MnCo_2O_{4.275}$ at 14 K apparently points to the presence of the compensation point on the temperature dependence of spontaneous magnetization. Complete removal of the impurity phase calls for temperatures above 600 °C.

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