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Magnetic properties of $La_{0.7}Sr_{0.3}Mn_{0.85}Nb_{0.15-x}Mg_xO_3$ system

Abstract. Structural and magnetization measurements have been performed on the $La_{0.7}Sr_{0.3}Mn_{0.85}Nb^{5+}_{0.15-x}Mg^{2+}_xO_3$ system. With rise of the Mg^{2+} content the formal oxidation state manganese increases from +3 (x=0) up to +3.55 (x=0.15). The substitution of Nb^{5+} with Mg^{2+} leads to a gradual weakening of the ferromagnetic component while in the x=0.15 compound A-type antiferromagnetic short-range order is stabilized in spite of macroscopic R-3c symmetry. It is suggested that ferromagnetism is originated from superexchange interactions via oxygen.

Streszczenie. Przeprowadzono pomiary strukturalne i namagnesowania układu $La_{0.7}Sr_{0.3}Mn_{0.85}Nb^{5+}_{0.15-x}Mg^{2+}_xO_3$. Wraz ze wzrostem zawartości Mg^{2+} formalny stopień utlenienia manganu wzrasta z +3 (x=0) aż do +3.55 (x=0.15). Zastąpienie Nb^{5+} poprzez Mg^{2+} prowadzi do stopniowego osłabienia składnika ferromagnetycznego podczas gdy w związku x=0.15 typu A antyferromagnetyczny porządek krótkiego zasięgu jest ustabilizowany pomimo makroskopowej symetrii R-3c. Sugeruje się, że ferromagnetyzm pochodzi z nadwymiany za pomocą tlenu.
  *(**Magnetyczne właściwości układu $La_{0.7}Sr_{0.3}Mn_{0.85}Nb_{0.15-x}Mg_xO_3$**).*

Keywords: magnetization measurements, ferromagnetism, superexchange interactions.
Słowa kluczowe: pomiary namagnesowania, ferromagnetyzm, nadwymiana.

Introduction

$La_{1-x}A_xMnO_3$ (A=Ca, Sr, Ba) manganites have been of interest for many years since they exhibit very intriguing magnetic and magnetotransport properties [1-3]. In order to explain the interplay between magnetic and transport properties Zener introduced a special form of exchange interactions through charge carriers – double exchange [2]. De Gennes [4] developed a theory of double exchange and predicted that a canted magnetic structure forms at intermediate concentrations between the antiferromagnetic and ferromagnetic states. However, nuclear magnetic resonance data strongly support the mixed phase scenario as two different hyperfine lines corresponding to ferromagnetic and antiferromagnetic regions were observed. [5-7]. All these different experimental results indicate that the understanding of the development of ferromagnetic interactions in manganites is still far from being clear.

Optimally doped $La_{0.7}Sr_{0.3}(Mn^{3+}_{0.7}Mn^{4+}_{0.3})O_3$ has the highest critical temperature (T_C=380 K) of the transition into the ferromagnetic state among mixed-valence manganites. The substitution of manganese with a two-valence ion such as Mg^{2+} leads to an increasing Mn^{4+}/Mn^{3+} ratio and enhances the role of the interactions between Mn^{3+}-Mn^{4+} pairs. Conversely, by replacing manganese ions with five-valence ions such as Nb^{5+} or Sb^{5+} the average manganese valence is lowered and, hence, Mn^{3+}-O-Mn^{3+} superexchange interactions via oxygen should be dominant. In this work we report the structure and properties of $La_{0.7}Sr_{0.3}Mn_{0.85}Nb_{0.15-x}Mg_xO_3$ series. In this series the formal oxidation state of manganese ions is changed from +3 (x=0) up to +3.55 (x=0.15) assuming oxygen stoichiometry. Our results indicate that superexchange interactions can be dominant in the formation of ferromagnetic state of studied manganites.

Experimental

Ceramic samples of $La_{0.7}Sr_{0.3}Mn_{0.85}Nb_{0.15-x}Mg_xO_3$ series were prepared by a solid-state reaction technique using high purity oxides La_2O_3, Mn_2O_3, Nb_2O_5, MgO and carbonate $SrCO_3$ taken in a stoichiometric ratio and thoroughly mixed in a planetary mill (Retsch, 300 rpm, 30 min). La_2O_3 was preliminary annealed at 1100°C in air in order to remove moisture. The synthesis was performed at 1500°C – 1550°C for 7 h in air, using a two-step procedure with an interim annealing at 1400°C for 5 h followed by a thorough grinding. The samples were cooled from the synthesis temperature with a rate of 300°C/h down to 300°C. The reference compound $La_{0.7}Sr_{0.3}Mn_{0.85}Ga_{0.15}O_3$ (gallium is in the three-valent state) has been prepared in a similar manner. Neutron powder diffraction (NPD) measurements of the x=0 and x=0.15 compounds were performed on the high intensity D1B (λ=2.520 Å) and high resolution D2B (λ=1.594 Å) diffractometers (Institute Laue-Langevin, Grenoble). The samples x=0.05; 0.08 and 0.1 were studied with Fine Resolution Powder Diffractometer E9 (FIREPOD) (λ=1.7982 Å) at the Helmholtz-Zentrum for Materials and Energy, Berlin. Rietveld refinement of data has been performed using FULLPROF soft package [8]. Magnetic properties of samples were investigated with PPMS set-up in magnetic fields up to 14 T and in the temperature range 5-320 K (Cryogenic Ltd).

Results

Magnetization dependencies on magnetic field at 5 K are shown in Fig.1. The evolution of a ferromagnetic component upon increasing Mg-doping is clearly evident. The compositions x=0 and 0.05 have approximately equal magnetization at T=5 K. For the compositions x=0.1 and x=0.15 spontaneous magnetization is significantly smaller than that for x=0. The coercive field for x=0 and x= 0.05 is around 0.01 T at 5 K and weakly increases with magnesium content increasing. Magnetic moments per manganese ion evaluated from magnetization data are around $3.5\mu_B$ (x=0) and $0.6\mu_B$ (x=0.15). The observed magnetic moment for Mg-free compound is close to the expected value for the purely ferromagnetic state.
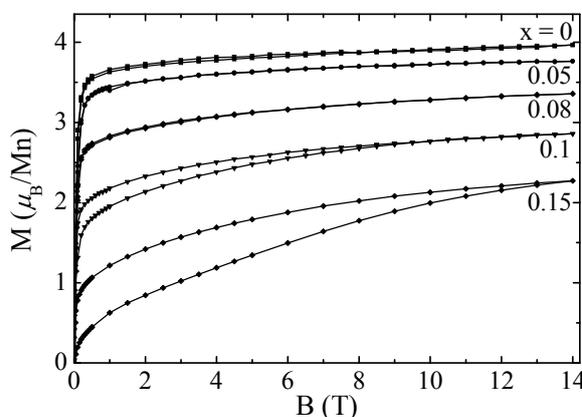

Fig.1. Field dependencies of magnetization for $La_{0.7}Sr_{0.3}Mn_{0.85}Nb_{0.15-x}Mg_xO_3$ samples measured at 5 K

One can suggest that the compositions $0<x<0.1$ are predominantly ferromagnetic. However, the presence of nonferromagnetic clusters embedded in a ferromagnetic matrix cannot be excluded. The contribution from nonferromagnetic clusters increases as the content of magnesium and therefore of Mn^{4+} ions rises. The Nb-free compound (x=0.15) exhibits a metamagnetic transition in the external magnetic field as can be seen from the field dependence of the magnetization in Fig.2. The fact that the hysteresis loop is not symmetric indicates that this transition is partially irreversible. The second magnetic field cycle leads then to a smaller magnetic hysteresis. The magnetic moment in a field of 14 T is significantly lower than the expected value for a pure ferromagnetic state. A rise in temperature suppresses the magnetic hysteresis. Note that a noticeable hysteresis in large magnetic fields has been detected as well for the x=0.1 sample (Fig.1).
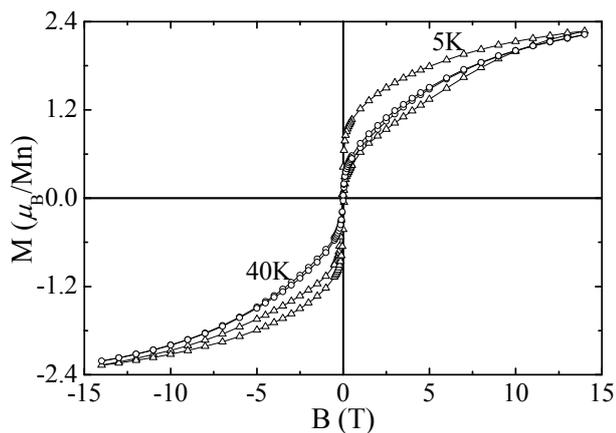

Fig.2. Field dependencies of magnetization for $La_{0.7}Sr_{0.3}Mn_{0.85}Mg_{0.15}O_3$ samples measured at 5 K and 40 K
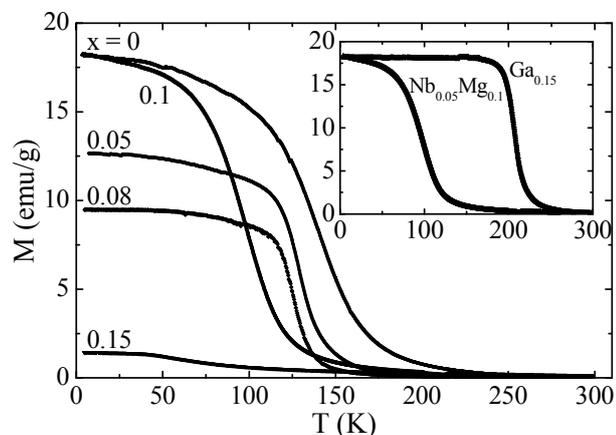

Fig.3. Temperature dependencies of magnetizations for $La_{0.7}Sr_{0.3}Mn_{0.85}Nb_{0.15-x}Mg_xO_3$ and $La_{0.7}Sr_{0.3}Mn_{0.85}Ga_{0.15}O_3$ (inset) samples measured in a field of 0.02 T

The temperature dependencies of magnetization measured in a small magnetic field upon cooling are presented in Fig. 3. One can see that substitution of Nb ions by Mg ones results in a lowering of the Curie temperature which is maximal (T_C=150 K) for the formally Mn^{4+} free compound (x=0).

NPD measurements show that the crystal structure of all the samples at room temperature can be successfully described in the frame of the rhombohedral space group R-3c. However, the samples with Mg content in the range $0<x<0.08$ show a structural transition with decreasing temperature. Rietveld refinement of the neutron diffraction

patterns at low temperature has been performed for these compounds using the Pnma space group resulting in a good agreement between experimental data and calculated patterns. The lattice parameters decrease smoothly with Mg doping (Fig.4). As the ionic radius of Mg^{2+} is larger than that of Nb^{5+} the decrease of the unit cell volume is the result of the appearance of Mn^{4+} ions, which have a much smaller ionic radius than Mn^{3+} ones. The connection between the lattice and orbital degrees of freedom, as investigated in several orthorhombic manganites [9, 10], suggests that the development of orbital ordering results in a contraction of the b parameter, and if $b/\sqrt{2}<c\le a$ the occurrence of orbital ordering can be conjectured [9, 10]. On the other hand, if $c>a\approx b/\sqrt{2}$, orbital disorder is expected. The observed relationship between the here determined structural parameters (Fig. 4) is in agreement with the absence of orbital order in the orthorhombic samples. The samples x=0.1 and 0.15 have rhombohedral symmetry down to helium temperature. Rietveld refinement of the neutron diffraction patterns using high-resolution data indicates that the refined oxygen contents correspond to a stoichiometric composition.
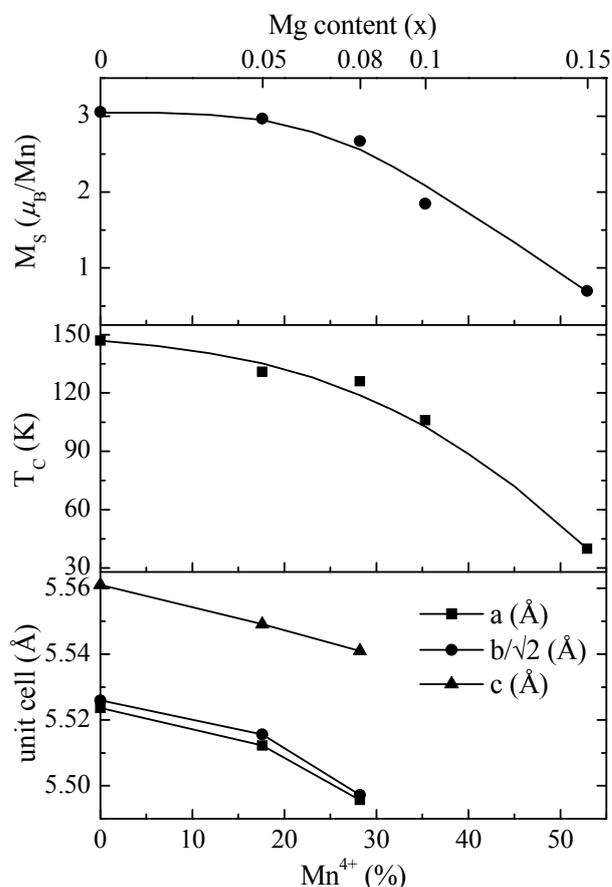

Fig.4. Spontaneous magnetization (top panel), temperature Curie (middle panel) and unit cell parameters (bottom panel) vs. Mn^{4+} concentration for $La_{0.7}Sr_{0.3}Mn_{0.85}Nb_{0.15-x}Mg_xO_3$ samples

The additional intensity contribution to some structural peaks observed below 150 K for the x=0 sample is associated with the ferromagnetic ordering. The refined magnetic moment is $3.1\mu_B$/Mn. Mg-doping leads then to a gradual decrease of the magnetic moment value (Fig.4). The dependencies of the Curie point and of the ferromagnetic moment value on the composition are shown in Fig.4. For the x=0.15 compound, one can notice that magnetic moment value determined from the ferromagnetic contribution to the Bragg peaks has decreased dramatically; indicating that only a very small fraction of the sample

shows long-range ferromagnetic order. Moreover, at the position where A-type antiferromagnetic peaks normally appear, a broad hump can be noticed. This suggests the existence of short-range A-type antiferromagnetic regions in the sample. This antiferromagnetic short-range order disappears at around 100 K. Note that the antiferromagnetic ordering is not accompanied by significant changes in the crystal structure.

All the samples show an insulating behavior of the resistivity. The x=0.15 sample exhibits strong magnetoresistance, however, its resistivity in a field of 14 T is still very large thus indicating the insulating character of the ferromagnetic phase.

Discussion

In contrast to the $La_{1-x}A_xMnO_3$ series (A=Ca, Sr, Ba) there is no enhancement of ferromagnetism under Mg^{2+} (Mn^{4+}) doping (Figs. 1, 3, 4). The conductivity is not strongly affected by the creation of Mn^{4+} through doping. Therefore, the ferromagnetism of the studied samples cannot be caused by orbital ordering or double exchange and is not associated with charge carriers. According to the Goodenough-Kanamori rules the sign of the 180-superexchange interaction between $Mn(e_g)$-O-$Mn(e_g)$ cannot be determined for the Mn^{3+} ion if the orbital ordering is removed [11, 12]. So, the antiferromagnetic and ferromagnetic components of the interactions can be equal. However, this statement is correct only in the case of a purely ionic bond. If, however, the chemical bond includes a covalent component hybridization occurs between the e_g orbitals of manganese and the $2p$ orbitals of oxygen. It results in a decreasing formal population of filled e_g orbitals of Mn as e_g electrons are partially located at the oxygen site leading to an increase of the ferromagnetic component of the superexchange interactions. In the ionic model a similar effect results by partially replacing La^{3+} ions with two-valent alkaline earth ions, in this case Mn^{4+} ions appear. This substitution leads to the decrease of the antiferromagnetic contribution in the superexchange interactions as the e_g orbitals of Mn^{4+} are empty.

Conclusions

We have presented a detailed magnetic analysis of the doping effect of Mn^{4+} ions in the $La_{0.7}Sr_{0.3}Mn_{0.85}Nb_{0.15-x}Mg_xO_3$ system. The parent compound (x=0) is basically ferromagnetic in spite of a formally single-valent Mn^{3+} state. The substitution of Nb^{5+} with Mg^{2+} is accompanied by an increase of the average manganese valence. The structural refinement shows that all the compositions are orbitally disordered. The increase of the Mn^{4+} content leads to a weakening of the ferromagnetic interactions and stabilizes gradually antiferromagnetic ones. The x=0.15 (55% Mn^{4+}) compound exhibits a metamagnetic behavior associated with the transformation of A-type short-range order into ferromagnetic one. The ferromagnetism of manganese single-valent compounds can be understood in terms of the superexchange scenario and orbital disorder

assuming a dominant role of covalency. It is suggested that a large local variation of the Mn-O-Mn bond angle due to Nb^{5+}/Mg^{2+} substitution destabilizes the ferromagnetic component. This angle is the key factor for p-d orbital hybridization and, hence, ferromagnetism. From our experimental data we do not see any need to invoke the strong double exchange interaction between Mn^{3+} and Mn^{4+} ions. Ferromagnetism in optimally doped mixed-valence manganites can be strongly supported by positive superexchange interactions between localized e_g electrons.

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REFERENCES
[1] Dagotto E., Hotta T., Moreo A., Colossal magnetoresistant materials: the key role of phase separation, *Physics Reports,* 344 (2001), No. 1-3, 1-153
[2] Zener C., Interaction between the d-shells in the transition metals. II. Ferromagnetic compounds of manganese with perovskite structure, *Phys. Rev.*, 82 (1951), No. 3, 403-405
[3] Şen C., Alvarez G., Dagotto E., Competing ferromagnetic and charge-ordered states in models for manganites: the origin of the colossal magnetoresistance effect, *Phys. Rev. Lett.*, 98 (2007), No. 12, 127202-1-4
[4] De Gennes P. G., Effects of double exchange in magnetic crystals, *Phys. Rev.*, 118 (1960), No. 1, 141-154
[5] Allodi G., De Renzi R., Guidi G., Licci F., Pieper M.W., Electronic phase separation in lanthanum manganites: evidence from ^{55}Mn NMR, *Phys. Rev. B*, 56 (1997), No. 10, 6036-6046
[6] Kumagai K., Iwai A., Tomioka Y., Kuwahara H., Tokura Y., Yakubovskii A., Microscopically homogeneous magnetic structure of $La_{1-x}Sr_xMnO_3$ beyond the range of 0<x<0,1 observed by La NMR, Phys. Rev. B, 59 (1999), No. 1, 97-99
[7] Choi K.-Y., Zhou H.D., Kuhns P.L., Reyes A.P., Dalal N.S., *Physica B*, 405 (2010), No. 1, 390–393
[8] Roisnel T., Rodriguez-Carvajal J., Winplotr: a windows tool for powder diffraction pattern analysis, *J. Mater. Sci. Forum*, 378-381 (2001), 118-123
[9] Zhou J.-S., Goodenough J.B., Orbital mixing and ferromagnetism in $LaMn_{1-x}Ga_xO_3$, *Phys. Rev. B*, 77 (2008), No.17, 172409-1-4
[10] Deisenhofer J., Paraskevopoulos M., Krug von Nidda H.-A., Loidl A., Interplay of superexchange and orbital degeneracy in Cr-doped $LaMnO_3$, *Phys. Rev. B*, 66 (2002), No.5, 054414-1-7
[11] Zhou J.-S., Goodenough J.B., Paramagnetic phase in single-crystal $LaMnO_3$, *Phys. Rev. B*, 60 (1999), No. 22, R15002-R15004
[12] Goodenough J.B., Magnetism and Chemical Bond, Interscience, New York/London, 1963.