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Spin-reorientational transitions in low-doped $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ manganites: the evidence of an inhomogeneous magnetic state

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Abstract

A study of crystal structure, elastic, and magnetic properties of low-doped $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x \leq 0.15$) perovskites has been carried out. The ferromagnetic component is shown to increase under hole doping and, simultaneously, the temperature of the orbital order–disorder phase transition decreases. The mechanism of the concentrational transition from a weak ferromagnetic state ($x = 0$) to a ferromagnetic one ($x > 0.15$) is discussed using a two-phase model, according to which the samples consist of weak ferromagnetic and ferromagnetic phases exchange coupled at their boundary. It is found that interaction between different magnetic phases leads to spin reorientation which takes place for $0.06 \leq x \leq 0.1$ compounds around $T_{\text{eff}} \sim 9$ K. In the temperature range from 5 to 20 K, metamagnetic behaviour is revealed for the $\text{Nd}_{0.92}\text{Ca}_{0.08}\text{MnO}_{2.98}$ sample. H versus T as well as T versus x magnetic phase diagrams, which are characterized by the missing of a canted phase, are proposed. The appearance of orientational transitions is explained on the basis of a magnetic analogue of the Jahn–Teller effect taking into account that the magnetic moments of Nd ions are ordered parallel to the moments of Mn ions in the ferromagnetic phase, and opposite to the direction of the weak ferromagnetic vector at $T > T_{\text{eff}}$ in the weak ferromagnetic phase.

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1. Introduction

Hole-doped manganites with the perovskite structure have attracted much attention in recent years. The interest in the study of manganites is due not only to an observation of the ‘colossal’ magnetoresistance effect [1], but also to a large variety of such physical phenomena as phase separation, charge, orbital ordering, etc [2]. The majority of investigations are devoted to the study of substituted lanthanum manganites $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{A} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Pb}^{2+}$). Under hole doping, these compounds exhibit a number of concentrational transitions from antiferromagnetic (weak ferromagnetic) insulating to ferromagnetic insulating, and then to a ferromagnetic metallic state at $x \sim 0.08\text{--}0.10$ and $\sim 0.15\text{--}0.20$, respectively [3, 4]. From a theoretical point of view, the ferromagnetic metallic state in manganites might be explained by the double exchange (DE) mechanism [5]. In the framework of the DE model, strong Hund’s rule coupling enhances the hopping of e_g holes between the two successive Mn sites by establishing ferromagnetic spin order. For the low-doped compounds ($x < 0.10$), the double exchange mechanism predicts the formation of a canted magnetic structure [6]. The recent magnetic phase diagrams of the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ systems were constructed assuming the homogeneous canted magnetic state at the low-doping range [7, 8]. However, double exchange alone cannot explain the existence of a ferromagnetic but insulating phase ($0.10 < x < 0.20$). Recently, theoretical and experimental investigations have argued in favour of the possibility of a magnetic phase separation in manganites [2, 9–12]. According to this conception, the concentrational transition from an antiferromagnetic state to a ferromagnetic one occurs via the formation of an inhomogeneous magnetic state. The driving force of such a separation can be either electronic [13] or structural phase separation [2]. In spite of numerous investigations, the mechanism of the antiferromagnet–ferromagnet phase transition in manganites is still a matter of discussion.

In contrast to lanthanum-based hole-doped compositions, there is small amount of research devoted to the study of low-doped rare-earth manganites. The decrease of the lanthanide ionic radius dramatically changes the properties of the manganites [14]. In addition to the dimensional effect, the magnetic properties of manganites depend on the magnetic state of a rare-earth ion. Eu^{3+} , Lu^{3+} as well as La^{3+} are characterized by $L = S = 0$ in the ground state. This means that the magnetic behaviour of the LaMnO_3 , EuMnO_3 , LuMnO_3 parent compounds is determined predominantly by the manganese sublattice. In contrast, the magnetic properties of other rare-earth manganites are conditioned not only by d–d interactions of manganese ions, but also by f–d and f–f interactions of rare-earth ions, and their contribution to the magnetic state at low temperature becomes comparable with the contribution from a manganese B-sublattice. Among the low-doped rare-earth manganites, the $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ series is distinguished by very unusual magnetic properties at low temperatures [15]. In this system, the interactions between magnetically active Nd- and Mn-sublattices lead to the appearance of well pronounced anomalies in the magnetization behaviour. The low-temperature magnetic properties arising from Nd–Mn magnetic coupling undergo striking changes depending on the hole-doping level; therefore an investigation of the magnetic properties of the $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ system can give immediate information about the mechanism of the antiferromagnet–ferromagnet phase transition in low-doped manganites.

The magnetic properties of parent NdMnO_3 have been studied using both magnetization and neutron diffraction (ND) methods [16]. According to ND data, NdMnO_3 is a canted ferromagnet. The antiferromagnetic component appears at 80 K whereas the ferromagnetic one appears at 70 K. Both components are associated with the manganese sublattice. The neodymium sublattice becomes ordered in the same direction as the ferromagnetic component only below 13 K. However, according to pioneering work [17] stoichiometric NdMnO_3 is an

antiferromagnet (weak ferromagnet) of A-type, as is the well known LaMnO_3 . We believe that the NdMnO_3 studied in [16] contains an excess of oxygen due to its preparation at 1000°C in air, whereas for the synthesis of the stoichiometric compound strongly reducing conditions are necessary (stoichiometric LnMnO_3 (Ln—lanthanide) is obtained only by firing at a very low partial pressure of oxygen; final heat treatment at $850^\circ\text{C} \leq T \leq 1300^\circ\text{C}$ in air gave $\text{LnMnO}_{3+\lambda}$ with $0.11 \geq \lambda \geq 0.04$ [18, 19]). The suggestion that the temperature of Nd-sublattice ordering is 13 K [16] or below 2 K [20] contradicts the results of the magnetization study of $\text{NdMnO}_{3.04}$ [15]. In [15] it was observed that the Nd contribution strongly modifies the magnetization behaviour slightly below the Néel point $T_N = 85$ K. This behaviour was interpreted in terms of a strong negative coupling between the manganese and neodymium sublattices. Moreover, a sharp drop in magnetization near 10 K was found for the $\text{Nd}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ compound [15]. However, this phenomenon has not been interpreted. Some unidentified peaks arising either from an unforeseen lowering of the unit cell symmetry with decreasing temperature (the *Pnma* space group was successfully used in room-temperature refinement) or from incorrect conditions of the diffraction experiment were observed on neutron diffraction patterns of an $\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_3$ sample at low temperatures [21]. The refinement of the magnetic structure was performed in a homogeneous canted model. It was shown that Nd moments are ordered along the ferromagnetic component associated with the Mn-sublattice. The origin of the forbidden reflections has not been found. In our present work we have tried to resolve these questions and we present a magnetic state model explaining the obvious contradictions between the observed experimental data [15, 16, 20].

Thus, in order to reveal the role of the Nd-sublattice in the formation of the magnetic properties of Nd-based manganites and to determine the possible scenario of the concentrational transition from a weak ferromagnetic state to a ferromagnetic one, we have carried out a study of the low-doped $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x \leq 0.15$) manganites using magnetization, heat capacity, and elastic modulus measurements. In the present paper we have shown that the process of low-temperature spin reorientation observed in the lightly doped $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ series can be successfully explained by the model of magnetic phase separation. The reasons for the orientational transitions are discussed on the basis of a magnetic analogue of the Jahn–Teller theorem.

2. Experiment

Polycrystalline samples of $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x \leq 0.15$) system were prepared by the standard solid state reaction method using high-purity Nd_2O_3 , CaCO_3 and MnO_2 reagents. To remove absorbed water, pre-firing of Nd_2O_3 (1000°C , 1 h) was carried out. After that, mixtures of reagents taken in stoichiometric cation ratio were annealed at 1000°C for 2 h. The products obtained were ground, pressed into pellets, annealed at $T = 1500^\circ\text{C}$ in air for 5 h and then cooled down to room temperature at a rate of 100°C h^{-1} . The oxygen content of the materials was determined by thermogravimetric analysis (TGA) in a reducing H_2/N_2 flow. The as-prepared samples had an excess of oxygen content in comparison with stoichiometric ones. In order to reduce the oxygen nonstoichiometry the samples were annealed in evacuated quartz ampoules. Metallic tantalum was used as a reducing agent. Selected samples were reduced below the stoichiometric oxygen value. The unit cell parameters as well as the phase purity of the samples were checked by x-ray analysis using a DRON-3 diffractometer with $\text{Cr K}\alpha$ radiation. The data were analysed with the FullProf program [22].

Measurements of the temperature dependence of the magnetization were carried out with a commercial IQ-3001 vibrating sample magnetometer in the temperature range 4.2–150 K. Measurements of the field dependence of the magnetization at different temperatures of the

Table 1. Unit cell parameters of the $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x \leq 0.15$) manganites (space group $Pnma$).

Composition	a (Å)	b (Å)	c (Å)	V (Å ³)
NdMnO_3	5.8423	7.5429	5.4130	238.54
$\text{NdMnO}_{3.02}$	5.7938	7.5512	5.4146	236.89
$\text{Nd}_{0.94}\text{Ca}_{0.06}\text{MnO}_3$	5.6840	7.5952	5.4152	233.78
$\text{Nd}_{0.92}\text{Ca}_{0.08}\text{MnO}_3$	5.6552	7.6011	5.4166	232.84
$\text{Nd}_{0.92}\text{Ca}_{0.08}\text{MnO}_{2.98}$	5.7225	7.5701	5.4107	234.39
$\text{Nd}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$	5.6346	7.6077	5.4169	232.20
$\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_3$	5.6075	7.6141	5.4125	231.09
$\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_{2.98}$	5.6580	7.5898	5.4204	232.77
$\text{Nd}_{0.85}\text{Ca}_{0.15}\text{MnO}_3$	5.6015	7.6158	5.4138	230.95

samples were performed with a SQUID magnetometer in fields up to 50 kOe. The elastic properties were studied by a resonance method in the low-frequency regime ($\nu \sim 10^4$ Hz) using cylindrical samples with a diameter of 5 mm and length of 40 mm. The specific heat data were obtained in the range from 5 to 300 K using a quasiadiabatic pulse technique.

Neutron diffraction measurements for the $\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_3$ sample were performed at the Laboratoire Leon Brillouin-CEA in Saclay (France) using a G4.2 2-axes (7×10 detectors) high-resolution diffractometer with a wavelength $\lambda = 2.3433$ Å. The data were analysed with the Rietveld method using the FullProf program [22].

3. Results

All the samples were found to crystallize in an orthorhombic structure without extra diffraction peaks indicative of impurities. Room-temperature unit cell parameters obtained from the FullProf refinement of the x-ray diffraction data are shown in table 1. The unit cell volume decreases as the calcium concentration increases. The decrease of the volume is supposed to be due to the conversion of Mn^{3+} ions into Mn^{4+} . The effective ionic radii of Mn^{3+} and Mn^{4+} ions in octahedral oxygen coordination are 0.645 and 0.530 Å, respectively [23]. All the samples have a ratio of unit cell parameters $b/\sqrt{2} < c < a$ corresponding to the so-called O' -orthorhombic structure [24].

An NPD pattern collected at a temperature of 160 K where the sample is paramagnetic was used for the refinement of the structure of the crystal with composition $\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_3$. In contrast to [21], all Bragg reflections of the new sample can be indexed in the orthorhombic space group $Pnma$ with unit cell parameters $a = 5.6108(1)$ Å, $b = 7.5979(1)$ Å, $c = 5.4068(1)$ Å. No change of the unit cell symmetry is observed with decreasing temperature. Apparently, the forbidden reflections observed in the case of $x = 0.12$ sample studied in [21] resulted from incorrect conditions of the neutron diffraction experiment. A satisfying agreement between the observed and calculated patterns is shown in figure 1. The structural parameters calculated by the Rietveld refinement are presented in table 2. The MnO_6 octahedrons are rather strongly distorted; the bond lengths vary in the range from 1.938 up to 2.075 Å. Such a distortion indicates static d_z^2 orbital ordering. The Mn–O–Mn bond angle value is less than that for the lightly doped La-based manganites [25, 26]. The smaller the Mn–O–Mn bond angle the more distorted is the perovskite structure. Selected interatomic distances and angles are presented in table 3.

The temperature dependences of magnetization for the NdMnO_3 and $\text{NdMnO}_{3.02}$ compounds are presented in figure 2. The magnetization was measured using both zero field cooled (ZFC) and field cooled (FC) modes at a relatively small external field of 100 Oe.

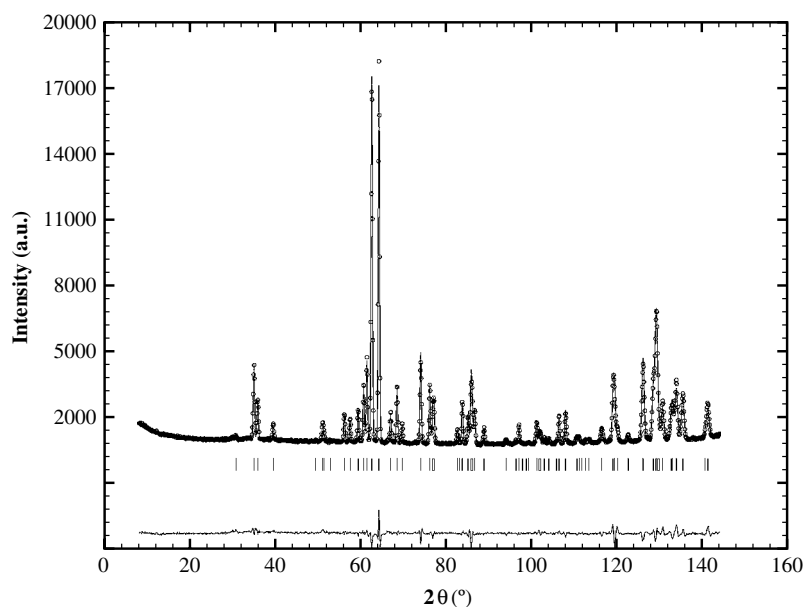


Figure 1. Observed and calculated neutron powder diffraction patterns for the $\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_3$ sample at $T = 160$ K. The difference between the observed and calculated patterns is also plotted.

Table 2. Structural parameters for the $\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_3$ sample obtained by Rietveld refinement of the NPD pattern at $T = 160$ K. Space group: $Pnma$.

Atoms	x	y	z	B (\AA^2)
(NdCa) 4c	$-0.053(5)$	0.2500	$0.0101(5)$	$0.65(6)$
Mn 4b	0.0000	0.0000	0.5000	$0.1(1)$
O1 4c	$0.5196(5)$	0.2500	$0.9177(5)$	$0.42(7)$
O2 8d	$0.3029(4)$	$-0.0429(3)$	$0.7119(4)$	$0.68(5)$
Cell	$a = 5.6108(1) \text{\AA}$	$b = 7.5979(1) \text{\AA}$	$c = 5.4068(1) \text{\AA}$	$V = 230.49(3) \text{\AA}^3$
Discrepancy factors	$R_p = 4.4\%$	$R_{wp} = 5.64\%$	$R_B = 6.2\%$	$\chi^2 = 7.2$

Table 3. Selected interatomic distances (in ångströms) and angles (in degrees) for the $\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_3$ compound at $T = 160$ K.

Mn-distances		Mn–O–Mn angles		(NdCa)-distances	
Mn–O1 $\times 2$	$1.954(7)$	Mn–O1–Mn	$152.86(3)$	(NdCa)–O1	$2.350(4)$
Mn–O2 $\times 2$	$1.938(2)$	Mn–O2–Mn $\times 2$	$152.21(9)$	(NdCa)–O1	$2.448(4)$
Mn–O22 $\times 2$	$2.075(2)$			(NdCa)–O2 $\times 2$	$2.375(3)$
Mn–Mn $\times 2$	3.80			(NdCa)–O22 $\times 2$	$2.655(3)$
Mn–Mn $\times 4$	3.90				

Though both compounds are characterized by an approximately equal temperature of magnetic ordering $T_N = 85$ K, the behaviour of FC magnetizations in the heating–cooling cycles is essentially different. Where broad hysteresis between cooling and heating runs is observed for the stoichiometric sample just below the Néel temperature, the $\text{NdMnO}_{3.02}$ compound exhibits

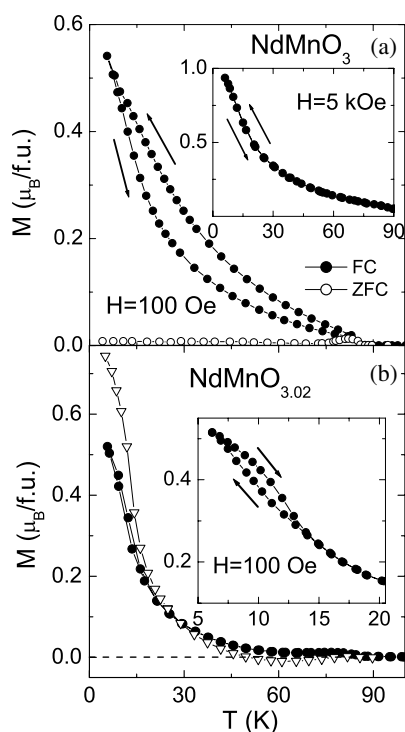


Figure 2. The temperature dependence of magnetization for the samples NdMnO_3 (top panel) and $\text{NdMnO}_{3.02}$ (bottom panel). The top inset shows the FC magnetization of the NdMnO_3 compound measured in a field of 5 kOe. The bottom inset shows the behaviour of the FC magnetization of the $\text{NdMnO}_{3.02}$ sample at low temperature. Open triangles are used for the curve obtained for $\text{NdMnO}_{3.02}$ in zero field on heating after cooling in a field of 15 kOe.

such a property only below 14 K (see the inset in figure 2(b)). For the stoichiometric compound, the increase of the external magnetic field leads to the suppression of the temperature hysteresis (inset in figure 2(a)). In the case of the $\text{NdMnO}_{3.02}$ sample, if the applied field increases, the hysteresis between cooling and heating FC runs becomes more pronounced. When measuring in zero field on heating after cooling in a relatively large magnetic field (in our case the field was equal to 15 kOe), negative magnetization is observed for both samples below the Néel point (figure 2(b)). Such behaviour can be explained by the negative exchange coupling between the manganese and neodymium sublattices.

The thermal evolution of the magnetization for $0.06 \leq x \leq 0.15$ compounds is shown in figure 3. The anomalous behaviour associated with the onset of magnetic ordering in the $x = 0.06$ sample was observed at $T_N = 73$ K. At around 68 K, the ZFC magnetization shows a peak; below this temperature a large difference between the ZFC and FC magnetizations begins to develop. It is well known that the difference between the ZFC and FC magnetizations as well as maxima in the ZFC magnetization versus temperature dependence result from a magnetic anisotropy in hard ferromagnetic materials [27]. So we can conclude that low-doped $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ are strongly anisotropic materials. A decrease in the FC magnetization is observed below 20 K, the total magnetization of the sample becoming equal zero at 9.5 K. At a temperature of $T_{\text{eff}} \sim 9$ K, the FC magnetization exhibits a jump, providing the orientation opposite to an external magnetic field of 100 Oe. At the same temperature the ZFC magnetization shows a maximum. The temperature hysteresis between cooling and heating

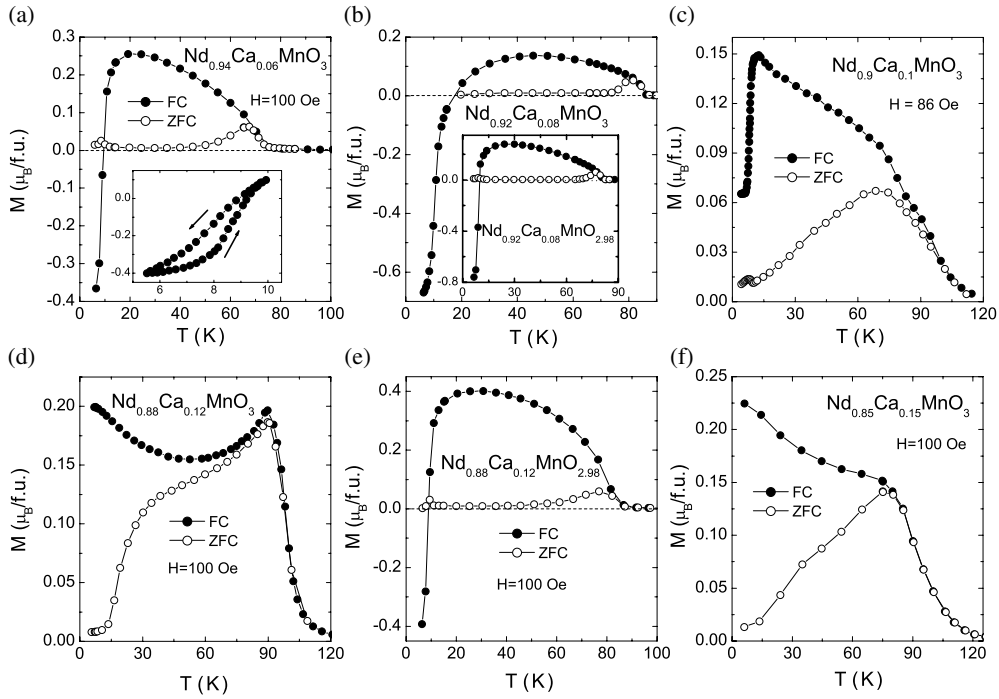


Figure 3. The temperature dependence of ZFC and FC magnetizations for the samples $0.06 \leq x \leq 0.15$. The inset shows enlargement near the phase transition.

runs indicates a first-order magnetic phase transition. An increase of magnetic field leads to the suppression of the above-mentioned effect. However, we observed anomalous behaviour of both ZFC and FC magnetizations at low temperature in a relatively large magnetic field of 14 kOe.

The temperature of magnetic ordering for the $\text{Nd}_{0.92}\text{Ca}_{0.08}\text{MnO}_3$ compound increases to 84 K. The reduction of oxygen content down to 2.98 leads to a decrease of the temperature of the magnetic transition into paramagnetic state and an increase of magnetic anisotropy. The anomalous behaviour of the magnetization around $T_{\text{eff}} \sim 9$ K is well pronounced for both these compounds; however, the effect is larger for the reduced one.

In the $x = 0.1$ sample, spontaneous magnetization begins to develop below 104 K. The low-temperature magnetic phase transition occurs at the same temperature $T_{\text{eff}} \sim 9$ K as for $x = 0.06$ and 0.08 compounds, though the magnitude of the anomaly is smaller, and compensation of magnetization in a field of 100 Oe is not observed.

The temperature of magnetic ordering for the $\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_3$ sample is 107 K. There is no anomalous behaviour of the magnetization near 9 K. Unlike $0.06 \leq x < 0.1$ compounds, an increase of the FC magnetization is observed for the $\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_3$ sample in the low-temperature range. However, well pronounced low-temperature anomalous behaviour appears in the reduced sample $\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_{2.98}$. A further increase of calcium content does not lead to a significant increase of T_C .

The magnetization measured in a field of 15 kOe after a field cooling procedure increases as the calcium or oxygen content increases, reaching a maximal value of $3 \mu_B \text{ fu}^{-1}$ for the stoichiometric $x = 0.12$ sample. A further increase of calcium content up to $x = 0.15$ does not lead to an increase of magnetization. It is worth noting that for the correct estimation of

the spontaneous magnetic moment a very strong magnetic field much above 15 kOe is needed because the magnetic anisotropy is very strong. The $\text{Nd}_{0.92}\text{Ca}_{0.08}\text{MnO}_{2.98}$ manganite was chosen for high magnetic field study because the effect associated with the low-temperature phase transition is the most pronounced for this composition. The results of magnetization measurements versus field for the $\text{Nd}_{0.92}\text{Ca}_{0.08}\text{MnO}_{2.98}$ compound at different temperatures are presented in figure 4. The measurements were performed after cooling the sample in zero field. At a temperature of 25 K, the sample shows the usual hysteresis loop. The coercive field reaches a value of 4.6 kOe, confirming that $\text{Nd}_{0.92}\text{Ca}_{0.08}\text{MnO}_{2.98}$ is a hard magnetic material. We did not observe saturation of magnetization apparently due both to the large magnetic anisotropy and the Nd-sublattice contribution.

Below 25 K, field dependence of magnetization becomes qualitatively different. Decreasing the temperature down to 20 K leads to the appearance of appreciable hysteresis in the field range from 20 to 50 kOe, which indicates a first-order magnetic phase transition. The hysteresis cycle shifts to lower fields as the temperature decreases. Moreover, there are noticeable magnetization jumps below 20 K.

It is worth noting that the jump in magnetization as the field increases is much smaller than the drop in magnetization as the magnetic field decreases. This unusual phenomenon is observed in a temperature range from 9 to 15 K: as the magnetic field decreases the magnetization shows a sharp drop and takes on a negative value in a positive field. This phenomenon is most pronounced at a temperature of 12.5 K, when the magnetization of the sample becomes equal to $-0.22 \mu_{\text{B}} \text{fu}^{-1}$ in a zero field. The subsequent decrease of temperature results in the disappearance of the above-mentioned effect: at 8.5 K the magnetization of the sample is equal to zero in a zero field. Below 8.5 K, the residual magnetization of the sample remains positive. At 5 K the sample is characterized by a residual magnetization of $1 \mu_{\text{B}} \text{fu}^{-1}$ and coercive field of 4 kOe. However, anomalous magnetization behaviour associated with a metamagnetic transition also has been observed. Note that the total magnetization of the sample gradually increases with decreasing temperature.

It is well known that the specific heat of a sample is very sensitive to changes in its magnetic structure. In order to reveal the features of specific heat behaviour near the temperatures of magnetic phase transitions we carried out a study of specific heat temperature dependence. The results obtained for selected samples are shown in figure 5. Stoichiometric NdMnO_3 shows a sharp peak associated with the transition from the paramagnetic to weak ferromagnetic state at 85 K. The temperature coincides with that obtained from the magnetization data. For the $\text{Nd}_{0.94}\text{Ca}_{0.06}\text{MnO}_3$ and $\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_3$ samples, the anomaly indicating the appearance of long-range magnetic order becomes significantly smaller. It is worth noting that such behaviour is typical for magnetically inhomogeneous systems. A phase transition with a large temperature width usually does not show any specific heat anomaly [28]. For instance, no specific heat anomaly is observed for spin glass [29]. More interestingly, a pronounced peak indicating a magnetic phase transition is observed for the $\text{Nd}_{0.94}\text{Ca}_{0.06}\text{MnO}_3$ sample at $T_{\text{eff}} \sim 9$ K.

The results of the study of elastic properties are presented in figure 6. It should be noted that the square of the resonance frequency is proportional to the value of Young's modulus. The $\text{Nd}_{0.92}\text{Ca}_{0.08}\text{MnO}_3$ sample shows a minimum of the Young's modulus near 600 K. A strong attenuation has been observed at this temperature. This type of behaviour supports a structural phase transition. The situation changes abruptly for the $\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_3$ sample. We did not observe any sharp anomaly associated with a structural phase transition; however, starting from 500 K Young's modulus increases strongly as the temperature increases. It is worth noting that such behaviour normally indicates a structural instability because Young's modulus usually decreases as the temperature increases. So we believe that the structural phase transition in the $x = 0.12$ sample occurs over a wide temperature range.

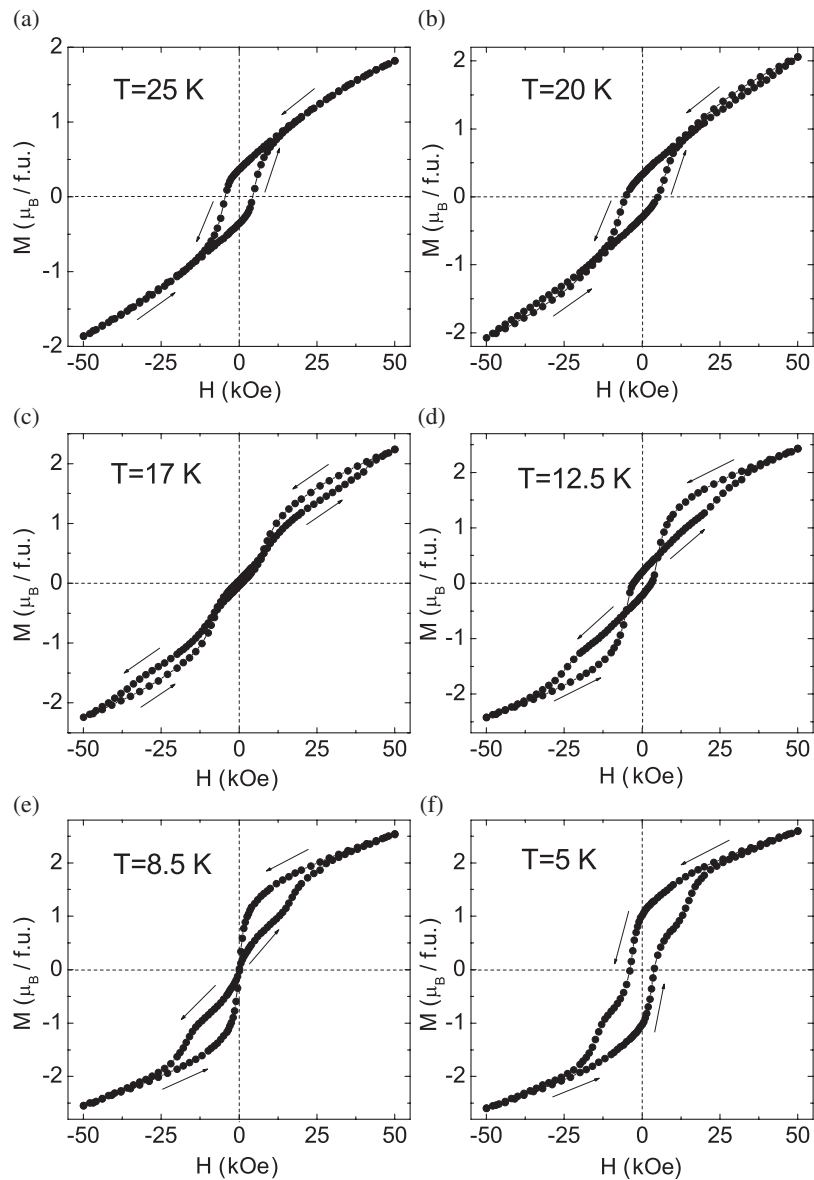


Figure 4. The field dependence of magnetization for the $\text{Nd}_{0.92}\text{Ca}_{0.08}\text{MnO}_{2.98}$ compound at different temperatures.

4. Discussion

The hypothetical magnetic phase diagram of the $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ system at low Ca doping level is presented in figure 7. Under hole doping the temperature of the transition into the paramagnetic state at first decreases and then at around $x = 0.1$ increases. We have observed two magnetic phase transitions in the range $0.06 \leq x \leq 0.1$ as the temperature decreases.

The $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ solid solutions contain two types of magnetically active sublattices: neodymium and manganese. At first we discuss the Nd contribution to the magnetic properties. The f-f exchange interaction in a rare-earth sublattice is as a rule rather weak in comparison with

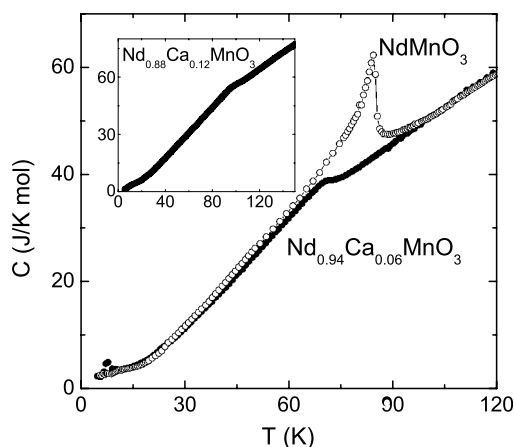


Figure 5. The temperature dependence of specific heat for the NdMnO_3 , $\text{Nd}_{0.94}\text{Ca}_{0.06}\text{MnO}_3$, and $\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_3$ samples.

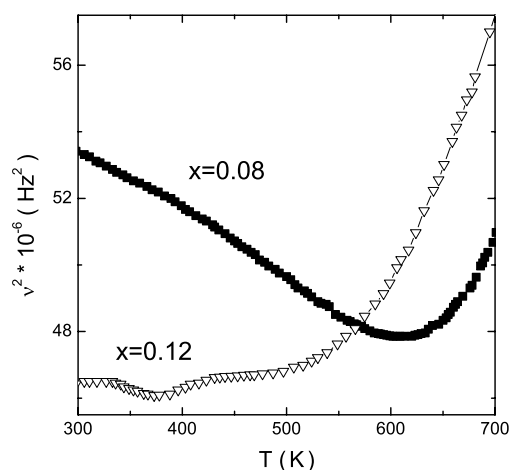


Figure 6. The square of the resonance frequency versus temperature for the $\text{Nd}_{0.92}\text{Ca}_{0.08}\text{MnO}_3$ and $\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_3$ samples.

the d–d interaction between manganese ions. The substitution of Nd ions for nonmagnetic Ca ones leads to a weakening of the f–f exchange. Hence, one can expect that neodymium magnetic moments should order as a result of f–d exchange interactions between the neodymium and manganese sublattices. A study of the magnetic properties of the NdMnO_3 and $\text{NdMnO}_{3.02}$ samples confirms this viewpoint. According to magnetization data (figure 2), the magnetic moments of neodymium ions are ordered slightly below $T_N = 85$ K, the f–d exchange being negative near T_N .

One can assume that the sign of the f–d interaction becomes positive with increasing Mn^{4+} ion content: for the $x = 0.15$ compound, we observe an increase in the FC magnetization in the entire temperature range (figure 3(f)) (see also [21]). The unusual behaviour of the FC curves observed for the $\text{Nd}_{0.9}\text{Ca}_{0.1}\text{MnO}_3$ and $\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_3$ compounds can be explained by a competition of two phases with a different sign of f–d exchange. The magnetic moment corresponding to the Nd^{3+} ion is about $1.2 \mu_B$ [16, 30].

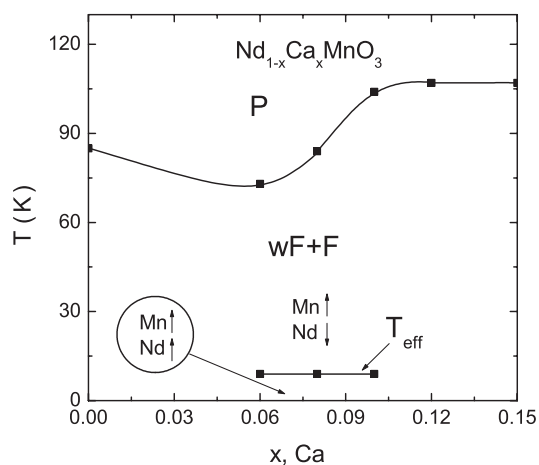


Figure 7. The magnetic phase diagram of the $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ low-doped manganites. wF—weak ferromagnet, F—ferromagnet, P—paramagnet, T_{eff} —the effective temperature at which the anomalous drop of the FC magnetization reflecting the orientational phase transition is the most pronounced. The relative directions of the magnetic moments of the Nd and Mn sublattices are given only for the weak ferromagnetic phase. The magnetic moments of the Nd and Mn sublattices for the ferromagnetic phase are parallel ordered in the whole temperature range below T_C .

On the other hand, the neutron diffraction results suggest that the neodymium sublattice in nonstoichiometric $\text{NdMnO}_{3+\lambda}$ orders ferromagnetically along the manganese ferromagnetic component below 13 K [16]. The refinement of the magnetic structure in [16] was carried out in a single canted magnetic phase model. However, we suggest that a two-phase model describes the magnetization, neutron diffraction and small-angle neutron scattering much more adequately [19]. In the framework of this model, disagreement between neutron diffraction [16, 20, 21] and magnetization data (present work) can be easily understood. According to our theory, samples in the range $0.06 \leq x \leq 0.15$ consist of antiferromagnetic (weak ferromagnetic) and ferromagnetic phases which are exchange coupled at the boundary. The $\text{NdMnO}_{3+\lambda}$ samples at a sufficiently large hole-doping level contain two magnetic phases too. The neodymium sublattice in both the weak ferromagnetic and ferromagnetic phases orders near the Néel point (Curie point). However, the orientation of the neodymium magnetic moments in both these phases is different: f–d exchange is positive for the ferromagnetic phase whereas it is negative in the weak ferromagnetic phase. In the two-phase model the sample studied in [16] consists of approximately 45% of the ferromagnetic phase and 55% of the antiferromagnetic one. Hence above 13 K, the average neodymium contribution from the weak ferromagnetic and ferromagnetic phases should be practically equal to zero. The ferromagnetic phase strongly affects the magnetic properties of the weak ferromagnetic phase due to exchange coupling at the boundary. This interaction may induce a reorientational transition from the antiparallel orientation of the neodymium moments and the weak ferromagnetic vector to a parallel one. One can see the features of such a transition in the $\text{NdMnO}_{3.02}$ sample below 14 K (figure 2(b)). Apparently, the spin reorientation of the neodymium ions in the weak ferromagnetic phase has been considered in [16] as a neodymium sublattice ordering. What is the reason for the spin reorientation? We believe that near a certain temperature the ground state of Nd^{3+} ions becomes degenerate because the opposing contributions from the exchange coupled ferromagnetic and weak ferromagnetic phases at the Nd site become equal. According to theoretical considerations this state should be unstable, thus leading to magnetic structure

transformation [31]. Due to the magnetic phase transition, the degeneracy is removed. The presence of electronic transitions between the closely located energy levels of Nd^{3+} ions is corroborated by spectroscopic study [32]. Submillimetre measurements revealed an intensive absorption in the transmission spectra of the nominal NdMnO_3 single crystal (the data on λ determination are not given) at a frequency $\sim 14 \text{ cm}^{-1}$. The observed excitation was attributed to the electron transition inside the Nd^{3+} Kramers doublet split by an Nd–Mn exchange field. It is interesting to note that a sharp decrease of the magnetic susceptibility along the c -axis was observed below 13 K [32] (see the inset in figure 2(b)). If our viewpoint is correct, no abrupt spin-reorientational transition taking place in a narrow temperature range can be observed for the stoichiometric NdMnO_3 compound which does not contain the ferromagnetic component. The temperature hysteresis observed between cooling and heating FC runs at 100 Oe just below the Néel point is suppressed by a stronger magnetic field (figure 2(a)). Taking into account that the d–f exchange field strongly depends on temperature, and the magnetic moment associated with Mn-sublattice in NdMnO_3 is very small, such behaviour can be explained by the gradual rotation of the easy direction of magnetization taking place in a low field with increasing or decreasing temperature.

The reorientational transition which occurs for compositions with $0.06 \leq x \leq 0.10$ has a number of peculiarities. The drop in magnetization observed in these compounds reaches a value of $1.1 \mu_{\text{B}}$ in a low field of 100 Oe, and the total magnetic moment is directed opposite to the external magnetic field (figure 3). In the case when the sample consists of 50% ferromagnetic and 50% weak ferromagnetic phase, the magnetization drop associated with the reorientation of Nd magnetic moments in the ferromagnetic phase should be about $0.6 \mu_{\text{B}}$. Therefore one can assume that manganese ions are involved in the spin reorientation process too. We believe that the dramatic changes in magnetization observed at low temperature result not only from the transformation of the weak ferromagnetic phase due to Nd^{3+} ion ground state degeneracy, but also from reorientation of the magnetic moment of the much less anisotropic ferromagnetic phase, which is exchange coupled with the weak ferromagnetic one. Thus, at low temperature all four sublattices of both phases have ions whose magnetic moments are directed opposite to the external magnetic field of 100 Oe. This assumption is in agreement with the results of the magnetic study in a strong magnetic field (figure 4). As one can see (figure 4) the remanent magnetization at 5 K practically coincides with the value obtained after cooling in a field of 100 Oe (figure 3). Moreover, a neutron diffraction study carried out for the $\text{NdMnO}_{3.11}$ sample which also exhibits the phenomenon of negative magnetization upon FC has revealed a significant increase of small angle neutron scattering intensity at low temperature [19]. The fragmentation of both ferromagnetic and weak ferromagnetic phases which takes place at the low-temperature spin reorientational transition can result in such behaviour⁸.

The metamagnetic behaviour of the magnetization observed in the $\text{Nd}_{0.92}\text{Ca}_{0.08}\text{MnO}_{2.98}$ sample in an external magnetic field (figure 4) has a similar origin. It is known that the splitting of the energy levels of a rare-earth ion in a magnetically ordered crystal is determined by the joint action of a crystal field, exchange interactions and an external field. If f–d exchange interaction causes an increase in the distance between the sub-levels of Nd ions, the external field should result in their decrease because in $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.06 \leq x \leq 0.1$) perovskites these fields are oppositely directed (whereas the f–d exchange field establishes the magnetic moments of the neodymium and manganese sublattices in the weak ferromagnetic phase in antiparallel directions, an external field aspires to establish them in parallel). A strong enough external magnetic field can lead to sublevel crossover, i.e. to their degeneracy. In [31] it was

⁸ The refinement of the magnetic structure of the $x = 0.08$ and 0.12 compounds by neutron diffraction methods will be carried out and the results will be reported in the near future.

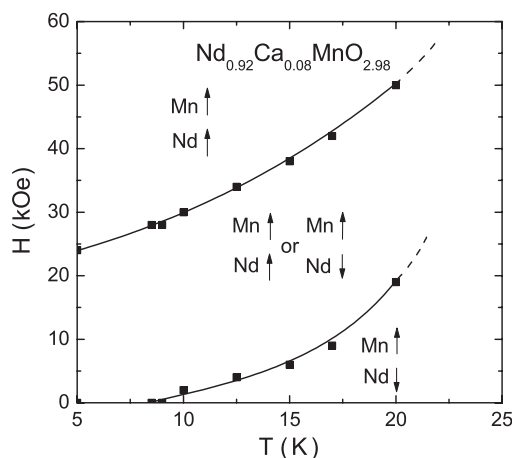


Figure 8. The H - T magnetic phase diagram for the $\text{Nd}_{0.92}\text{Ca}_{0.08}\text{MnO}_{2.98}$ compound. The relative directions of the magnetic moments of the Nd and Mn sublattices in the weak ferromagnetic phase are shown by arrows.

shown that the magnetic structure in which the ground state of f-ions is degenerate or close to that at sufficiently low temperature is unstable. The degeneracy is removed due to the deformation of the magnetic structure. Thus, magnetization jumps observed with increasing and decreasing field are a display of the magnetic analogue of the Jahn-Teller effect.

Below 17 K, the magnitude of the magnetization drop observed with decreasing magnetic field is much larger than the value of the magnetization jump which takes place as the field increases. This means that different processes occur with decreasing and increasing the magnetic field. We suggest that increasing the external field leads to a reorientation of the magnetic moments of the neodymium ions in the weak ferromagnetic phase in the direction of the moment of the ferromagnetic phase and the weak ferromagnetic vector. In contrast, decreasing the field results in a reorientation of the weak ferromagnetic vector and exchange coupled ferromagnetic phase, thus leading to a much stronger drop in the magnetization in comparison with the increasing field case. Taking into account that the investigated compound is a strongly anisotropic material, we could understand the negative remanent magnetization in terms of the competition between the magnetostatic energy and anisotropy.

On the basis of the data presented here we propose the H - T magnetic phase diagram for the $\text{Nd}_{0.92}\text{Ca}_{0.08}\text{MnO}_{2.98}$ compound (figure 8). Depending on the prehistory, phases with parallel or antiparallel orientation of the Nd and Mn sublattices in the weak ferromagnetic phase can be realized over a wide range of magnetic field. One can see that the value of the magnetic field which is required to change the relative orientation of the magnetic moments of the Nd and Mn ions in the weak ferromagnetic phase increases as the temperature rises. The width of the field range in which hysteresis is observed is practically temperature independent. This type of magnetic phase diagram is in agreement with the crossover of the energy sub-levels of Nd ions.

The two-phase model presented here is capable of explaining the unusual magnetic properties of $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ manganites, but what is the origin of the phase separation? Some scientists have suggested that the two-phase mixed state in manganites is realized through electronic separation into a hole-rich ferromagnetic phase and a hole-poor antiferromagnetic one [13]. The electronic phase separation scenario is based on the idea that the energy of a charge carrier in a magnetic semiconductor depends on the type of magnetic ordering being

minimal for the ferromagnetic state. For this reason free charge carriers tend to establish a parallel ordering of magnetic moments. In this scenario the ferromagnetic regions should contain an excess of holes. The size of these regions should be comparable with the lattice constant due to a limitation resulting from the electro-neutrality condition. The transition to metallic conductivity taking place with an increase of the doping level occurs when ferromagnetic clusters percolate. However, the ferromagnetic state in $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ solid solutions is not metallic [15], so advantages in energy due to electronic phase separation are not evident.

Moreover, a change from 2D ferromagnetic interactions characteristic of LnMnO_3 to 3D ones may be induced not only by Mn^{4+} but also by diamagnetic Nb^{5+} [33], Al^{3+} , Sc^{3+} [34] doping of the parent LnMnO_3 (Ln—lanthanide). The appearance of ferromagnetic order in spite of the absence of Mn^{4+} ions contradicts both double exchange and electronic phase separation scenarios. According to Goodenough's consideration, the removal of static Jahn–Teller distortions should lead to the appearance of isotropic ferromagnetic interaction [24, 35]. In the cases when one dopes the LnMnO_3 with non-Jahn–Teller ions such as Mn^{4+} (Nb^{5+} , Sc^{3+} etc), the e_g orbitals of all the Mn^{3+} sites surrounding the Mn^{4+} (Nb^{5+} , Sc^{3+} etc) ion tend to be directed towards the central ion, forming an orbital polaron as was shown in [36]. According to the Goodenough–Kanamori rules, an important consequence of such a type of orbital ordering is ferromagnetic exchange interactions between Mn^{3+} and Mn^{4+} ions in this cluster. The diamagnetic doping (Nb^{5+} , Sc^{3+} etc) also favours ferromagnetism converting 2D-type orbital ordering intrinsic to LnMnO_3 into a 3D cluster-like one with much faster orbital dynamics. An interaction of ferromagnetic clusters may lead to long-range ferromagnetic order if the Mn–O–Mn angle is enough large. The mixed phase state in $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ most likely results from the orbital phase separation mechanism. In this scenario the 2D orbitally ordered clusters are antiferromagnetic (weak ferromagnetic) whereas the 3D quasistatically orbitally ordered ones are ferromagnetic [24]. Apparently, both phases have a slightly different composition. A recent x-ray absorption fine structure measurement of the Sr and La K edges of the lightly doped solid solutions $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ has revealed intrinsic chemical and structural inhomogeneity [37]. The development of the ferromagnetic state in the $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ series strongly correlates with the removal of Jahn–Teller distortions. The Jahn–Teller distortions in stoichiometric NdMnO_3 remove the first-order phase transition at $T = 1080$ K [38]. In the $\text{Nd}_{0.92}\text{Ca}_{0.08}\text{MnO}_3$ sample, the cooperative Jahn–Teller effect disappears at $T = 600$ K (figure 6). For the almost ferromagnetic $\text{Nd}_{0.88}\text{Ca}_{0.12}\text{MnO}_3$ sample the temperature dependence of Young's modulus (figure 6) has not revealed sharp changes associated with an orbital order–disorder transition. The anomalous increase in the magnitude of Young's modulus observed with increasing temperature above $T = 500$ K could be attributed to a broad crystal structure transition into an orbitally disordered state. We ascribe this anomalous behaviour to the structural inhomogeneity of solid solutions. Note that the orbital order–disorder transition in the ferromagnetic $\text{Pr}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ studied by x-ray resonant scattering occurs over a wide temperature range, 300–800 K [39]. A key influence of the type of orbital state on the magnetic and transport properties of low-doped manganites as well as the possibility of the coexistence of orbitally ordered and orbitally disordered phases are confirmed by x-ray and neutron diffraction data [40, 41].

5. Conclusions

The evolution of the magnetic properties of $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ samples with doping was investigated. It was shown that the magnetic properties of the investigated compounds can be successfully explained in the framework of a two-phase model according to which the samples with $x \leq 0.15$ consist of exchange coupled ferromagnetic and weak ferromagnetic phases.

The phases differ in the sign of the f – d exchange. The magnetic moments of the neodymium ions are ordered parallel to the moments of the manganese ions in the ferromagnetic phase, and opposite to the direction of the weak ferromagnetic vector at $T > T_{\text{eff}}$ in the weak ferromagnetic phase.

The low-temperature magnetic phase transition associated with the reorientation of the weak ferromagnetic vector and the ferromagnetic phase in the direction of the magnetic moments of the neodymium ions in the weak ferromagnetic phase is observed in the concentrational range $0.06 \leq x \leq 0.1$ near $T_{\text{eff}} \sim 9$ K.

The magnetization jumps observed with increasing external field for $\text{Nd}_{0.92}\text{Ca}_{0.08}\text{MnO}_{2.98}$ are associated with the reorientation of the magnetic moments of the neodymium ions in the weak ferromagnetic phase along the moments of the ferromagnetic phase and the weak ferromagnetic vector. In contrast, decreasing the field results in the reorientation of the weak ferromagnetic vector and the moment of the ferromagnetic phase while the magnetic moments of the neodymium ions in the weak ferromagnetic phase remain directed along the field.

On the basis of the data presented we proposed T versus x and H versus T magnetic phase diagrams which are characterized by the missing of a canted phase. The appearance of orientational transitions was explained within the framework of a magnetic analogue of the Jahn–Teller theorem.

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