Giant magnetostructural coupling in $\text{Gd}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$

Correa V. F. 1, Sänger N. 2, Jorge G. 3, Nieva G. 1, Haberkorn N. 1

1 Comisión Nacional de Energía Atómica, Centro Atómico Bariloche, 8400 S. C. de Bariloche, Argentina
2 Fachbereich Physik, Universität Konstanz, D-78457 Konstanz, Germany
3 Departamento de Física, FCyN, Universidad de Buenos Aires, Argentina

E-mail: victor.correa@cab.cnea.gov.ar

Abstract. We report high magnetic field magnetostructural studies on $\text{Gd}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ single crystals. A giant linear magnetostrictive effect is observed in a wide temperature range ($T < 120$ K). Above 25 K a large hysteresis is seen reflecting the $\text{Mn}$ magnetic moments ordering. At lower temperature ($T < 15$ K), a rather complicated field dependence arising from the competition between the $\text{Mn}$ and $\text{Gd}$ magnetic sublattices is observed. The relevance of the $\text{Gd}$ ions in the low temperature behavior is further corroborated by specific heat experiments.

1. Introduction

Manganite compounds are mostly known for their spectacular colossal magnetoresistance (CMR). But CMR is not the only superb effect observed in these systems. Less known, but as formidable as CMR, they show what is called giant linear magnetostriction (MS): any linear dimension of the sample is strongly affected by an applied magnetic field. The effect is comparable in magnitude ($\lambda = \Delta L/L \geq 10^{-3}$ at several Tesla) to the highest MS values ever reported. In some members of the family, even giant volume MS ($\Delta V/V$) is seen. In this sense, they are not only excellent candidates for applications in magnetic memories making use of their CMR properties but also good candidates for applications as actuators, sonar systems or ultrasound devices due to their giant MS properties.

For some doping levels, manganites show a metal-insulator (MI) transition associated with the onset of $\text{Mn}$ ions ferromagnetic ordering at the Curie temperature $T_c$. As it happens with magnetoresistance, the magnetostrictive effect is particularly large around $T_c$, implying that CMR and giant MS could be related phenomena [1]. In fact, their overall field dependence is quite similar displaying, both resistivity $\rho$ and $\lambda$, a rapid increase at low fields followed by saturation above the same field that magnetization saturates.

In zeroeth order, metal-insulator transition as well as magnetoresistance can be easily understood in terms of a double-exchange mechanism: ferromagnetic ordering (spontaneous or field induced) favors metallic character. However, as pointed out by Millis et al. [2], many aspects of manganites cannot be explained by such a simple mechanism and the need of a more sophisticated model was suggested. Particularly, the need to include the Jahn Teller (JT) effect to better describe the MI transition.

In this way, by introducing not only double-exchange hopping but also JT distortion, Zeeman and elastic energies a simple correlation between metallic character, magnetoresistance and magnetostriction can be obtained [3]: at certain temperature, the JT effect in $\text{Mn}$ ions favors
the lattice distortion at the cost of elastic energy. When lowering the temperature, the ions order ferromagnetically inducing a MI transition. The system can further lower the energy by killing the JT splitting, thus placing more electrons at the bottom of the \( e_g \) bands and gaining elastic energy. If around \( T_c \) a magnetic field is applied, magnetic ordering is even more favorable. Then, CMR and giant MS naturally follow.

So far so good with metallic manganites. But, what happens with doping levels for which no MI transition is observed? Well, it turns out to be that CMR as well as giant MS are detected down to very low temperature [4]. Naively, it can be thought that the exchange is not strong enough as to induce spontaneous magnetic ordering but an external magnetic field does it, giving CMR and giant MS. And, what happens if the system is further complicated introducing a second magnetic ion?

In this work we present magnetostriction experiments on single crystals of the insulating ferrimagnet \( \text{Gd}_{2/3} \text{Ca}_{1/3} \text{MnO}_3 \) [5, 6, 7]. The \( \text{Gd} \) and \( \text{Mn} \) magnetic sublattices compete each other giving rise to a non monotonic field dependence at low temperature. At higher temperature \( (T \geq 25 \text{ K}) \) a large hysteresis associated with the ferrimagnetic order is seen. Even though a negligible magnetoresistance was reported [5], the magnetostructural effect is giant in a wide temperature range suggesting that an extra mechanism besides double-exchange and Jahn Teller distortion should be considered for a proper description of this system.

2. Results

\( \text{Gd}_{2/3} \text{Ca}_{1/3} \text{MnO}_3 \) single crystals were grown by the floating zone technique [7]. Magnetostriction experiments were carried out using a capacitive dilatometer with sub-Angstrom resolution [8] while specific heat measurements were performed in a \( \text{SiN} \) membrane micro-calorimeter with the thermal relaxation time technique [9].

![Figure 1](image)

**Figure 1.** Temperature dependence of the magnetization/magnetic field ratio at two different applied fields (for FCC and FCW procedures). Small differences between FCC and FCW around \( T_{\text{comp}} \) are discussed in Ref. 7.

Fig. 1 displays the temperature dependence of the magnetization/magnetic field ratio \( M/H \) for field cooling cooling (FCC) and field cooling warming (FCW) procedures at two different applied fields: 1000 and 7500 Oe. It is the typical behavior of ferrimagnetic systems. Around \( T_c \approx 80 \text{ K} \) the \( \text{Mn} \) magnetic moments start to order ferromagnetically. The \( \text{Gd} \) moments behaves basically as paramagnetic free ions reacting to the internal field created by the ferromagnetic \( \text{Mn} \) sublattice. Hence, they start to align in the opposite direction giving rise to the peak seen around 50 K. At \( T_{\text{comp}} \approx 15 \text{ K} \), the two sublattices magnetism compensate and the magnetization \( M \) vanishes. Below \( T_{\text{comp}} \) the \( \text{Gd} \) moment is larger and \( M \) is negative. Applying a field higher than the coercive field the net magnetization can be flipped over switching to positive as the 7500 Oe curve shows.
Linear magnetostriction $\Delta L_c/L_c$ along the c-axis (direction [002] of the orthorrombic $Pnma$ phase) in a parallel field can be seen in Figs. 2 and 3. Large hysteresis is observed above 25 K (Fig. 2). Also, and not shown here, a strong lattice relaxation effect (with a characteristic time of the order of 15 min.) is found between 40 and 70 K. Both phenomena have already been reported [10] in other manganite systems and they were ascribed to metastable states arising from a phase coexistence of ferromagnetic and paramagnetic domains.

Below $T_{comp}$ the behavior changes dramatically: a non monotonic field dependence where $\lambda$ changes sign twice is observed (see Fig. 3). The effect is more remarkable as $T$ is lowered and it may be a consequence of the interplay between $Mn$ and the now more relevant $Gd-Mn$ interaction as can be inferred from magnetization curves.

Further evidence of the role played by $Gd$ moments at low temperature can be extracted from zero field specific heat experiments shown in Fig. 4. Even though no particular feature is associated with $T_c$, $C_p$ flattens below $T_{comp}$ showing even a small bump. It is interesting to note as well that, down to 5 K, $C_p$ is still quite large. This means an appreciable amount of missing entropy at low $T$ that could be possible related to a short-range magnetic order of $Gd$.

**Figure 2.** High temperature ($T > T_{comp}$) field dependence of c-axis magnetostriction. Curves are vertically shifted for clarity.

**Figure 3.** Low temperature ($T < T_{comp}$) field dependence of c-axis magnetostriction. Curves are vertically shifted for clarity.

**Figure 4.** Zero field specific heat vs. temperature.
3. Conclusions
Magnetostriction experiments were carried out in Gd$_{2/3}$Ca$_{1/3}$MnO$_3$ single crystals. Even though no magnetoresistance is found [5], a giant magnetostructural effect is seen in the whole temperature range studied (1 K $\leq T \leq$ 120 K). The overall behavior can be separated in two well differentiated regimes. The high $T$ regime ($T \geq T_{\text{comp}} \sim 15$ K) is dominated by the $Mn$ interactions showing large hysteresis associated with the magnetic order. On the other hand, $\lambda$ offers a non monotonic field dependence in the low $T$ regime ($T \leq T_{\text{comp}}$) reflecting the increasing strength of Gd-$Mn$ and Gd-Gd interactions and their competition with $Mn$ magnetism. These results suggest that extra microscopic mechanisms (other than double-exchange and Jahn Teller effect), like superexchange, $Mn$-$Gd$ magnetic interactions and/or a strain dependence of the exchange/hopping parameters should be considered for a suitable description of the observed phenomena.

Finally, we would like to stress the following issue: an extrapolation of the linear field dependence of magnetization curves [5] up to the expected full polarization of both Gd and $Mn$ sublattices (8.34 $\mu_B$/unit cell) gives a saturation field of about 30 Tesla. Doing the same linear extrapolation of the magnetostriction curves, we get $\lambda$(30 Tesla) $\sim 3-4 \cdot 10^{-3}$, the largest value ever observed in manganites.

Acknowledgments
The authors would like to acknowledge B. Alascio and D. García for helpful discussions and R. Fuentes for technical assistance. V.F.C., G.J., G.N. and N.H. are members of CONICET, Argentina. Work partially supported by ANPCyT PICT05-32900.

References
[1] Ibarr a M R, Algarabel P A, Marquina C, Blasco J and Garcia 1995 Phys. Rev. Lett. 75 3541
[2] Millis A J, Littlewood P B and Shraiman B I 1995 Phys. Rev. Lett. 74 5144
[3] Ghatak S K and Chaudhuri I 2003 J. Magn. Magn. Mater. 261 442
[4] Kimura T, Tomioka Y, Asamitsu A and Tokura Y 1998 Phys. Rev. Lett. 81 5920
[5] Snyder G J, Booth C H, Bridges F, Hiskes R, DiCarolis S, Beasley M R and Geballe T H 1997 Phys. Rev. B 55 6453
[6] Peña O, Bahout M, Ghanimi K, Duran P, Gutierrez D and Moure C 2002 Spin reversal and ferrimagnetism in (Gd,Ca)MnO$_3$ J. Mater. Chem. 12 2480
[7] Haberkorn N, Larregola S, Franco D and Nieva G 2008 Inhomogeneous ferrimagnetic-like behavior in Gd$_{2/3}$Ca$_{1/3}$MnO$_3$ single crystals J. Magn. Magn. Mater. (in press) Preprint arXiv:0808.3922
[8] Schmiedeshoff G M, Lounsbury A W, Luna D J, Tracy S J, Schramm A J, Tozer S W, Correa V F, Hannah S T, Murphy T P, Palm E C, Lacerda A H, Bud’ko S L, Canfield P C, Smith J L, Lashley J C and Cooley J C 2006 Rev. Sci. Instrum. 77 123907
[9] Denlinger D W, Abarra E N, Allen K, Rooney P W, Messer M T, Watson S K and Hellman F 1994 Rev. Sci. Instrum. 65 946
[10] Matsukawa M, Alasaka K, Noto H, Suryanarayanan R, Nimori S, Apostu M, Revcolevschi A and Kobayashi N 2005 Phys. Rev. B 72 064412