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Reappearance of Antiferromagnetic Order in $Nd_{0.9}Ca_{0.1}BaCo_2O_{5+\delta}$ for $\delta > 0.51$

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The absence of the antiferromagnetic order in $Nd_{0.9}Ca_{0.1}BaCo_2O_{5.5}$ has been found to remain unchanged by applying a hydrostatic pressure of 10 kbar. In magnetic studies of polycrystalline $Nd_{0.9}Ca_{0.1}BaCo_2O_{5+\delta}$ ($\delta = 0.07-0.69$), we have found a reappearance of the antiferromagnetic phase, caused by an increase in oxygen index δ above 0.51 related to extra oxygen ions addition into the NdO_δ plane. For the samples with $\delta = 0.555$ and 0.59, a coexistence of well developed antiferromagnetic phase with ferrimagnetic one is evidenced.

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1. Introduction

The layered perovskites $RBaCo_2O_{5+\delta}$ (R = lanthanide ion or Y, $\delta = 0.5$) are characterized by the sequence of complex magnetic and electronic phase transitions observed with increasing temperature: antiferromagnet–ferromagnet (AFM-FM, $T_N = 200-250$ K), ferromagnet–paramagnet ($T_C = 280-310$ K), and insulator–metal transition ($T_{MIT} = 330-360$ K), which can be tuned by a substitution at the R-, Ba-, and Co-sites or by a change of oxygen content $5+\delta$ [1–6]. The perovskite-related structure [3] consists of aligned along the c-axis layers of RO_δ–CoO_2–BaO–CoO_2. Each Co ion is coordinated by 5 or 6 oxygen ions, forming pyramid or octahedron, depending on the oxygen index δ. The variation of δ index leads to addition or removal of oxygen ions from the RO_δ planes, changing the ratio of the Co octahedral/pyramidal coordination, and altering charge doping of the CoO_2 planes. For $\delta = 0$, i.e. for the compound with no oxygen in RO_δ layer, all Co ions are pyramidally coordinated (CoO_5) and gradual increase of δ up to 1 leads to transition to octahedral coordination of all Co ions (CoO_6). For the compound with $\delta = 0.5$, there is an additional order of octahedrally and pyramidally coordinated planes along the b-axis. Variation of δ value leads to the changes in the formal valence of Co ions. For $\delta = 0.5$, only Co^{3+} ions are present. A small shift from that value leads to hole-doping (Co^{4+}) or electron-doping (Co^{2+}). Taskin et al. [4] have shown very strong dependence of the ground state on oxygen content; i.e., on simultaneous changes of coordination and charge doping for $GdBaCo_2O_{5+\delta}$: from charge-ordered insulating antiferromagnet ($\delta = 0$), to optimally doped insulator ($\delta = 0.5$), and finally to metallic ferromagnet ($\delta = 0.7$). On the contrary, the heterovalent substitutions at R- and Ba-sites for the fixed oxygen content do not affect oxygen vacancy ordering but only alter charge doping of the CoO_2 planes.

The hole doped system of $Nd_{1-x}Ca_xBaCo_2O_{5.5}$ ($x = 0-0.2$) is characterized by mixed valence of Co^{3+} and Co^{4+} ions with ferrimagnetic interactions between them. Upon Ca^{2+} substitution for Nd^{3+} at the R-site the temperature of antiferro–ferrimagnetic phase transition is drastically suppressed. At 10% Ca content this magnetic transition is completely absent and antiferromagnetic order does not appear [5, 6]. In this work we show that the reappearance of antiferromagnetic phase is possible by variation of δ in $Nd_{0.9}Ca_{0.1}BaCo_2O_{5+\delta}$.

2. Experimental details

Polycrystalline samples of $Nd_{0.9}Ca_{0.1}BaCo_2O_{5+\delta}$ with $\delta = 0.07-0.69$ have been obtained by using a standard solid-state synthesis method described in detail in Ref. [3]. Single-phase samples were annealed in argon or oxygen at various temperatures and the oxygen content was established by thermogravimetric measurements. X-ray diffraction experiments were performed in a Rigaku diffractometer. Magnetic measurements were carried out using a Magnetic Property Measurement System (Quantum Design) in the temperature range of 5–380 K in magnetic fields up to 50 kOe. An external hydrostatic pressure up to 10 kbar was applied, using an easyLab Technologies Mcell 10 pressure cell. A high-purity Sn wire (0.25 mm in diameter) was employed as an *in situ* manometer.

3. Results and discussion

X-ray diffraction patterns for the studied $Nd_{0.9}Ca_{0.1}BaCo_2O_{5+\delta}$ samples are presented in Fig. 1. The evolution of the crystal structure with δ is similar to the one for undoped $RBaCo_2O_{5+\delta}$ [4]. For $\delta \leq 0.25$, this material adopts a tetragonal structure. In the range $0.40 \leq \delta \leq 0.555$, the vacancy-ordered orthorhombic structure is observed, in particular from the splitting of the 040 and 200 peaks between 46 and 47 deg. Further oxidation for $\delta \geq 0.59$ changes the structure into tetragonal one with smaller lattice parameters. Figure 2a presents the temperature dependence of magnetization for $Nd_{0.9}Ca_{0.1}BaCo_2O_{5+\delta}$ with $\delta = 0.43-0.69$, measured

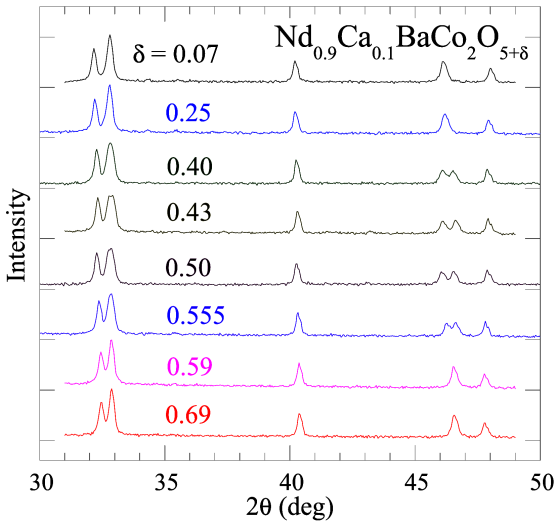

Fig. 1. X-ray diffraction spectra for $Nd_{0.9}Ca_{0.1}BaCo_2O_{5+\delta}$. The intensity data are presented in a logarithmic scale and shifted for clarity.

using "field-cooling" procedure (M_{FC}) in a magnetic field of 1000 Oe. An antiferromagnetic phase is not present for the oxygen content δ varying from 0.5 down to 0.43. The T_C decreases from 310 K for the sample with $\delta = 0.5$ [5] to 295 K for $\delta = 0.43$. For $\delta = 0.555$, we have observed a significant decrease of magnetization with a small cusp near 235 K (Fig. 2b). Below 235 K, the M_{FC} decreases, but not falls to zero, which may be an indication of appearance of antiferromagnetic ordering in ferrimagnetic matrix. At around 140 K, a smooth plateau is well developed. From $M(T)$, we can estimate $T_N = 230$ K and $T_C = 245$ K, which is considerably lower than T_C for the samples with $\delta \approx 0.5$. The Ca^{2+} hole-doping results in mixed valence of Co^{3+}–Co^{4+}.

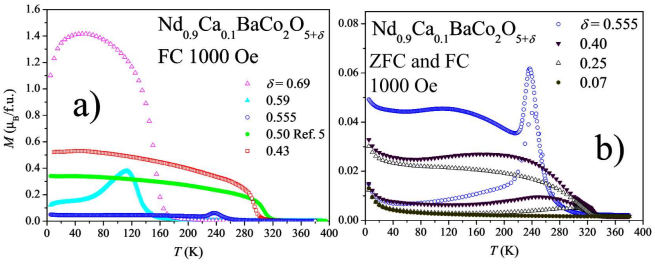

Fig. 2. The temperature dependence of magnetization recorded in magnetic field of 1000 Oe for $Nd_{0.9}Ca_{0.1}BaCo_2O_{5+\delta}$ with $\delta \geq 0.43$ (a) and with $\delta = 0.07$–0.555 (b).

It was suggested [5] that interactions between Co^{3+} and Co^{4+} ions lead to ferrimagnetic ordering. An increase of δ up to 0.555 results in further hole-doping, which increases the number of Co^{3+}–Co^{4+} pairs, but also disorders Co–O network by formation of larger number of CoO_6 octahedra at the expense of CoO_5 pyramids. It seems that disorder, induced by oxygen content change, is responsible mainly for a decrease of T_C for $Nd_{0.9}Ca_{0.1}BaCo_2O_{5.555}$ since the same tendency was reported by Taskin et al. [4] for $GdBaCo_2O_{5.5+\delta}$.

Further increase in oxygen content results in shift of a cusp in $M(T)$ dependence down to about 110 K for $\delta = 0.59$, correlated with an increase in magnetization value. One can observe a further decrease in T_N and T_C for higher oxygen contents, which confirms the important role of oxygen vacancy ordering in regulating of both T_N (= 90 K) and T_C (= 130 K). Then, the reappearance of the phase transition from antiferromagnetic to ferrimagnetic phase by degrading the oxygen vacancy ordering is possible. Further increase in oxygen content for δ above 0.6 results in a complete collapse of oxygen vacancy ordering, evidenced by a vast increase in magnetization. Here, the material adopts a tetragonally distorted perovskite structure with oxygen vacancies distributed randomly across the crystal lattice. Figure 2b presents the $M(T)$ dependence for $Nd_{0.9}Ca_{0.1}BaCo_2O_{5.555}$ and for selected electron-doped compositions with $\delta \leq 0.4$, recorded in M_{ZFC} and "field-cooling" mode. Taskin et al. [4] have shown a decrease in both T_N and T_C as a result of electron doping by oxygen removal from $GdBaCo_2O_{5.5+\delta}$. In our case, the situation is different. Starting from 295 K for $\delta = 0.43$, the T_C increases to 340 K with a decrease in δ down to 0.34 (not shown in the figure), and again decreases to 295 K with a further decrease in δ to 0.25. In the case of removing the oxygen ions from RO_δ, we have found a gradual decrease in magnetization, but the compositions remain ferrimagnetic without a noticeable decrease in T_C for oxygen content lowered to $\delta = 0.07$, where a complete disappearance of spontaneous ordering for the whole investigated temperature range is noticed.

Figure 3a presents the field dependences of the magnetization recorded at 5 K for the samples with δ values of 0.5 and above. One can see the smallest value of M at the highest applied field for the sample with $\delta = 0.555$, and the highest value of M at the highest applied field for the one with $\delta = 0.69$. For $\delta > 0.555$ we observe a clear hysteretic behavior, characteristic of ferrimagnetic ordering, and a linear $M(H)$ dependence in the high-field region, characteristic of an antiferromagnetic contribution to the net magnetization. This is in line with conclusions based on the results of $M(T)$ measurements that some antiferromagnetic fraction exists at low temperatures for the samples with $\delta = 0.59$ and 0.69. For $\delta < 0.5$, the shape of $M(H)$ is different, indicating a competition of antiferromagnetic and ferrimagnetic interactions at low temperatures. The hysteretic behavior weakens for $\delta = 0.59$ in the ferrimagnetic region (Fig. 3b). For $\delta = 0.555$, we observe a completely different shape of the hysteresis loop recorded at 150 K, characteristic of domination of ferrimagnetic interactions, with an invar effect and the saturation of the magnetization for 50 kOe (Fig. 3c). The same shape of the $M(H)$ dependence is observed for the already ferrimagnetic sample with $\delta = 0.43$, in the full

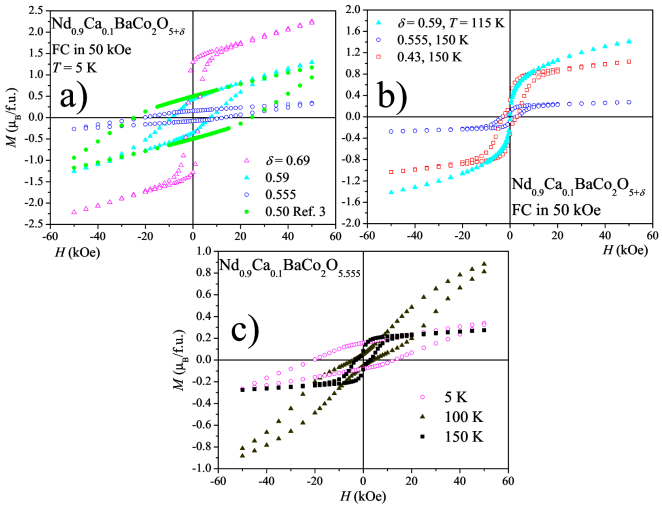

Fig. 3. The magnetic field dependence of magnetization for $Nd_{0.9}Ca_{0.1}BaCo_2O_{5+\delta}$ with $\delta \geq 0.43$, measured at 5 K (a) and at 150 K (b). Evolution of $M(H)$ dependence with temperature for the sample with $\delta = 0.555$ (c).

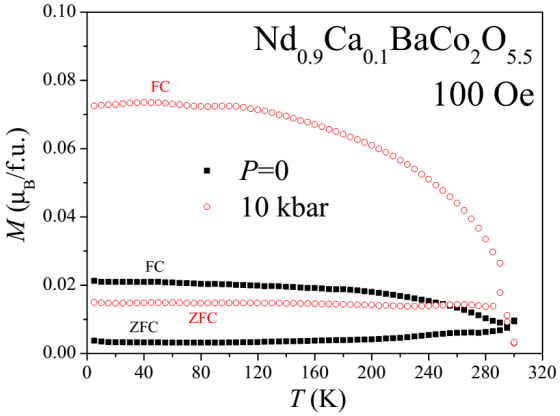

Fig. 4. The temperature dependence of magnetization of $Nd_{0.9}Ca_{0.1}BaCo_2O_{5.5}$ measured under ambient pressure and under a hydrostatic pressure of 10 kbar in a magnetic field of 100 Oe.

studied temperature range of appearance of magnetically ordered phase, from 295 K down to 5 K. The smooth plateau observed at about 140 K (Fig. 2a) may be attributed to the second ferrimagnetic phase, which seems to exist up to about 180 K.

Figure 4 shows that under applied hydrostatic pressure up to 10 kbar it is not possible to induce an appearance of antiferromagnetic phase in $Nd_{0.9}Ca_{0.1}BaCo_2O_{5.5}$. Under a pressure of 10 kbar, one can see a sudden decrease in magnetization with increasing temperature at around 300 K and a transition to the paramagnetic state above T_C. Such a decrease in T_C under applied pressure is in agreement with the results of dT_C/dP obtained for the samples with lower Ca^{2+} substitution levels, for which the pressure coefficient of T_C was found to decrease with increasing x and become negative at $x = 0.06$, contrary to that for undoped $NdBaCo_2O_{5.5}$ with positive dT_C/dP [7].

4. Conclusions

We have shown a strong variation of magnetic properties with the oxygen content changed over wide range for $Nd_{0.9}Ca_{0.1}BaCo_2O_{5+\delta}$ ($\delta = 0.07-0.69$). We have found a reappearance of the antiferromagnetic phase, caused by an increase of the oxygen index δ above 0.51. Under applied hydrostatic pressure up to 10 kbar we did not observe an appearance of the antiferromagnetic phase for the optimally doped $Nd_{0.9}Ca_{0.1}BaCo_2O_{5.5}$.

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