Giant magnetostructural coupling in $Gd_{2/3}Ca_{1/3}MnO_3$

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Abstract. We report high magnetic field magnetostructural studies on $Gd_{2/3}Ca_{1/3}MnO_3$ 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 Mn magnetic moments ordering. At lower temperature ($T < 15$ K), a rather complicated field dependence arising from the competition between the Mn and Gd magnetic sublattices is observed. The relevance of the 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 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 ρ and λ, 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 can not 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 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 $Gd_{2/3}Ca_{1/3}MnO_3$ [5, 6, 7]. The Gd and Mn magnetic sublattices compete each other giving rise to a non monotonic field dependence at low temperature. At higher temperature ($T \geq 25$ 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

$Gd_{2/3}Ca_{1/3}MnO_3$ 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 SiN membrane micro-calorimeter with the thermal relaxation time technique [9].
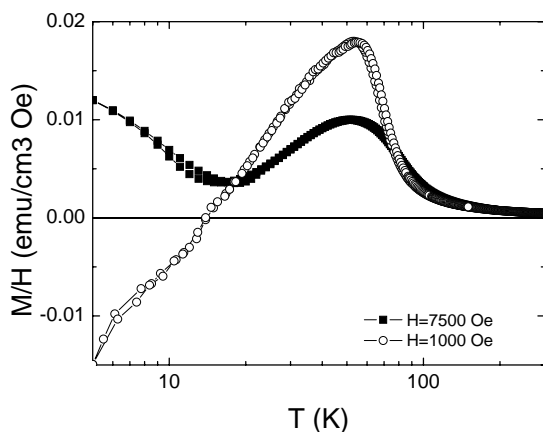

Figure 1. Temperature dependence of the magnetization/magnetic field ratio at two different applied fields (for FCC and FCW procedures). Small differences between FCC and FCW around T_{comp} are discussed in Ref. 7.

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 $T_c \sim 80$ K the Mn magnetic moments start to order ferromagnetically. The Gd moments behaves basically as paramagnetic free ions reacting to the internal field created by the ferromagnetic Mn sublattice. Hence, they start to align in the opposite direction giving rise to the peak seen around 50 K. At $T_{comp} \sim 15$ K, the two sublattices magnetism compensate and the magnetization M vanishes. Below T_{comp} the 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 adscribed to metastable states arising from a phase coexistence of ferromagnetic and paramagnetic domains.
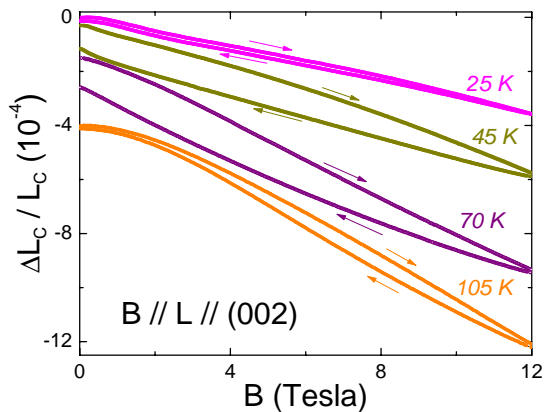

Figure 2. High temperature ($T > T_{comp}$) field dependence of c-axis magnetostriction. Curves are vertically shifted for clarity.
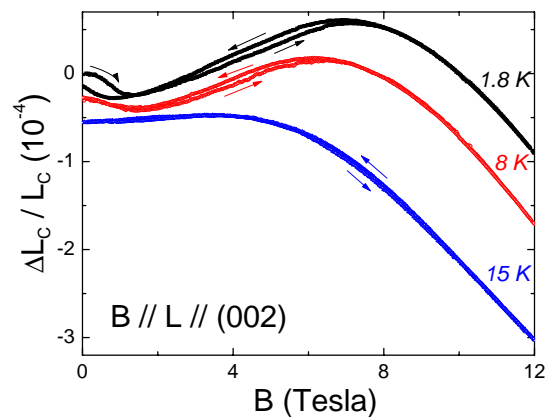
Figure 3. Low temperature ($T < T_{comp}$) field dependence of c-axis magnetostriction. Curves are vertically shifted for clarity.

Below T_{comp} the behavior changes dramatically: a non monotonic field dependence where λ 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 extracted from zero field specifc 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.
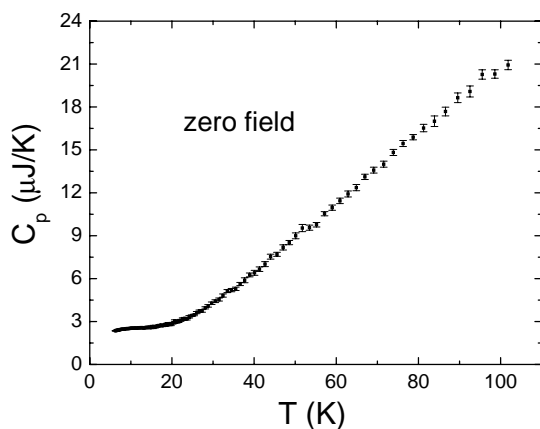

Figure 4. Zero field specific heat vs. temperature.

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 ($T \geq T_{comp} \sim 15 K$) is dominated by the Mn interactions showing large hysteresis associated with the magnetic order. On the other hand, λ offers a non monotonic field dependence in the low T regime ($T \leq T_{comp}$) 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: a 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 $\lambda(30 \text{ Tesla}) \sim 3\text{-}4 \cdot 10^{-3}$, the largest value ever observed in manganites.

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