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Phase transition from *Pnma I* to *Pnma II* in the ^{57}Fe-doped $LaMnO_{3+\delta}$ compound

V. Sedykh *, G.E. Abrosimova, V.Sh. Shekhtman, I.I. Zver'kova,
A.V. Dubovitskii, V.I. Kulakov

Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow 142432, Russia

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Abstract

The structural phase transition from *Pnma I* to *Pnma II* in the 3% ^{57}Fe-doped lanthanum manganite $LaMnO_{3+\delta}$ has been investigated under heat treatment. It has been shown that the phase transition in the $LaMnO_{3+\delta}$ compound goes through the formation of the intermediate phase *Pnma II** under vacuum annealing at $T = 650$ °C (from 2 to 22 h). The transition from one phase to another, *Pnma I* → *Pnma II** → *Pnma II*, occurs virtually by jump. It follows from the Mössbauer investigations that two types of environments with stronger and weaker distortion exist in the *Pnma II** and *Pnma II* phases in contrast to *Pnma I* and $R\bar{3}c$, in which one type of environment takes place only.

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1. Introduction

Recently an interest to the new structural class of lanthanum manganites belonging to the extensive perovskite family and having unique properties has strongly increased. These materials find a wide application in different areas of current technologies because the doping of the compounds with bivalent Ca or Sr cations induces colossal magnetoresistance (CMR).

To understand a behavior of the doped systems the structure specific features of the basis non-doped $LaMnO_{3+\delta}$ compound should be thoroughly investigated. According to the data of literature [1–3] four structure modifications of this compound have been established: a rhombohedral phase of space group $R\bar{3}c$, two orthorhombic phases (named *Pnma I* and *Pnma II*) of space

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* Corresponding author. Tel.: +7 095 993 27 55; fax: +7 096 524 97 01.
E-mail address: sedykh@issp.ac.ru (V. Sedykh).

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group *Pnma* and a monoclinic phase of space group $P112_1/a$. It is known that the formation of these phases strongly depends on the conditions of synthesis of a complex oxide. In this connection it is interesting to find out the polymorphous bonds and the conditions of phase transitions under heat treatment.

In the present work the structural phase transition from *Pnma I* to *Pnma II* in the ^{57}Fe-doped $LaMnO_{3+\delta}$ compound has been investigated under vacuum annealing by X-ray diffraction analysis and Mössbauer spectroscopy.

2. Experimental

To synthesize the ^{57}Fe-doped $LaMnO_{3+\delta}$ compound a lanthanum oxide or carbonate (La_2O_3, $La_2(CO_3)_3\,6H_2O$), manganese oxides Mn_2O_3 or MnO_2 and 3% ^{57}Fe dissolved in HNO_3 have been used. Chemical analysis has shown that an oxide content in the specimens of the original compound was 99.5%. The specimens of the original compound taken in a stoichiometric ratio were ground and mixed in a ball micromill. Then the mixture was preliminary annealed in air at 900 °C for 10 h. After annealing the mixture was again ground. The final synthesis was made in air at 1100 °C for 20 h.

A quantity of oxygen excess δ (or relation between Mn^{3+} and Mn^{4+} ions) was determined by a direct weight method or potassium iodide titration.

An orthorhombic phase *Pnma I* was synthesized when quenching a specimen at 1100 °C. The specimen composition was $LaMn_{0.97}Fe_{0.03}O_{3.08}$ (Mn^{4+}, 17%, Mn^{3+}, 83%).

The orthorhombic *Pnma II* phase was obtained under subsequent vacuum annealing of *Pnma I* at 650 °C for 10 h (vacuum is $\sim 10^{-3}$ Torr). The specimen composition was $LaMn_{0.97}Fe_{0.03}O_3$.

To investigate the process of phase transition from *Pnma I* to *Pnma II* a series of vacuum annealing at 650 °C for different annealing time (from 2 to 22 h) was performed.

X-ray diffraction measurements were carried out at a diffractometer SIEMENS D500 (CuK_α-radiation). The special programs allowing us to smooth, to correct the background, to separate overlapping maxima etc. have been used when processing the diffraction data. A survey together with a reference was used to determine the lattice parameters.

The ^{57}Fe Mössbauer measurements were carried out on the polycrystalline specimens at room temperature by using a conventional Mössbauer spectrometer operating in the constant acceleration mode. To analyze the absorption spectra, the thin-foil approximation was used and a least-square fit was performed assuming a sum of Lorentz functions.

3. Results and discussion

X-ray diffraction patterns of the $LaMn_{0.97}Fe_{0.03}O_{3+\delta}$ specimens obtained for different vacuum annealing time are shown in Fig. 1. The upper and lower patterns illustrate the initial *Pnma I* and final *Pnma II* phases, respectively. The intermediate case for the mixture of two phases is shown in the middle pattern. It should be noted that the diffraction pattern is typical; when varying the vacuum annealing time a ratio of the *Pnma I* and *Pnma II* phases changes only; the lines with largest intensity of both phases coincide. The lattice parameters of phase components are tabulated in Table 1. A low degree of accuracy of the lattice parameters for *Pnma I* is due to a small amount of this phase in the specimens.

To determine a quantitative ratio of the mentioned phases and its variation in the process of heat treatment the computer simulation and comparison of the experimental and calculated data have been performed. For this purpose the program PowderCell (Werner Kraus and Gert Nolze, BAM Berlin) and the known lattice parameters and atomic positions in each of the lattices have been used [1]. The possible changes in both the structure parameters and the portion of each phase in the mixture have been considered for calculation and analysis. The calculation results of the reflection intensities of two phases are tabulated in Table 2. As is seen in Table 2 the *Pnma II* phase has the main contribution to the diffraction pattern for the specimen annealed for 8 h; as for the