



# Effect of porosity on FMR linewidth of $\text{Ln}_{0.67}\text{A}_{0.33}\text{MnO}_3$ (Ln = La, Pr; A = Ca, Sr)

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## Abstract

Magnetization and ferromagnetic resonance (FMR) measurements near the Curie temperature have been taken from sol-gel and ceramic samples of  $\text{Ln}_{0.67}\text{A}_{0.33}\text{MnO}_3$  (Ln = Pr, La; A = Ca, Sr). We demonstrate that the demagnetizing fields arising from the pores in polycrystalline samples cause the FMR line broadening observed below  $1.1 T_C$ , with respect to the values of the equivalent single crystals. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Colossal magnetoresistance; Electron spin resonance

The presence of chemical and magnetic inhomogeneities in CMR manganites that seem to be single phase is at present controversial due to the recent ferromagnetic resonance (FMR) results [1,2]. Variations in the local chemistry of these compounds produce large  $T_C$  and magnetization ( $M$ ) distributions, which could seriously affect their transport properties. The above-mentioned FMR data show a systematic increase of the linewidth ( $\Delta H$ ) below  $T \leq 1.1 T_C$  in polycrystalline samples with respect to the equivalent single crystals. For  $T \leq 1.1 T_C$  the interaction between the localized moments of the manganese ions become significant. At first sight, this is opposed to Gilbert's equation [3], which predicts a  $\Delta H$  independent of temperature for  $T < 0.9 T_C$ . Dominguez et al. [1] suggested that additional contributions to the intrinsic linewidth can arise from  $M$  and  $T_C$  distributions present in polycrystalline samples. However, a similar increase in the linewidth below  $1.1 T_C (= T_{\min})$  has recently been reported as a consequence of surface polishing of  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  single crystals by Causa et al.

[4]. Moreover, a strong frequency dependence of  $T_{\min}$  has been observed for all the samples studied. These results indicate that the origin of the wider linewidth in polycrystalline samples is not due only to the chemical inhomogeneity of the material. In this work, we propose that the dipole demagnetizing fields arising from pores between grains in non-single crystal samples (ceramic, as-grown thin films, etc.) are responsible for the observed  $\Delta H(T < T_{\min})$  spread. Ceramic samples of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ,  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ , and  $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  were prepared by solid-state reaction and in the final sintering process annealed at  $1300^\circ\text{C}$  for 100 h. Sol-gel samples of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  were prepared as described in Ref. [5]. Powder X-ray diffraction patterns show single phases. From TEM and SEM analysis, the mean size of the particles ( $\approx 20 \mu\text{m}$  for ceramics) and pores ( $< 1.5 \mu\text{m}$  for ceramics) was determined. The nominal oxygen content was close to 3.00 as determined by iodometric titration. FMR measurements were performed at 1.2, 9.4 and 34 GHz with an ESP-300 Bruker Spectrometer between 240 and 400 K. Initial magnetization curves were measured using a vibrating sample magnetometer (VSM) from 0 to 12 kG between 240 and 400 K ( $\Delta T = 2 \text{ K}$ ). The values of  $M$  to fit the FMR data

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were taken at  $H = H_r$ , where  $H_r = \omega/\gamma$  is the resonance field ( $\omega = 2\pi\nu$  and  $\gamma = g|\mu_B|/2mc$ ). In Fig. 1 we present  $\Delta H(T < T_{\min})$  measured at 34 GHz (Q-Band) and magnetization ( $H = 12$  kOe) for sol-gel particles of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  with different grain sizes. The experimental data definitively show the existence of a line broadening mechanism operative below  $1.1T_C$ , proportional to  $4\pi MF$ , like

$$\Delta H(T < T_{\min}) = 4\pi MF \quad (1)$$

$F$  being a dimensionless fitting parameter. Although FM interaction between localized moments below  $1.1T_C$  causes the non-coincidence of  $T_{\min}$  and  $1.1T_C$ , there is a good correlation between experimental data and Eq.

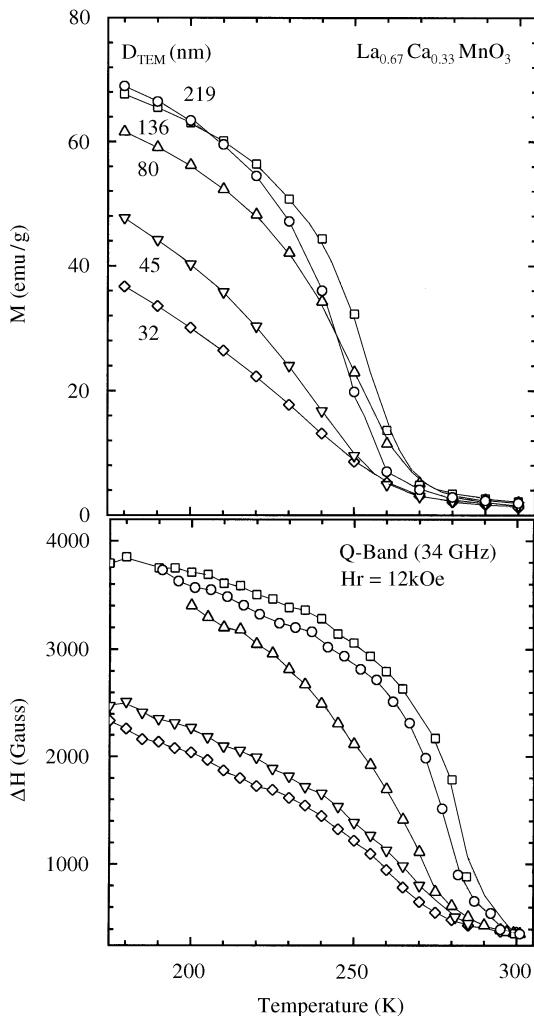


Fig. 1. Evolution of  $M$  (top) and  $\Delta H(T < T_{\min})$  (bottom) versus  $T$  for sol-gel particles of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  with different sizes (TEM diameters are indicated).  $\Delta H(T < T_{\min})$  shows a good scalability with  $M$ .

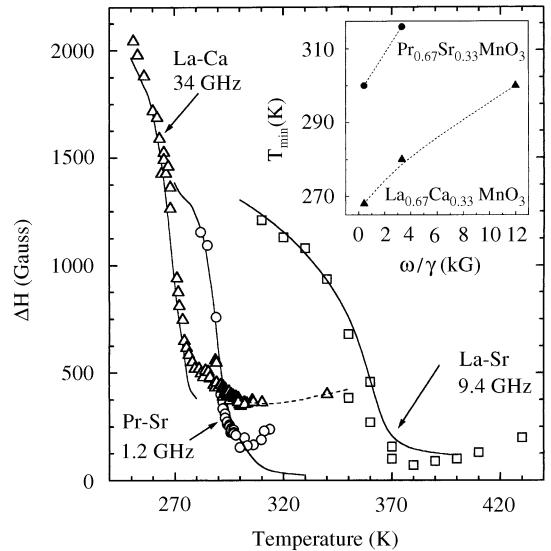


Fig. 2.  $\Delta H(T < T_{\min})$  for  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  (triangles),  $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  (circles) and  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  (squares) at several frequencies. Lines are fits to Eq. (1). In the inset, the frequency dependence of  $T_{\min}$  for ceramic samples of  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  and  $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  is shown.

(1). Following the Sparks theory [6] we can relate  $F$  with the porosity of the sample ( $\rho$ ) and some geometrical factors of the pores ( $\beta$ ), such as the shape of the pores, etc. The usual FMR linewidth is the relaxation frequency of the spin wave mode with all the spins parallel ( $k = 0$ ). But in polycrystalline samples, the pores between grains (or surface craters in polished single crystals) induce a relaxation into other spin wave modes ( $k = 0 \rightarrow k \neq 0$ ). The pores introduce a new demagnetizing term in the Hamiltonian of the system, which produces the observed  $M$  dependence. Another source of line broadening in polycrystalline samples can arise from the random orientation of anisotropy energy axes from grain to grain. Lofland et al. [7] determined the crystalline anisotropy field in a single crystal of  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$  yielding a maximum value of  $\approx 230$  G at 100 K. This cannot be the mechanism of line broadening in our samples, in view of the much large values of  $\Delta H$  observed ( $\approx 1500$  G at 300 K). We have measured the porosity of the ceramic samples as the difference between X-ray and macroscopic densities. The value obtained were always in the range 7.5–9%. In Fig. 2,  $\Delta H(T < T_{\min})$  of  $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ ,  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ , and  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  is shown, together with the fit to Eq. (1) for several frequencies. It is noticeable that we have not observed the peak due to  $T_C$  spread reported by Dominguez et al. [1] in any of our samples at any frequency. The  $\beta$  values derived from fits ( $3.95 \pm 0.03$ ) are slightly higher than typical values derived from the Sparks theory considering ideal spherical pores ( $\approx 1.5$ ). Moreover, TEM and SEM analysis

revealed very irregular shaped pores. Typical values between 0.23 and 0.3 were obtained for  $F$ .

In summary, we have demonstrated that without including the presence of local chemical inhomogeneities, the  $\Delta H(T < T_{\min})$  broadening can be satisfactorily fitted considering only the demagnetizing fields arising from pores between grains in polycrystalline samples.

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