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NMR study of $LaMn_{1-x}Co_xO_3$ perovskites

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Abstract

The perovskite compounds of $LaMn_{1-x}Co_xO_3$ ($0.2 \leqslant x \leqslant 0.5$) have been studied by means of NMR spectroscopy in powder samples prepared by the solid state reaction and sol–gel methods. The NMR signals were observed in the frequency range 250–650 MHz at 4.2 K in zero external magnetic field. A relatively narrow spectral line assigned to ^{55}Mn in Mn^{4+} is situated around 270–320 MHz in all spectra. Additional spectral lines are observed at higher frequencies. Line intensities and forms are dependent on the cobalt concentration and preparation techniques.

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1. Introduction

During the past decade a high interest was devoted to perovskite manganites due to the variety of their electric transport and magnetic properties resulting from the competition of the lattice, charge, spin and orbital degrees of freedom. Besides studies of their macroscopic characteristics also local methods of investigation were successfully employed to provide insight into the micro-, meso- or nanoscopic subject matter. Nuclear magnetic resonance (NMR) was applied to the basic composition $LaMnO_3$, e.g. Ref. [1], as well as to the manganite perovskites with cationic substitutions including mixed valence compositions, to probe the manganese valence state, magnetic phase separation and other effects. Cationic substitutions of La^{3+} were studied quite often by NMR (see e.g. Refs. [2–6]). Systems with manganese ions partially replaced by other cations were studied only rarely [7,8] and the published spectra covered a limited spectral range around 300 MHz.

This paper reports the NMR results obtained for $La(Mn_{1-x}Co_x)O_3$ compounds where manganese cations of valency 3+ or 4+ are supposed to coexist with cobalt cations of valency 3+ or 2+. The accent was put on the proper technique of NMR experiments with respect to the broad spectral range of the detected spectra. The aim was to obtain reliable results for comparising spectra of samples which differ in amount of cobalt and also in preparation processes.

Solid solutions $La(Mn_{1-x}Co_x)O_3$ form perovskite structures with orthorhombic Pbnm (for $x < 0.46$) or rhombohedral R-3c (for $x > 0.46$) crystal symmetry. While $LaMnO_3$ is antiferromagnetic below 140 K (manganese valency is 3+ and spin $S = 2$), $LaCoO_3$ is diamagnetic below 100 K (cobalt ion is in a low spin state having valency 3+ and spin $S = 0$). For intermediate ratios of Mn/Co ferromagnetic order is observed, and at about $x \sim 0.5$ a possibility of higher and lower transition temperatures were reported [9]. These two phases were identified as the Mn/Co ordered ($T_c \sim 220$ K) and disordered ($T_c \sim 160$ K) one. Importantly, the valence distribution is close to Mn^{4+}/Co^{2+} in the former case and Mn^{3+}/Co^{3+} in the latter case [10,11].

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Electrical resistivity strongly depends on x. The samples are insulating for both $x = 0$ and 1 limiting values and the minimum of resistivity appears about $x \sim 0.2$.

2. Samples

Polycrystalline samples of $LaMn_{1-x}Co_xO_3$, $0.2 \leqslant x \leqslant 0.5$ were synthesised both by the standard solid state reaction and using the precursors prepared by sol–gel process.

In case of solid state reaction, homogenised mixtures of La_2O_3, $MnCO_3$ and $Co(NO_3)_2 \cdot 6H_2O$ were calcined at $600-900\,^{\circ}C$. The pre-reacted powder was pressed in the form of pellets, which were sintered at 1300 °C for 40 h and cooled down to the room temperature. The samples are same as used in [11–13].

For the sol–gel process the starting compounds La_2O_3, $MnCO_3$ and $Co(NO_3)_2 \cdot 6H_2O$ were separately dissolved in nitric acid, mixed together with citric acid and ethylene glycol in the ratio of 1:1.5:2.25, respectively, and pH was adjusted to 9 by addition of NH_4OH. Further steps included evaporation of water at 90 °C, drying at 160 °C and calcination at 400 °C (4 h) and then at $600-900\,^{\circ}C$. The pre-reacted powder was pressed in the form of pellets, which were sintered at $1200-1300\,^{\circ}C$ in air for 40 h and cooled down to the room temperature.

A list of the samples is given in Table 1 together with detailed parameters of their additional thermal treatment in oxygen atmosphere.

3. Experiment

NMR measurements were performed at 4.2 K in zero external magnetic field. Two pulse spin echo sequence was used.

The spectrometer used for our NMR measurements is a system based on a commercial BRUKER AVANCE high-resolution console. The original apparatus was adapted to cover broad frequency range needed for experiments carried out on magnetic materials. It works as a fully coherent one channel device in both transmitter and receiver sections and covers frequency range of 6–650 MHz. Coherent summation of NMR signals in the time domain for required number of scans enables to reach a high sensitivity.

Table 1
The list of measured samples with specification of Co content x, preparation method and additional thermal treatment

Sample	x	Method of synthesis	Additional treatment
0.2sg	0.2	sg	–
0.3sg	0.3	sg	–
0.4sgt	0.4	sg	$1200\,^{\circ}C\ O_2 + 750\,^{\circ}C\ O_2$
0.5sgt	0.5	sg	$1200\,^{\circ}C\ O_2 + 750\,^{\circ}C\ O_2$
0.5sg	0.5	sg	–
0.5sr	0.5	sr	–

The frequency of rf field was successively changed in steps of 1–2 MHz to cover the needed frequency range. Evaluating of the broadband spectra was based on the fast Fourier transformation (FFT) of the time domain data for each exciting frequency. Finally magnitudes of FFT at excitation frequencies were plotted.

The sample was placed into the broad-band probe. Attention was paid to the conditions of excitation as well as of detection of NMR spectra with respect to their frequency dependences. The parameters of rf pulses were optimised to get maximal NMR signal. Because the sensitivity of the detection line depends on the frequency, a calibration of receiver line was carried out (for each sample) to achieve reliable relative intensities in the broadband spectra. Details of the calibration procedures will be published elsewhere. To take into account the differences in nuclear Zeeman energy level populations, linear scaling of the intensity with increased frequency was applied. No corrections for the frequency dependence of enhancement factor were done.

4. Results and discussion

Spectra of $LaMn_{1-x}Co_xO_3$ samples measured at 4.2 K are plotted (normalised to unit area) in Figs. 1–3. All the spectra exhibit the relatively narrow spectral line at 270–320 MHz which can be unambiguously assigned to ^{55}Mn NMR in Mn^{4+} ions. Additional broad lines and, in some samples, another narrow line are observed at higher frequencies. Line intensities and forms are dependent on the cobalt concentration and preparation techniques.

NMR spectra of samples with the same x ($x = 0.5$) but prepared in different ways are compared in Fig. 1. While spectra 0.5sr and 0.5sg are rather similar and contain very broad structureless band between 330 and 600 MHz, spectrum 0.5sgt exhibits a dominating spectral line of width about 70 MHz situated around 520 MHz and another narrow line at 538 MHz. These spectral lines belong to the ^{55}Mn or ^{59}Co nuclei of transition metals. Their assignment to a certain resonating isotope and its valence state is though impossible at the moment; that is

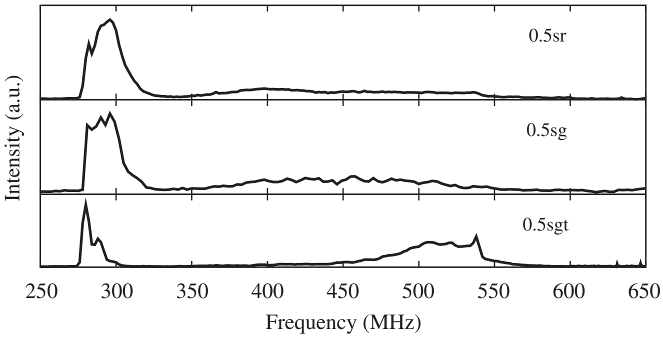

Fig. 1. NMR spectra of $LaMn_{1-x}Co_xO_3$ with $x = 0.5$ prepared by different techniques.

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