BOLETIN DE LA SOCIEDAD ESPAÑOLA DE
Cerámica y Vidrio
A R T I C U L O

Spin reversal in Gd(*Me*,Mn)O_3 (*Me* = Co, Ni)

O. PEÑA, K. GHANIMI , C. MOURE*, D. GUTIÉRREZ*, P. DURÁN*
Chimie du Solide et Inorganique Moléculaire, UMR 6511. CNRS - Université de Rennes 1 - Institut de Chimie de Rennes, 35042 Rennes cedex, Frrancia
*Instituto de Cerámica y Vidrio, CSIC, Departamento de Electrocerámica, 28049 Cantoblanco, Madrid, SPAIN

Partial substitution of the rare-earth by calcium at the cationic site of the ABO_3 perovskites may show extraordinary effects of spin reversal due to a negative polarization between the rare-earth and the manganese networks, as it occurs in the solid solution $Gd_{1-x}Ca_xMnO_3$. We present herein similar effects in gadolinium perovskites of the Gd(*Me*,Mn)O_3 type, in which the manganese sublattice has been partially substituted by transition metal elements *Me*, leaving the gadolinium network intact. The spin reversal phenomena is observed at a critical concentration of x(*Me*) = 1/3, which implies an optimum number of pairs Mn^{3+}-Mn^{4+}. Néel temperatures of 48 and 67 K are obtained for *Me* = Co and Ni, respectively, at the optimum concentration of substituent. A comparison between these different solid solutions allows us to generalize the interpretation of two interacting magnetic sublattices : a Mn-based ferromagnetic one and a negatively-aligned gadolinium network.

Keywords : spin reversal, magnetic exchange, ferromagnetic perovskites, substitution effects

Inversión de espín en perovskitas Gd(*Me*,Mn)O_3 (*Me* = Co, Ni)

La sustitución parcial del lantánido por el elemento calcio en el sitio catiónico (sitio A) de la perovskita ABO_3 puede dar lugar a efectos importantes ligados a una inversión del espín. Dicha inversión se debe a una interacción negativa entre la tierra rara y la subred de manganeso, tal como ocurre en la solución solida $Gd_{1-x}Ca_xMnO_3$. Se presentan en este trabajo efectos similares que ocurren en las perovskitas de gadolinio de fórmula Gd(*Me*,Mn)O_3, en las cuales la subred de manganeso (sitio B) ha sido reemplazada parcialmente por otros metales de transición *Me*, dejando intacta la subred de gadolinio. Se observa el fenómeno de inversión de espín para una concentración crítica x(*Me*) = 1/3, para la cual se logra una cantidad óptima de pares Mn^{3+}-Mn^{4+}. Para esta concentración crítica se observan temperaturas de Néel antiferromagnéticas del orden de 48 y 67 K, respectivamente para *Me* = Co y Ni. Un análisis comparativo entre estos diferentes sistemas permite generalizar la interpretación de la existencia de dos subredes magnéticas que interactúan : una subred ferromagnética relacionada con el Mn, y una subred de gadolinio cuyos espines se orientan en sentido contrario a la primera.

Palabras clave : inversión de espín, interacciones de canje, perovskitas ferromagnéticas, fenómenos de sustitución

1. INTRODUCTION

Presence of two well-defined crystallographic and magnetic networks in the (RE,*A*)MnO_3 manganites (RE = rare-earth, *A* = alkaline-earth) leads to interesting features, due to the relative orientations of their respective magnetic moments. The most classical situation is encountered when both the ferromagnetic Mn lattice and the rare-earth spins show a cooperative behavior, i.e., their moments add together in a canted-antiferromagnetic geometry. However, if the exchange interaction J between networks becomes negative and, in addition, the magnitude of the rare-earth moment is much higher than the one due to the ferromagnetic Mn lattice, a ferrimagnetic-like state occurs, which may lead to some unusual situations. Thus, a net inversion of the magnetization, due to antiferromagnetically coupled sublattices has been reported in the (Gd,Ca)MnO_3 and (Dy,Ca)MnO_3 solid solutions [1-3]. Among other closely related compounds, the lanthanum-praseodymium orthochromate $La_{0.5}Pr_{0.5}CrO_3$ presents a spin reversal, even though none of the end-members of the solid solution $LaCrO_3$ and $PrCrO_3$ show any anomalous behavior [4]. A similar phenomenon occurs in the non-substituted gadolinium orthochromate $GdCrO_3$, for which the magnetization reverses its sign at T_{comp} = 130 K [5]. The common feature to all the above cited compounds is the presence of a homo-nuclear transition-metal ferromagnetic sublattice, that is, 100 % Mn or Cr, since the substitutions are only operated at the A-site of the perovskite compound.

On the other hand, it is well known that double-exchange ferromagnetic interactions in these perovskites materials may also be enhanced by partial substitution at the B-site, since a transformation mechanism $Mn^{3+} \rightarrow Mn^{4+}$ will occur. In such a case, two manganese atoms will be involved in the transformation : for each divalent ion *Me* replacing one manganese atom, a second manganese will convert into Mn^{4+}, leading to the general formulation $RE^{3+}\ Me^{2+}_x\ Mn^{3+}_{1-2x}\ Mn^{4+}_x\ O^{2-}_3$ [6]. In order to investigate if the spin reversal phenomena may also occur in perovskites containing a partially substituted manganese network, we synthesized gadolinium-based compounds of general formula Gd(*Me*,Mn)O_3, where *Me* is a transition element like Ni, Co or Cu. We present herein the magnetic behavior of these new perovskites, emphasizing their response to low field excitations. A comparison is made with both (Gd,Ca)MnO_3 [2] and Y(*Me*,Mn)O_3 [7-9] systems in order to generalize, if appropriate, the basic exchange-interaction mechanisms occurring in these materials.

2. EXPERIMENTAL

$GdNi_xMn_{1-x}O_3$, $GdCo_xMn_{1-x}O_3$, and $GdCu_xMn_{1-x}O_3$ compositions with x(*Me*) ranging from 0 to 0.50, were prepared by solid state reaction of *Me*O and Gd_2O_3 oxides. The mixtures were calcined at 1150 C for 2h, milled again and uniaxially pressed. Pellets were then sintered between 1325 C and 1450 C, dependent on composition and on the transitional metal, and slowly cooled in air at 1 C/min. Apparent densities reached 94-96 % of the theoretical values.

Bol. Soc. Esp. Ceram. V., 43 [3] 706-709 (2004)

Lattice parameters were determined by X-ray diffraction on a D-5000 Siemens diffractometer using CuK_α radiation and Si as an internal standard. A scanning rate of 1/4° 2Θ/min was used to calculate the lattice parameters. While most of the heavy rare-earth (including Y) pure manganites $REMnO_3$ crystallize in a hexagonal symmetry (S.G. $P6_3cm$), their solid solutions of the $RE_{1-x}Ca_xMnO_3$-type show a phase transition from a biphasic region (hexagonal + orthorhombic) towards a single-phase orthorhombic region at approximately x ~ 0.2, depending on the rare-earth size. However, in the specific case of the gadolinium-based manganites $Gd_{1-x}Ca_xMnO_3$, and $GdMe_xMn_{1-x}O_3$, the solid solutions extend over a large range of the alkaline Ca or the transition-metal *Me* substituents, including the pure manganite, all of them belonging to a single-phase region of orthorhombic perovskite-like symmetry, S.G. *Pbnm*. It should be noticed that, contrary to the Y(*Me*,Mn)O_3 series, compounds of formula $GdMe_{0.3}Mn_{0.7}O_3$ crystallize in the O′-type orthorhombic structure, that is, with $c/\sqrt{2} < a < b$ (Table I).

TABLE I. LATTICE PARAMETERS OF $GdMe_{0.3}Mn_{0.7}O_3$ COMPOUNDS (*Me* = Co, Ni, Cu)

Sample	a±0.0001 (nm)	b±0.0001 (nm)	c±0.0001 (nm)	V±0.0001 (nm³)	$c/\sqrt{2}$ ±0.0001 (nm)
$GdCo_{0.3}Mn_{0.7}O_3$	0.5310	0.5755	0.7483	0.2287	0.5291
$GdCu_{0.3}Mn_{0.7}O_3$	0.5314	0.5793	0.7439	0.2290	0.5254
$GdNi_{0.3}Mn_{0.7}O_3$	0.5306	0.5748	0.7485	0.2283	0.5293

S.G. = Pbnm, O′-type ($c/\sqrt{2} < a < b$)

Magnetic measurements were performed in a SHE VTS-906 SQUID susceptometer, between 5 K and 300 K. All measurements were done after cooling the samples in the absence of a magnetic field, then performing ZFC/FC cycles under 50 Oe or susceptibility measurements under a 500-Oe applied field. These properties were measured in specimens cut from ceramic bulks and glued to a thin rod in order to avoid disorientation due to torque forces exerted on the sample. Additional characterization by a.c. techniques was performed using a home-made mutual-inductance susceptometer [10].

3. RESULTS AND DISCUSSION

3.1. Paramagnetic regime.

Figure 1 shows the inverse susceptibility measured under an applied field of 500 Oe, for three $GdMe_{0.15}Mn_{0.85}O_3$ samples (*Me* = Cu, Ni, Co). The paramagnetic regime for these three samples extends from about 50 K up to room temperature. Below T ~ 50 K, deviations to the Curie behavior are observed, due to the ordered state which takes place at low temperatures ; in such a case, the proportionality between the magnetization and the applied field is not valid anymore, and the magnetic susceptibility should be understood in terms of M/H ratios. The inverse susceptibility was then fitted by a Curie-Weiss law in the region [50 K ≤ T ≤ 300 K], yielding a magnetic moment of the order of 8.9 to 9.1 μ_B/formula-unit. The Weiss parameter Θ ranged between -11 K ($GdNi_{0.15}Mn_{0.85}O_3$) and -21 K ($GdCu_{0.3}Mn_{0.7}O_3$), suggesting quite constant antiferromagnetic exchange interactions, almost independent of the *Me* substituent. By taking a constant gadolinium contribution (μ = 7.94 μ_B/Gd^{3+}-atom) to the overall effective moment, then the remaining contribution of the *Me* transition metal can be estimated from

$$\mu_{Mn+Me} = [\mu_{eff}^2 - \mu_{Gd}^2]^{1/2} = [\mu_{eff}^2 - 7.94^2]^{1/2} \ ,$$

yielding values of μ_{Mn+Me} = 4.37, 4.11 and 3.97 μ_B, for the [Mn+*Me*] network, *Me* = Co, Ni and Cu, respectively. These values fully agree with those obtained for the series Y(*Me*,Mn)O3, for similar *Me* concentrations, in which the rare-earth element (Y) does not contribute to the overall moment (μ_{Mn+Me} = 4.64, 4.47 and 3.81 μ_B, for $YCo_{0.3}Mn_{0.7}O_3$ [8], $YNi_{0.3}Mn_{0.7}O_3$ [7], $YCu_{0.3}Mn_{0.7}O_3$ [9], respectively).

3.2. Ordered state

3.2.1. a.c. SUSCEPTIBILITY

Figure 2 shows the a.c. susceptibility of $GdCo_{0.3}Mn_{0.7}O_3$ and $GdNi_{0.3}Mn_{0.7}O_3$ measured under an applied field of about 30-50 mOe, at a fixed frequency of 119 Hz. Well defined maxima are observed at T_{max} = 48 K and 67 K, respectively, suggesting predominant antiferromagnetic-type interactions, typical of a spin-glass behavior or AF-canted materials. Further experiments under low applied fields (see below) make us to prefer the second possibility (then, $T_{max} = T_{Néel} = T_N$) rather than the first one. Unfortunately, the presence of gadolinium in these samples handicaps any further investigation of the magnetic structure through neutron diffraction techniques. For less-substituted specimens (x = 0.15), T_N decreases enormously (e.g., T_N ~30 K, for $GdNi_{0.15}Mn_{0.85}O_3$) and becomes almost undetectable for the cobalt-based compound $GdCo_{0.15}Mn_{0.85}O_3$. No anomaly was detected on the copper-based perovskite $GdCu_{0.3}Mn_{0.7}O_3$. For this reason, most of the remaining experiments were performed at the optimum concentration of x(*Me*) = 0.3, which leads to the best observation of the magnetic phenomena.

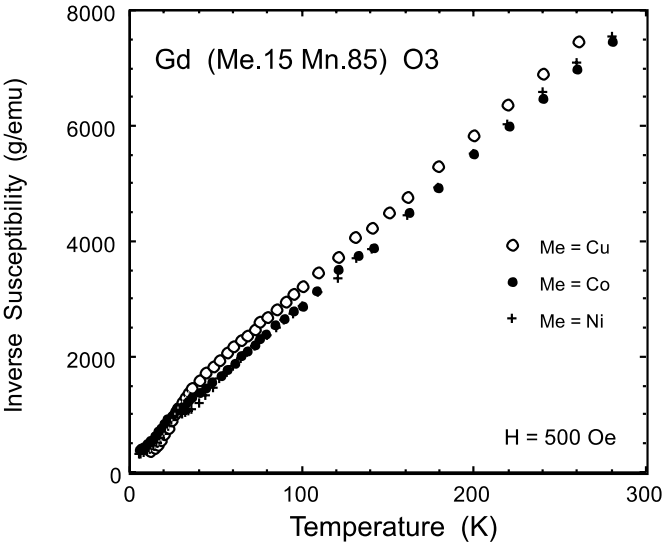

Fig. 1. Inverse magnetic susceptibility of $GdMe_{0.15}Mn_{0.85}O_3$ (*Me* = Cu, Ni, Co), measured under a 500-Oe applied field. Magnetic moments were calculated by Curie-Weiss fits on the range [50 K ≤ T ≤ 300 K]

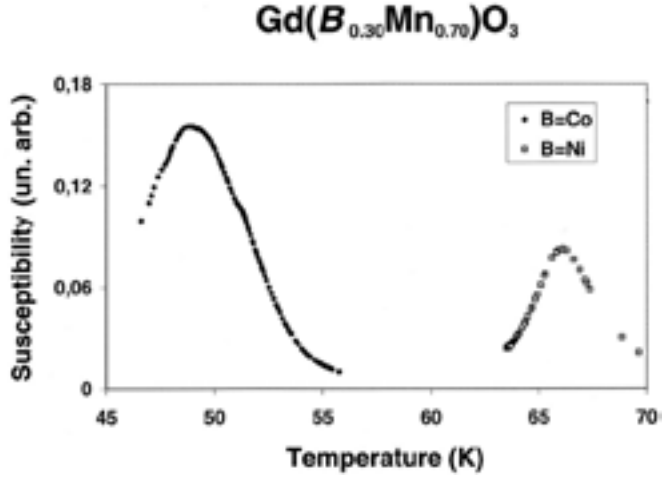

Fig. 2. a.c. susceptibility ($h_{a.c.}$ ~ 30-50 mOe) of $GdCo_{0.3}Mn_{0.7}O_3$ (closed symbols) and $GdNi_{0.3}Mn_{0.7}O_3$ (open symbols).

3.2.2. ZFC/FC CYCLES

The magnetic ordering transitions were studied by ZFC/FC methods, performed at 50 Oe, in the temperature range between 5 K and 300 K. Figures 3 and 4 show the temperature dependence of the magnetization ratio M/H, for samples $GdCo_{0.3}Mn_{0.7}O_3$ and $GdNi_{0.3}Mn_{0.7}O_3$. During the ZFC branch, that is, while warming the samples after they have been cooled under no magnetic field, a small decrease of the magnetization is first observed. This decrease is just the Curie-Weiss dependence of the susceptibility of the gadolinium moments. With further warming, steep maxima are observed, centered at about 60 K, for $GdNi_{0.3}Mn_{0.7}O_3$, and about 45 K, for $GdCo_{0.3}Mn_{0.7}O_3$. These maxima agree with those observed by $\chi_{a.c.}$ (§. 3.2.1), and suggest little or no dependence of T_N with the applied field. This process should be attributed to the canted-type structure of the manganese spins, where antiferromagnetic interplane interactions compete with a ferromagnetic in-plane exchange, as usually observed in ferromagnetic perovskites [11-13]. Above $T_c \sim 70$ K ($GdNi_{0.3}Mn_{0.7}O_3$) or $T_c \sim 60$ K ($GdCo_{0.3}Mn_{0.7}O_3$), the compounds reach the paramagnetic state, characterized by a Curie-Weiss behavior and a reversible thermal variation of the susceptibility.

On cooling under the external field of 50 Oe (FC process), the magnetization follows a reversible path down to T_c. At this temperature the [Mn+*Me*] sublattice orders ferromagnetically and imposes an internal field to the Gd sublattice. The magnetization increases abruptly, reaching higher values than those observed in the warming process. By supposing a negative exchange interaction J between the [Mn+*Me*] and the Gd moments, the rare-earth sublattice will polarize in the opposite direction to the internal field created by the [Mn+*Me*] network.

One of the key points in the magnetic behavior of these compounds is the fact that the rare-earth spins should be considered as free ions, and as such, they should follow a Curie-Weiss dependence, with a magnetic contribution which increases as 1/T when the temperature decreases. Since the gadolinium free ion moment ($\mu_{Gd} = 7.94\ \mu_B$) is much larger than the one associated to the transition-metal lattice μ_{Mn+Me}, the total magnetization of the Gd lattice will counteract the [Mn+*Me*] contribution. At a temperature defined as the compensation temperature $T = T_{comp}$, both contributions reach the same absolute value (then, $M_{tot} = M_{Mn+Me} + M_{Gd} = 0$), and when $T < T_{comp}$, the overall magnetization changes its sign and becomes negative.

3.2.3. MEAN-FIELD APPROXIMATION

As stated above, the ZFC/FC curves can be easily interpreted, as in ferrimagnetic systems, by the superposition of two interacting magnetic networks : a Mn-based sublattice, « frozen » in its ferromagnetic state, and a negatively-polarized sublattice, composed of paramagnetic free Gd spins, whose magnetization varies as 1/T. Then, when cooling under the presence of small fields (FC process), the [Mn+*Me*] network orders ferromagnetically, enhancing the local field at the Gd sites. In a mean-field approximation, if H_{Gd} (the local field at the Gd site) is mainly due to the magnetic moment of the [Mn+*Me*] sublattice, then

$$M_{Gd} = \chi Gd(T).H_{Gd} \sim \chi Gd(T).M_{Mn+Me}$$

By supposing a negative exchange interaction J between the transition-metal and the Gd spins, it follows

$$M_{tot} = M_{Mn+Me} + M_{Gd} = M_{Mn+Me} + |J|.\chi Gd(T).M_{Mn+Me}$$

Then the total magnetization may be written as

$$M_{tot} = \{1 + |J|.\chi Gd(T)\}.M_{Mn+Me} = \{1-\delta\chi Gd\}.\ M_{Mn+Me}$$

where δ takes into account the strength and the sign of the magnetic interaction between sublattices. From the above relation, it is immediately seen that, at low temperatures, when the gadolinium susceptibility ($\chi Gd \sim 1/T$) becomes sufficiently large, the total moment will reverse its sign. Obviously, at a macroscopic level, the resulting behavior would be of a ferrimagnetic type.

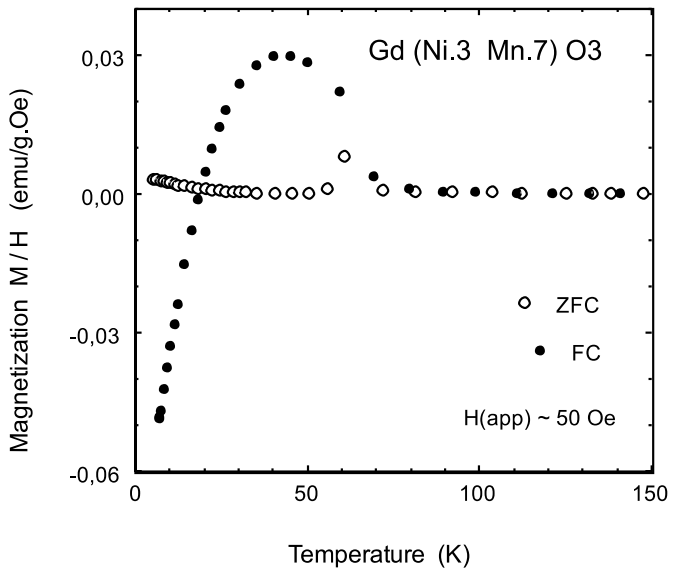

Fig. 3. Thermal variation of the M/H ratio for $GdNi_{0.3}Mn_{0.7}O_3$, during a ZFC/FC cycle performed under a 50-Oe applied field

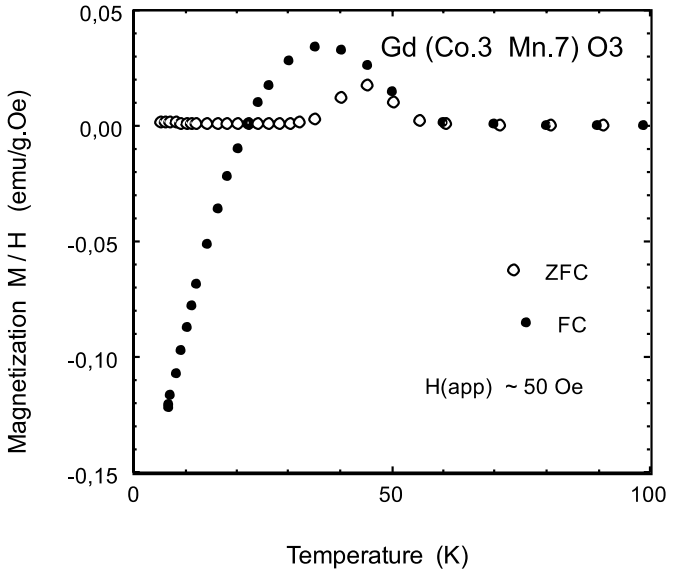

Fig. 4. Thermal variation of the M/H ratio for $GdCo_{0.3}Mn_{0.7}O_3$, during a ZFC/FC cycle performed under a 50-Oe applied field

4. CONCLUSIONS

From all perovskite materials known up today presenting the spin reversal phenomena, none of them -to our knowledge- concerned a mixed transition-metal sublattice and a 100 % rare-earth network. Indeed, even if the case of the pure ternary orthochromate $GdCrO_3$ compound also presents a reversal of the magnetization [5], no other examples concerning ferromagnetic manganites are known to have a 100% homogeneous rare-earth network. The originality of the present work mainly concerns the possibility to partially substitute the B-site network, preserving the ferromagnetic character and the spin reversal phenomenon. On the other hand, it is also interesting to notice that the copper ion seems to be a not good candidate for this purpose, perhaps due to its high Jahn-Teller nature which prevents an effective Mn^{3+}-O-Mn^{4+} double-exchange interaction.

REFERENCES

1. G.J. Snyder, C.H. Booth, F. Bridges, R. Hiskes, S. DiCarolis, M.R. Beasley, T.H. Geballe. "Local structure, transport, and rare-earth magnetism in the ferrimagnetic perovskite $Gd_{0.67}Ca_{0.33}MnO_3$". Phys. Rev. B., **55**, 6453-6459 (1997)
2. O. Peña, M. Bahout, K. Ghanimi, P. Duran, D. Gutierrez, C. Moure. "Spin reversal and ferrimagnetism in (Gd,Ca)MnO_3". J. Mater. Chem., **12**, 2480-2485 (2002)
3. M. Mouallem-Bahout, O. Peña, D. Gutierrez, P. Duran, C. Moure. "Peculiar magnetic properties of (Dy,Ca)MnO_3". Solid State Comm., **122**, 561-564 (2002)
4. K. Yoshii, A. Nakamura. "Reversal of magnetization in $La_{0.5}Pr_{0.5}CrO_3$". J. Solid State Chem., **155**, 447-450 (2000)
5. K. Yoshii. "Magnetic properties of perovskite $GdCrO_3$". J. Solid State Chem., **159**, 204-208 (2001)
6. C. Moure, D. Gutierrez, O. Peña, P. Duran. "Structural characterization of $YMe_xMn_{1-x}O_3$ (*Me* = Cu, Ni, Co) perovskites". J. Solid State Chem., **163**, 377-384 (2002)
7. O. Peña, M. Bahout, D. Gutierrez, J.F. Fernandez, P. Duran, C. Moure. "Critical behavior in the perovskite-like system Y(Ni,Mn)O_3". J. Phys. Chem. Solids, **61**, 2019-2024 (2000)
8. D. Gutierrez, O. Peña, K. Ghanimi, P. Duran, C. Moure. "Electrical and magnetic features in the perovskite-type system Y(Co,Mn)O_3". J. Phys. Chem. Solids, **63**, 1975-1982 (2002)
9. O. Peña, D. Gutierrez, P. Duran, C. Moure. "Magnetic properties of manganese-site substituted Y(Cu,Mn)O_3 perovskites". Bol. Soc. Esp. Ceram. V., this conference
10. O. Peña. "An easy and non-destructive induction method to characterize superconducting materials with planar geometry". Meas. Sci. and Technol. **2**, 470-475 (1991)
11. M. Hennion, F. Moussa, J. Rodriguez-Carvajal, L. Pinsard, A. Revcolevschi. "Coherent waves of magnetic polarons propagating in $La_{1-x}Ca_xMnO_3$: an inelastic-neutron-scattering study". Phys. Rev. B, **56**, R497-R500 (1997)
12. B. Dabrowski, X. Xiong, Z. Bukowski, R. Dybzinski, P.W. Klamut, J.E. Siewenie, O. Chmaissem, J. Shaffer, C.W. Kimball, J.D. Jorgensen, S. Short. "Structure-properties phase diagram for $La_{1-x}Sr_xMnO_3$ ($0.1 \le x \le 0.2$)". Phys. Rev. B, **60**, 7006-7017 (1999)
13. J.M. De Teresa, C. Ritter, M.R. Ibarra, P.A. Algarabel, J.L. Garcia-Muñoz, J. Blasco, J. Garcia, C. Marquina. "Charge localization, magnetic order, structural behavior, and spin synamics of $(La,Tb)_{2/3}Ca_{1/3}MnO_3$ manganese perovskites probed by neutron diffraction and muon spin relaxation". Phys. Rev. B, **56**, 3317-3324 (1997)