Crystal structure and magnetic ordering of the LaCo$_{1-x}$Fe$_x$O$_3$ system

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Abstract
The $LaCo_{1-x}Fe_xO_3$ compounds have been investigated by means of neutron
powder diffraction (NPD), x-ray powder diffraction (XPD) and magnetization
measurements. The NPD and XPD patterns were successfully refined as
rhombohedral ($x \leqslant 0.5$) and orthorhombic ($x \geqslant 0.6$). The temperature-
induced transition from the rhombohedral phase into the orthorhombic one
is characterized by a two-phase crystal structure state. Magnetization and
neutron powder measurements have revealed that compounds with $x < 0.4$
exhibit a paramagnetic-like behaviour, whereas for $x \geqslant 0.4$ samples a weak
ferromagnetic component was observed. The NPD patterns were successfully
refined by admitting a G_z spatial orientation of the antiferromagnetic vector.
The magnetic properties of the $LaCo_{1-x}Fe_xO_3$ samples can be explained
assuming a low spin state of the Co^{3+} ions, whereas antiferromagnetism is
caused by magnetic interactions between the Fe^{3+} ions. Based on the obtained
data the combined crystal and magnetic phase diagram has been constructed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

It is known [1, 2], that if the crystal field splitting of the 3d states of the Co ions in octahedral
coordination and the Hund's rule intra-atomic exchange energy are comparable, the energy
gap between the t_{2g} and e_g states is rather small. Thus, entropic forces can cause different spin

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states of the Co ions. Specifically, the energy gap between the t_{2g} and e_g states of the Co ions in $LaCoO_3$ can be of the order of 10 meV, and then the t_{2g} electrons can be thermally excited into the e_g state, resulting in an intermediate or high spin state [1, 2]. That is accompanied by an anomaly in the magnetic susceptibility curve near 100 K. Most of the researches have supposed the spin-crossover phenomenon around 100 K in $LaCoO_3$ not to be a phase transition, but a thermal excitation of Co ions from a low spin (LS) state into an intermediate spin (IS) one. However, this mechanism is controversial at present. According to resonant soft x-ray emission spectroscopy investigations on $LaCoO_3$ [3] in the temperature range 50 K $< T <$ 120 K, the gradual thermal excitation of Co ions into the IS state indeed appears, but not the LS/IS energy level crossover. The ionic radius of the Co^{3+} ion in the intermediate spin state is significantly larger than that of the low spin state [4]. So, eventually an unit cell volume increase favours the spin state transition.

It is known [5] that a unit cell volume increase can also be induced by chemical substitution in the A and B perovskite positions. In particular, it is found that for the Sr-doped system, i.e. $La_{1-x}Sr_xCoO_3$, the spin state transition near 90 K disappears and that the Co ions remain magnetic down to the lowest temperatures [6]. In a $LaCo_{0.5}Ni_{0.5}O_3$ 'solid solution' compound, the e_g state occupation is much higher than in $LaCoO_3$. This is evidenced by fact that the unit cell volumes of the $LaCoO_3$ and $LaNiO_3$ compounds are less than those of $LaCo_{0.5}Ni_{0.5}O_3$ [7]. The unit cell volume increase favours the Co spin transition from the low spin state into the intermediate spin state for that compound, as well as the one in Ba_2CoNbO_6 [8, 9]. However, substitution of the Co ions by the Ga does not lead to a spin state transition regardless of an observed unit cell volume increase [10].

There are data in the literature [11–13] proving that application of external pressure as a rule stabilizes the low spin state. This has opened the possibility to control the spin state via the correlation between the ion electronic configuration and peculiarities of the cobaltite crystal structure. However, this correlation is far from being unambiguous and there are further investigations necessary to clarify the situation.

In the present work, it is shown that in spite of significant unit cell volume increase as the Fe ion concentration increases in $LaCo_{1-x}Fe_xO_3$, an intermediate spin state stabilization does not occur; thus Co^{3+} ions apparently remain in the low spin state.

2. Experimental section

Polycrystalline samples of $LaCo_{1-x}Fe_xO_3$ ($0.15 \leqslant x \leqslant 0.7$) were prepared by a conventional solid state reaction method. The appropriate amounts of La_2O_3, Co_3O_4 and Fe_2O_3 were ground and calcined at 1420 K for 6 h. The calcined samples were then ground again, sintered at 1770 K for 2 h and cooled down to the room temperature at a slow rate. The neutron diffraction study was carried out using the FIREPOD diffractometer ($\lambda = 1.7971$ Å) at the Hahn-Meitner Institute (BENSC, Berlin). The x-ray structure analysis was performed on diffractometer DRON-3M with Cu Kα irradiation. The structures were refined by the full-pattern Rietveld method using the program 'FullProf'. Magnetic measurements were performed using a Quantum Design MPMS SQUID magnetometer (IFPAN, Warsaw).

3. Results

3.1. Crystal structure

The x-ray powder patterns of the $LaCo_{1-x}Fe_xO_3$ samples at room temperature were successfully refined as rhombohedral ($x \leqslant 0.5$), orthorhombic ($x \geqslant 0.6$) and as a mixture

of rhombohedral and orthorhombic phases for $0.5 < x < 0.6$ region. In order to clarify the origin of a two-phase crystal structure and correlation between magnetic properties and crystal structure we selected two samples on which to perform neutron powder diffraction measurements—LaCo$_{0.5}$Fe$_{0.5}$O$_3$ and LaCo$_{0.42}$Fe$_{0.58}$O$_3$.

The crystal structure refinement, carried out on the basis of LaCo$_{0.5}$Fe$_{0.5}$O$_3$ neutron diffraction measurements at 300 K (figure 1(a)), revealed that the best reliability factors were obtained assuming the $R\bar{3}c$ space group. For the LaCo$_{0.5}$Fe$_{0.5}$O$_3$ sample, besides rhombohedral peaks, additional peaks appear in the neutron powder pattern as the temperature decreases. Such reflections, like (111), (101) are forbidden for the $R\bar{3}c$ space group, but allowed for the orthorhombic one. With a further temperature decrease the rhombohedral peak intensities become quite low and they vanish at 200 K. Below this temperature the LaCo$_{0.5}$Fe$_{0.5}$O$_3$ sample has a pure orthorhombic structure ($Pbnm$ space group) (figure 1(b)). Such a behaviour suggests a two-phase crystal structure in the temperature range 200 K $< T < 300$ K. With respect to the LaCo$_{0.42}$Fe$_{0.58}$O$_3$ sample the situation is similar. At room temperature the structure is a mixture of rhombohedral and orthorhombic phases. The neutron pattern recorded at 400 K shows a two-phase structural state of the LaCo$_{0.42}$Fe$_{0.58}$O$_3$ sample (figure 1(c)). The refinement of this NPD pattern reveals that the crystal structure consists of 80% rhombohedral phase and 20% orthorhombic one. According to the NPD data the two-phase crystal structure exists up to higher temperatures, i.e. 310 K $< T < 420$ K. Lattice parameters, coordinates, some interatomic distances and angles as obtained from the neutron data are shown in table 1.

3.2. Magnetic structure

According to the low-temperature neutron powder measurements one can conclude that for the LaCo$_{0.5}$Fe$_{0.5}$O$_3$ sample the most noticeable magnetic contribution is observed from the (101), (011), (013), (121) reflections, which are close to the 23.2°, 45.5° angles, respectively (figure 1(b)). It is worth noting that magnetic reflections which are indicative of a G-type magnetic structure, should be in accordance with the requirements $h + k = 2m + 1, l = 2n + 1$. It is easy to see that the observed reflections fulfil these conditions, meaning a magnetic structure which is similar to that of the LaFeO$_3$ compound [15]. The spatial orientation of the antiferromagnetic vector can be concluded from the (101), (011) peaks intensities. However, because of large overlap of these reflections it is difficult to evaluate their intensities, but from the peak shape we can conclude that they are almost equal. Therefore the antiferromagnetic vector has a spatial orientation G_z. The same reflections are observed for the LaCo$_{0.42}$Fe$_{0.58}$O$_3$ sample, resulting in basically the same magnetic structure for that compound.

As extracted from the neutron diffraction data on the LaCo$_{0.5}$Fe$_{0.5}$O$_3$ sample, the magnetic moment per B ion is about 1.6 μ_B at 6 K. Assuming a low spin state of the Co^{3+} ions, only Fe^{3+} would carry a magnetic moment. That would yield about 3.2 μ_B. For the LaCo$_{0.42}$Fe$_{0.58}$O$_3$ sample the same assumptions give a value of $\sim$4 μ_B per Fe^{3+} ion, though it should be 5 μ_B with a 3+ valence state of the cations. Possibly, the difference between calculated and expected values is caused by the unavoidable covalence component of the B-ion chemical bond.

3.3. Magnetization measurements

The temperature dependences of the magnetization were measured in a magnetic field of 100 Oe in the field cooled (FC) and zero field cooled (ZFC) modes. For the purposes of clarification only a few data are presented (figure 2). Samples with low iron concentration ($x < 0.3$) exhibit a paramagnetic-like behaviour, i.e. the FC and ZFC curves almost coincide. At $x = 0.3$ Fe concentration the samples develop spin-glass-like properties with a cluster freezing temperature
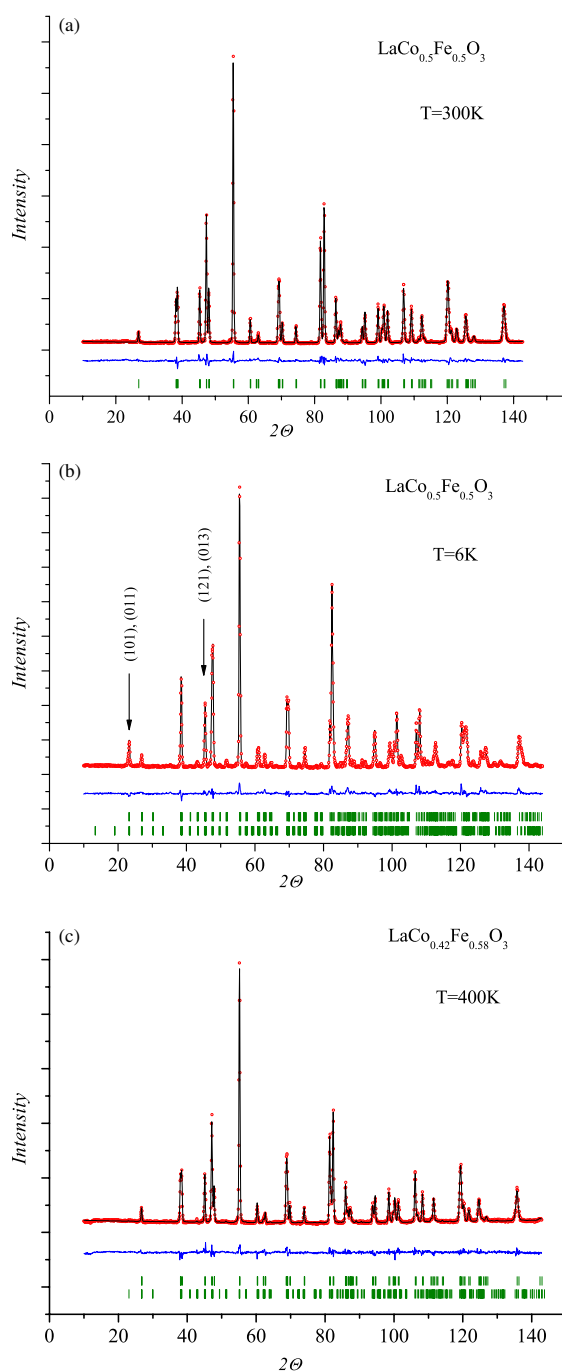
Figure 1. Refinement patterns for a La(Co$_{0.5}$Fe$_{0.5}$)O$_3$ sample at 300 K (a), for a La(Co$_{0.5}$Fe$_{0.5}$)O$_3$ sample at 6 K (b), and for a La(Co$_{0.42}$Fe$_{0.58}$)O$_3$ at 400 K (c), using neutron powder diffraction data. The observed intensities are shown by dots and the calculated ones by solid line. The positions of the Bragg reflections are shown by the small vertical lines below the patterns (for figures (b) and (c) the Bragg reflections in the upper line denote rhombohedral phase, and the lower ones orthorhombic phase). The line at the bottom indicates the intensity difference between the experimental and the refined patterns.

Table 1. The results of crystal structure refinements of $LaCo_{0.5}Fe_{0.5}O_3$ and $LaCo_{0.42}Fe_{0.58}O_3$ samples.

	x = 0.50			x = 0.58	
Temperature	6 K	300 K	4.2 K	400 K	400 K
Space group	$Pbnm$	$R\bar{3}c$	$Pbnm$	$R\bar{3}c$	$Pbnm$
a	5.4854(8)	5.4923(1)	5.4988(3)	5.5156(8)	5.5200(5)
b	5.4351(8)	—	5.4592(1)	—	5.4766(3)
c	7.7021(1)	13.2306(1)	7.7386(1)	13.3065(1)	7.7633(6)
La:	4c	6a	4c	6a	4c
x	−0.0029(3)		−0.0028(5)		−0.0063(2)
y	0.1879(3)		0.2054(4)		0.0179(2)
M:	4b	6b	4b	6b	4b
O(1):	4c	18e	4c	18e	4c
x	0.0630(4)		0.0647(6)		0.0562(4)
y	0.4948(5)	0.4461(1)	0.4948(7)	0.4458(4)	0.4947(4)
z					
O(2):	8d		8d		8d
x	−0.2712(3)	—	−0.2716(5)	—	−0.2763(2)
y	0.2707(3)	—	0.2715(5)	—	0.2705(3)
z	0.03359(2)	—	0.03506(3)	—	0.0420(1)
M–O(1)	1.958	1.954	1.976	1.963	1.965
M–O(2)	1.951		1.963		1.956
M–O(3)	1.957		1.963		1.976
M(1)–O–M(2)	162.07	162.60	161.362	162.50	161.75
M(1)–O–M(2)	159.04		159.01		158.20
R_p (%)	5.09	4.85	5.09	5.15	5.15
R_{wp} (%)	6.57	6.32	6.62	6.73	6.73
R_{Bragg} (%)	5.92	4.53	5.40	4.79	10.1
χ^2	3.65	5.07	1.25	1.35	1.35
Fraction %				79.33(3)	20.67(2)

of $\sim$50 K, whereas for $x = 0.4$ samples long-range magnetic ordering apparently arises. All the samples rich in iron ($x \geqslant 0.4$) are characterized by a small spontaneous magnetic moment. The magnetic properties of the intermediate Fe concentration samples show closer resemblance to those of $LaFeO_3$ than those of $LaCoO_3$. So, $LaCoO_3$ exhibits diamagnetic properties at low temperature as a result of the low spin state of Co^{3+} ions, whereas $LaFeO_3$ is known to be a weak ferromagnet with a Néel temperature of 740 K [16]. For the $LaCo_{0.5}Fe_{0.5}O_3$ sample a temperature-induced transition into the paramagnetic state occurs at 300 K, consistent with the neutron powder measurements, whereas for $LaCo_{0.42}Fe_{0.58}O_3$ the transition occurs at 380 K. The field dependences of the magnetization show that these samples are characterized by a strong magnetic anisotropy and the coercive force is about 3.5 kOe at 5 K. The saturation magnetization could not be estimated precisely from the magnetic measurements, but it is estimated to be less than 0.1 μ_B. Such a small value makes its exact determination from our neutron investigations also impossible.

4. Discussion

It is well known that Co^{3+} in the uncompensated spin state is a Jahn–Teller ion, which leads to CoO_6 octahedron distortions. These distortions can be identified by a difference in the Co(Fe)–O bond lengths. It has been found that for the $LaCo_{0.5}Fe_{0.5}O_3$ sample at low temperatures the
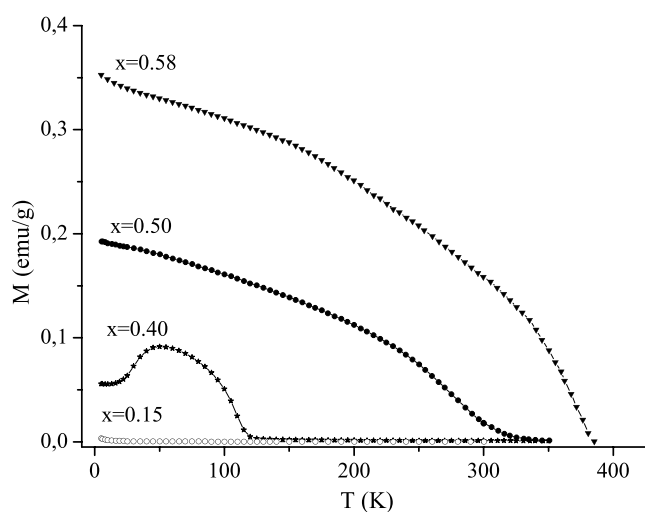
Figure 2. Temperature dependences of the magnetization as measured in the FC mode for the $LaCo_{1-x}Fe_xO_3$ samples with $x = 0.15, 0.4, 0.5$ and 0.58 at $H = 100$ Oe.

Co–O bond lengths in the CoO_6 octahedron differ from each other insignificantly, indicating only very small oxygen octahedron distortions. Almost the same small distortions are found with the $LaCo_{0.42}Fe_{0.58}O_3$ sample in the low-temperature region. Specifically, the average Co(Fe)–O bond lengths for $LaCo_{0.5}Fe_{0.5}O_3$ and $LaCo_{0.42}Fe_{0.58}O_3$ samples are equal to 1.955 and 1.968 Å respectively, which is slightly larger than for the $LaCoO_3$ (1.934 Å [4] at room temperature). This reduces the stability of the low spin state of Co^{3+} ions in comparison with the $LaCoO_3$ sample. At higher temperatures the situation is more complicated. Since the best reliability factors for the $LaCo_{0.5}Fe_{0.5}O_3$ sample were obtained with the $R\bar{3}c$ space group, we can suppose that if a difference in bond lengths really exists, it is insignificant. For the $LaCo_{0.42}Fe_{0.58}O_3$ sample, data obtained at 400 K for the *Pbnm* space group also confirm a small difference only in the Co(Fe)–O bond lengths.

Unit cell volume changes which are connected with a modification of the type of lattice distortion are less than 0.1%. It is found that the unit cell volume of $LaCo_{1-x}Fe_xO_3$ samples grows linearly with the Fe concentration, and the difference in the $LaFeO_3$ and $LaCoO_3$ volumes is about 8%. The temperature-induced lattice expansion is less than 1% (taking into account changes in the lattice distortion type), whereas for $LaCoO_3$ the unit cell volume at liquid helium and at room temperature is different by about 2%. So, despite the lower Co^{3+} ion spin state stability in the $LaCo_{1-x}Fe_xO_3$ system, the most likely ground state of Co ions is a low spin one for both the orthorhombic and rhombohedral phases. So, the obtained data are in accordance with the hypothesis of a thermal spin excitation of the Co ions in a $LaCoO_3$-based 'solid solution'.

The magnetization measurements confirm our assumption. The magnetic properties of the $LaCo_{1-x}Fe_xO_3$ system can be explained assuming a Co^{3+} low spin state. For $x < 0.4$ compounds, Fe-enriched clusters are isolated from each other, whereas near $x = 0.4$ a percolation of Fe-rich clusters takes place, leading to long-range magnetic ordering. Apparently, Co^{3+} ions being in a low spin state do not participate actively in the magnetic interactions, and so the magnetic properties of the compound can be explained predominantly by the magnetic coupling of the Fe^{3+} ions. The presence of a small spontaneous magnetization in heavily Fe-doped samples can be explained by antiferromagnetism developing a weak
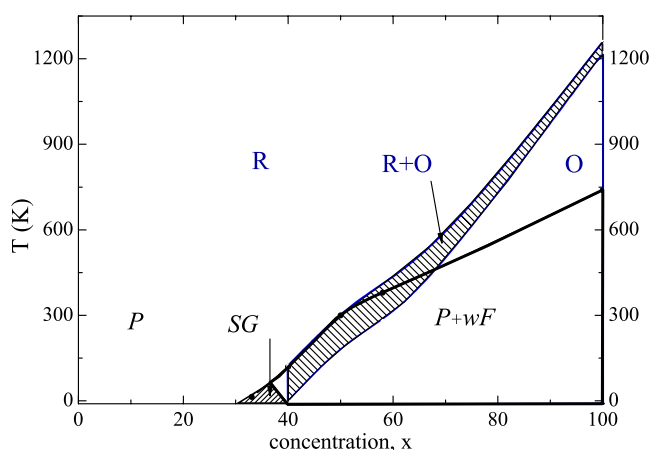
Figure 3. The combined crystal and magnetic phase diagram for the LaCo$_{1-x}$Fe$_x$O$_3$ system (O and R denote orthorhombic and rhombohedral phases whereas P, SG and wF denote paramagnet, spin-glass and weak ferromagnet respectively).

ferromagnetic component. In the case of a G_z configuration of the antiferromagnetic vector, a *Pbnm* space group permits only the F_x configuration of the weak ferromagnetic vector [17]. Most likely, the origin of the weak ferromagnetic component is similar to that proposed in orthoferrities; there it has been assigned to Dzialoshinsky–Moriya antisymmetric exchange interactions [18].

This suggestion is supported by the fact that almost in all of the heavily Fe-doped compounds a significant divergence in the FC and ZFC curves was observed, especially in the low-temperature region. This fact as well as a large coercive field evidences a significant magnetic anisotropy.

We failed to calculate any magnetic contribution from neutron measurements at high temperatures, i.e. at 300 K for LaCo$_{0.5}$Fe$_{0.5}$O$_3$ and 400 K for LaCo$_{0.42}$Fe$_{0.58}$O$_3$. That is to be expected from our magnetic investigations. Based on neutron and magnetic measurements one can conclude that below the magnetic transition temperature the samples with $x > 0.4$ consist of paramagnetic and weak ferromagnetic components, whereas at $x < 0.4$ the samples are paramagnets. Although, based on limited data we constructed a first-order combined magnetic and structural phase diagram for the LaCo$_{1-x}$Fe$_x$O$_3$ system (figure 3). The data for the LaFeO$_3$ compound were taken from [14]. So, there is some correlation between the magnetic ordering and the crystal structure type, in accordance with the assumption about the low spin state of Co ions.

The two-phase crystal region is narrowed with increasing Fe concentration and shifts simultaneously with a temperature increase. The most likely two-phase crystal structure is caused by the martensitic nature of the orthorhombic to rhombohedral phase transition and by the local chemical inhomogeneities, playing a key part in the middle concentration range.

5. Conclusion

The magnetic properties of the LaCo$_{1-x}$Fe$_x$O$_3$ system can be described using a model according to which Co^{3+} ions are predominately in the low spin state and do not participate actively in the magnetic interactions. Weak ferromagnetism and a large magnetic anisotropy are caused by the magnetically active subsystem of the Fe^{3+} ions. Their interactions result in the

appearance of long-range magnetic order at $x \sim 0.4$. Based on obtained data a combined structural and magnetic phase diagram has been constructed, confirming the envisioned correlation between magnetic properties and crystal structure in these compounds.

Acknowledgments

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