Effect of oxygen nonstoichiometry on magnetic phase transitions in frustrated cobaltites $YBaCo_4O_{7+x}$ ($x = 0, 0.1, 0.2$)

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Abstract. Experimental studies were carried out for structural and elastic properties of cobaltites $YBaCo_4O_{7+x}$ (x = 0, 0.1, 0.2) obtained by various technologies and distinguished by oxygen content. Correlation was revealed between the structure distortion at room temperature and a hysteresis in a $\Delta E(T)/T_0$ curve in the temperature range 80 – 280 K, as well as the anomaly value in the region of T_N. It was found, that small deviations from stoichiometry (x = 0.1, 0.2) result in suppression of structural transition, reduce a hysteresis, quickly smooth out and reduce anomalies of the Young's modulus $\Delta E(T)/T_0$ in the range of magnetic phase transition. This behavior indicates that structural and magnetic transitions are suppressed in nonstoichiometric samples and only short range correlations of order parameters are retained

1 Introduction

Rare-earth cobaltites $RBaCo_4O_7$, which are characterized by geometrical frustration of exchange interactions, mixed valence and coupled 3d- and 4f- subsystems, have attracted considerable interest due to their remarkable magnetic, electronic and magnetoelectric properties [1 – 5]. Frustrations result in a degenerate ground state and in absence of a long-range magnetic order even at significant constants of exchange interaction. A small orthorhombic distortion $\Delta a/a \approx 10^{-2}$ of the structure at the phase transition [6, 7] removes frustration of exchange bonds and leads to occurrence of the distinct magnetic order in the Co subsystem.

The data on the magnetic configuration, ground state, temperatures and peculiarities of structural and magnetic phase transitions for cobaltites of various preparation procedure are often incoincident, that allows to assume essential influence of technology of preparation and oxygen contents on their properties. In the present work effect of oxygen nonstoichiometry on structural and elastic characteristic as well as on phase transition is investigated in cobaltite $YBaCo_4O_{7+x}$ with only magnetic cobalt subsystem.

2 Experimental details

Polycrystalline samples $YBaCo_4O_{7+x}$ (x = 0, 0.1, 0.2) for studies have been synthesized by standard ceramic technology with three-step annealing in air and quenching sample from 900–950ºC after each stage [8]; the oxygen content after this procedure corresponds to x ~ 0.05–0.10. Further ceramic samples were exposed to additional heat treatment by using the $x(t)$ dependence from annealing time. Samples with x = 0 were obtained by annealing in vacuum at 500ºC, and samples with x = 0.10 and x = 0.20 were obtained by annealing at T = 210ºC within several days. The oxygen content in the samples was measured by change of weight of a tablet after heat treatment with a resolution $\Delta x \approx 0.001$ and absolute accuracy ± 0.01. For comparison, we also investigated samples Q_1 and Q_2, which were quenched from 900 - 950ºC and not exposed to additional heat treatment, the sample Q_2 being exposed to one more additional step of trituration, pressing and annealing.

X-ray diffraction (XRD) measurements were performed on a Stoe powder diffractometer using monochromated Co$K_{\alpha 1}$ radiation. All lines in the XRD patterns of the $YBaCo_4O_{7+x}$ samples measured at room temperature were indexed in the frameworks of a hexagonal or weakly distorted hexagonal structures. A full-profile analysis of XRD patterns in the 18–120° range by Full_Prof software allowed to determine the change of structure at a small deviation from the stoichiometry. The Young's modulus E and internal friction coefficient q^{-1} were measured by the composite resonator method at frequency ~100–200 kHz in the temperature range 4.2–300 K on polycrystalline samples $YBaCo_4O_{7+x}$ in the steady-state regime.

3 Results and discussion

3.1 XRD analysis

Influence of oxygen nonstoichiometry on structure was investigated at room temperature for the series of the samples $YBaCo_4O_{7+x}$ with oxygen excess x = 0, 0.1, 0.2 and also for quenched samples Q_1 and Q_2. Three types of XRD patterns were observed for samples with various deviation from stoichiometry. Sample with x = 0.1 and quenched sample Q_1 have undistorted hexagonal

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structure and don't reveal structural transition down to helium temperatures. On the XRD pattern of the stoichiometric sample, appreciable difference is observed for a number of peaks sensitive to the orthorhombic distortion and its structure is characterized by a small orthorhombic distortion $\varepsilon_o = (a_o - b_o/\sqrt{3})/a_o \approx 3\cdot10^{-3}$, where the relation between the hexagonal and orthorhombic lattice parameters is as follows $a_o = a_h$, $b_o = \sqrt{3}a_h$. Fig. 1 shows the part of the XRD pattern, containing peaks sensitive to orthorhombic distortion and/or presence of the two-phase state of a sample.

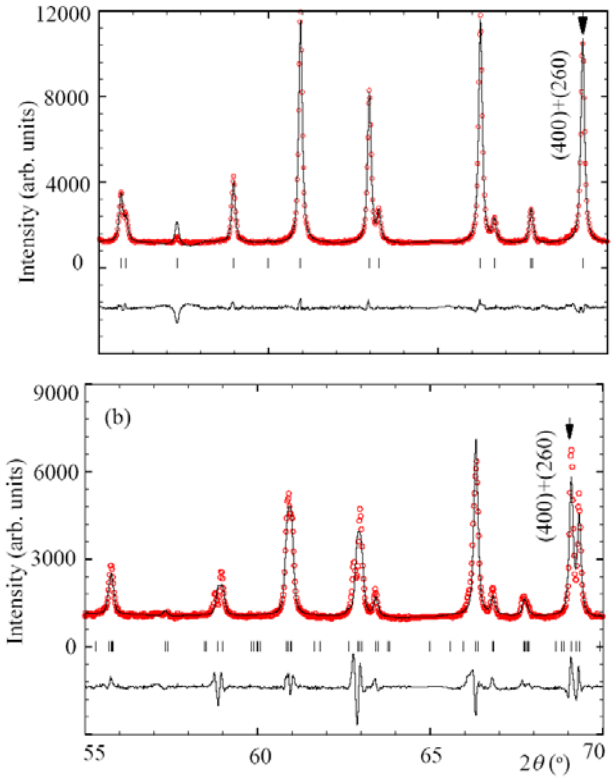

Fig. 1. Experimental (lines) and calculated (points) XRD patterns and their difference (lines below) for the series of the $YBaCo_4O_{7+x}$ samples with $x = 0.1$ (a) and $x = 0$ (b) on $CoK_{\alpha1}$ radiation. Bars show positions of Bragg peaks according to space group.

This difference comes to light most precisely for the peak (400) + (260), having the Bragg's angle $2\theta = 69°$. The small orthorhombic distortion for the sample with $x = 0$ results in the peak splitting into two lines (Fig. 1 b), the ratio of the intensities $I_1/I_2 = 2 : 1$ for the split lines corresponding to statistical value for such type of distortion. Unsplit line is observed for the sample with $x = 0.1$, since $d_1 = d_2$ at $a_o = b_o/\sqrt{3}$ (Fig. 1 a).

According to full-profile analysis, the quenched sample Q_2 is a mix of two phases with hexagonal/quasi hexagonal structures. The difference of the cell parameters $\Delta a/a$ ($\Delta a = a_{h1} - a_{h2}$) for two phases is of the same value, as the value of the orthorhombic distortion ε_o for the sample with $x = 0$, and the content of the minor phase is ~20%. This tendency of cobaltites to form a two-phase state at the oxygen deviation from the stoichiometry was discussed earlier for system $YbBaCo_4O_{7+x}$ [9]. The character and value of splitting reflexes on the XRD pattern for the sample with the oxygen excess $x = 0.2$ qualitatively differs from those observed for the samples with $x = 0$ and 0.1.

Thus, the development of two scenario is possible in ceramic samples at a small oxygen deviation from stoichiometry for x near to 0.1 value. It depends both on oxygen excess and synthesis procedure of ceramics (porosity of ceramics, temperatures and time of annealing, etc.). In the sample with $x = 0.1$ and quenched sample Q_1 the distortion of the hexagonal structures is absent, apparently because of irregular distribution of excess oxygen ions in the lattice. The structure becomes defect, that prevents the correlated ordering of local structural distortions thought the sample. Under other conditions, it is also possible a separation of the sample into two phases with different oxygen contents.

3.2 Young's modulus and internal friction

Due to the distortion of the crystal structure in the stoichiometric samples, frustrations are removed and subsequently the long-range magnetic order appears in the cobalt subsystem. In this case, one should expect the occurrence of the well defined magnetic phase transitions accompanied by the distinct anomalies of elastic properties of the samples. For this purpose, in this work the temperature dependences of Young's modulus $E(T)$ and internal friction coefficient $q^{-1}(T)$ were investigated for the series of $YBaCo_4O_{7+x}$ ($x = 0$, 0.1, 0.2) compounds distinguished by the oxygen content and value of the structure distortion. In figures relative

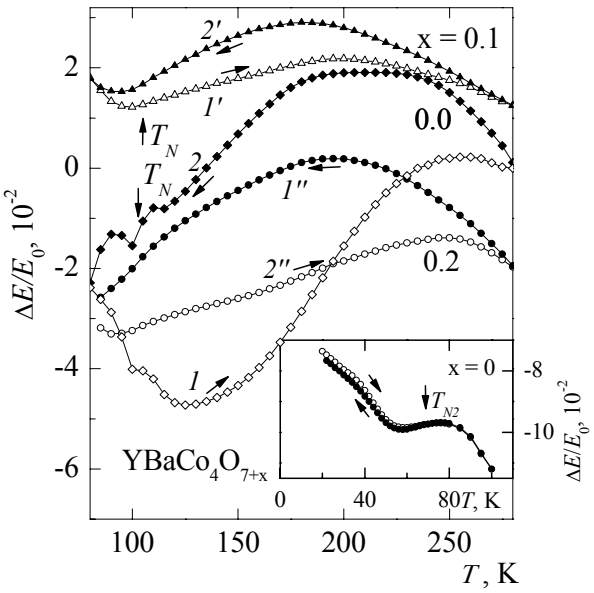

Fig. 2. Temperature dependence of the relative change $\Delta E/E_0$ of the Young's modulus for the series of samples $YBaCo_4O_{7+x}$ measured on heating (open symbols) and cooling (closed symbols; curves for $x = 0.1$, 0.2 are shifted along the vertical axis). The insert shows dependence $\Delta E/E_0(T)$ in the range of the spin reorientation transition for the sample with $x = 0$.

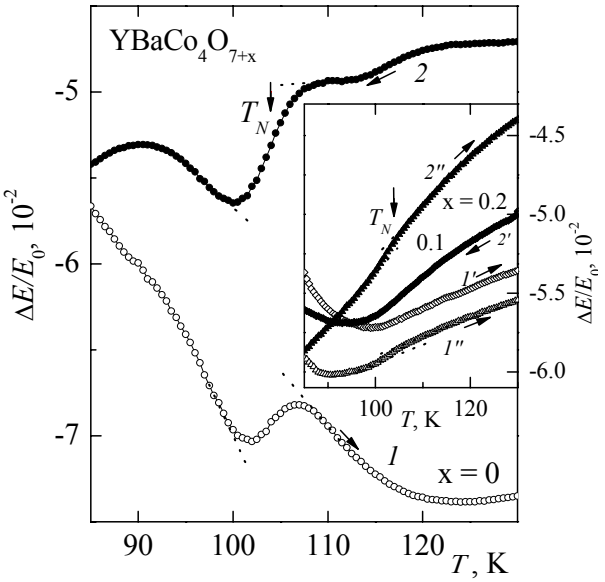

Fig. 3. Temperature dependence of the relative change $\Delta E/E_0$ of the Young's modulus for the series of the $YBaCo_4O_{7+x}$ samples measured on heating (open symbols) and cooling (closed symbols) in the range of the magnetic phase transition temperature T_N. (curves for various x are shifted along the vertical axis; the dotted line shows extrapolation of the temperature trend outside of anomaly).

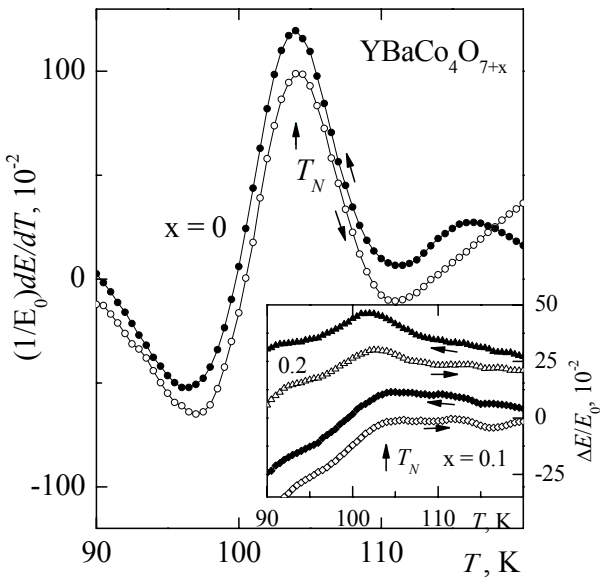

Fig. 4. Temperature dependence of the temperature derivative of the of Young's modulus $(1/E_0)\mathrm{d}E/\mathrm{d}T$ for the series of the $YBaCo_4O_{7+x}$ samples measured on heating (open symbols) and cooling (closed symbols) in the range of the magnetic phase transition temperature T_N (curves for various x are shifted along the vertical axis).

changes of the modulus $\Delta E(T)/E_0$, normalized on its value E_0 at $T = 280$ K, are shown ($\Delta E(T) = E(T) - E_0$; $E_0 = E(T = 280\ \mathrm{K})$).

The structural phase transition at temperature T_s in RE cobaltites, as was found previously, is accompanied by a softening (decrease) of the Young's modulus with decreasing temperature, which begins considerably above T_s, and then by its back jump at T_s and subsequent increase. Similarly, the magnetic phase transition is also accompanied by a softening of the Young's modulus, which begins above T_N,. Thus, in the interval between two temperatures T_s and T_N, a complicated behavior may be observed due to two opposite tendencies to increase and decrease of the Young's modulus [7].

For the series of the samples with different x, correlation is traced between the structure distortion and the deviation from stoichiometry on the one side and features in the curves $\Delta E(T)/E_0$, such as the value of the hysteresis, full softening of the module in the temperature range (80 – 280) K, the value of the anomaly in the range of T_N on the other side (compare curves for samples with x = 0, 0.1, 0.2 in Fig. 2, 3). The $\Delta E(T)/E_0$ curve for the quenched sample Q_1 is similar to that observed for the sample with x = 0.1, only softening begins with lower temperatures ~130 K and is a little bit less in value. On the contrary, the behavior of the quenched sample Q_2 is close to that observed for the stoichiometric sample with x = 0.

For the stoichiometric and distorted sample with x = 0, a jump of the Young's modulus is observed (Fig. 3) in the range of the magnetic phase transition temperature $T_N \sim 105$ K. In view of the temperature variation in the curves $\Delta E(T)/E_0$ on the background of monotonous change of $\Delta E/E_0$ (the dotted line shows extrapolation of the temperature trend in the range of T_N), the values of jump at cooling and heating practically coincide and are $\delta E(T_N)/E_0 \approx 1 \cdot 10^{-2}$. The phase transition temperature T_N corresponds to the jump in the $\Delta E(T)/E_0$ curve or to the maximum of the temperature derivative of Young's modulus (Fig. 4). The similar anomaly of the modulus (comparable in character and value) is also observed in the range of T_N for the quenched sample Q_2. These anomalies are caused by the magnetic phase transition of the second order, the transition temperature coinciding well with the literary data. For the stoichiometric compound with x = 0 (as well as for quenched sample Q_2), similar anomalies are observed in the range of the second magnetic phase transition with $T_{N2} \sim 70$ K (insert in Fig. 2).

The jumps in temperature dependences of Young's modulus $\Delta E(T)/E_0$ at T_N decrease very sharply, smooth out and become practically unobservable at oxygen increase in the nonstoichiometric samples $YBaCo_4O_{7.1}$ and $YBaCo_4O_{7.2}$ (Fig. 3). Their traces can only be found out in the temperature derivative $(E_0^{-1})(\mathrm{d}E/\mathrm{d}T)$ (Fig. 4), having a maximum in the range of T_N. The transition temperature, determined by the maximum in the curve $(E_0^{-1})(\mathrm{d}E/\mathrm{d}T)$, is $T_N = (104.0 \pm 0.2)$ K, and does not appreciably vary at the change of the stoichiometry.

Thus, the distortion of the structure at structural phase transition for the stoichiometric $YBaCo_4O_7$ samples removes frustration of exchange bonds and promotes to a formation of the long-range magnetic order as the distinct magnetic phase transition. This phase transition is accompanied by the anomaly taking place both at heating and cooling, and reproducing at repeated thermo cycling. Structures for the

nonstoichiometric samples remain undistorted, and frustrations in system are kept. As consequence, the short-range magnetic order develops gradually at temperature lowing, but the correlation length for magnetic order does not reach the sizes of crystallites.

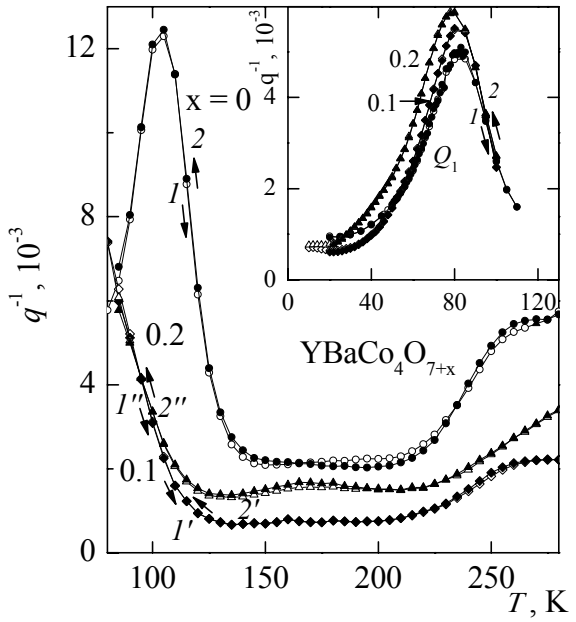

Fig. 5. Temperature dependence of the internal friction coefficient q^{-1} for the series of the $YBaCo_4O_{7+x}$ samples measured on heating (open symbols) and cooling (closed symbols). The insert shows comparison of absorption maxima of $q^{-1}(T)$ for the samples with $x = 0.1$, 0.2 and quenched sample Q_1.

Similarly, one can trace regularity in the behavior of the internal friction coefficient depending on the oxygen contents and distortion of the structure (Fig. 5). For the stoichiometric and distorted sample with $x = 0$ there is the large maximum consisting of two adjoined peaks close in temperature whereas for the nonstoichiometric samples with $x = 0.1, 0.2$, one low-temperature maximum at $T \sim 80$ K is only kept. The value of the $q^{-1}(T)$ maxima in the range of $T_N \sim 105$ K decreases for the quenched sample Q_2 which was not exposed to additional heat treatment in air. For the quenched sample Q_1, the behavior of the absorption maxima of the $q^{-1}(T)$ in the range of $T \sim 80$ K is very close to that observed for the nonstoichiometric samples with $x = 0.1$, 0.2 (insert in Fig. 5).

4 Summary

In this work, we performed experimental investigations of the structural and elastic properties for the series of the cobaltites $YBaCo_4O_{7+x}$ ($x = 0$, 0.1, 0.2) obtained by various technology and distinguished by oxygen content. Correlation was revealed between the structure distortion at room temperature and the hysteresis in $\Delta E(T)/T_0$ curve in the temperature range (80–280) K, as well as the anomaly value in the region of T_N. These compounds are found to exhibit significant hysteresis and irreversible elastic effects over a wide temperature range of (80–280) K between the temperatures of the structural and magnetic phase transitions. For the stoichiometric and distorted sample $YBaCo_4O_{7,}$ the magnetic phase transition is accompanied by weak and distinct anomaly of the elastic properties, that is according to low dimension of exchange interactions in the Co subsystem. The small deviations from the stoichiometry for $x = 0.1$, 0.2 result in suppression of the structural transition, reduce the hysteresis, quickly smooth out and reduce the anomaly of the Young's modulus $\Delta E(T)/T_0$ in the range of the magnetic phase transition. This behavior indicates that structural and magnetic transitions are suppressed in nonstoichiometric samples and only short-range correlations of order parameters are retained.

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