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Electron-spin-resonance line broadening around the magnetic phase transition in manganites

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We report magnetization and electron-spin-resonance (ESR) measurements around the Curie temperature on single-crystal and ceramic colossal magnetoresistance manganites. The temperature dependence of the ESR linewidth below $\approx 1.1T_C$ is well described in terms of a two-magnon scattering relaxation mechanism induced by the demagnetization fields of the pores between crystallites. [S0163-1829(99)09241-3]

The possible technological applications of mixed-valence manganites based on their intrinsic colossal magnetoresistance (CMR) have recently promoted a large number of theoretical and experimental studies.[1] However, the presence of chemical and magnetic inhomogeneities in CMR manganites that seem to be single phase is at the present controversial. Electron-spin-resonance (ESR) results[2] show a systematic increase of the linewidth (ΔH) with $T > T_{\min}$ ($T_{\min} \approx 1.1T_C$). On the other hand, for $T < T_{\min}$, ΔH increases suddenly in as-grown thin films and ceramic samples with respect to the equivalent single crystals.[2,3] Nevertheless, the linewidth derived from the Gilbert equation,[4] which accounts for the ferromagnetic resonance (FMR), is found to be independent of temperature for $T < 0.9T_C$. To explain this contradiction between experimental behavior and theoretical predictions, the possibility has been suggested that additional contributions to the intrinsic linewidth can arise from magnetization and T_C distributions present in polycrystalline samples, due to variations in the local chemical homogeneity.[3] But a similar increase in the linewidth below a certain $T_{\min}$ has recently been reported as a consequence of surface polishing for $La_{0.67}Sr_{0.33}MnO_3$ single crystals by Causa *et al.*[2] This result makes it hard to assume that the origin of the wider linewidth in polycrystalline samples with respect to those in single crystals is mainly due to the chemical inhomogeneity of the material itself. For a better understanding the origin of the observed line broadening below $T_{\min}$, we have measured the ESR spectrum at different frequencies in $A_{0.67}B_{0.33}MnO_3$ ($A = La,\ Pr$; $B = Ca,\ Sr$) ceramic and single crystals. We report here that the dipole demagnetization fields arising from pores between grains in nonsingle-crystal samples (ceramic, as-grown films, etc.) are the origin of the observed $\Delta H(T < T_{\min})$ spread.

Single crystals of $La_{0.67}Sr_{0.33}MnO_3$ and $Pr_{0.67}Sr_{0.33}MnO_3$ were grown by the optical floating zone method as has been previously described in Refs. 5 and 6. Single crystals were cut with a diamond saw. Spherical-shaped polished single crystals were made by air propelling the specimens around the walls of an abrasive cup. In this way, the size of surface craters induced by polishing can be controlled by the texture of the abrasive. The size of these craters was studied by scanning electron microscopy (SEM).

Ceramic samples of $La_{0.67}Ca_{0.33}MnO_3$, $La_{0.67}Sr_{0.33}MnO_3$, and $Pr_{0.67}Sr_{0.33}MnO_3$ were prepared by solid-state reaction. In the final sintering process the pellets were annealed at 1300 °C for 100 h, with an intermediate grinding step at 30 h. Powder x-ray diffraction patterns show single phases. From transmission electron microscopy (TEM) and SEM analysis of ceramic samples, the mean size of the particles ($\approx 20\ \mu m$) and pores ($< 1.5\ \mu m$) was determined. The nominal oxygen content was found to be close to 3.00 as determined by iodometric titration. ESR measurements were performed at 1.2 GHz (L band), 9.4 GHz (X band), and 34 GHz (Q band) with an ESP-300 and an EMX Bruker spectrometer covering the temperature range from 200 to 500 K. The line shapes for single crystals and fine-powdered ceramic samples were Dysonian and Lorentzian, respectively. For Dysonian line shapes, linewidths and resonance fields were derived by fitting the line to the proper combination of the absorptive and dispersive part of a Lorentzian shape line, following the method proposed by Peter *et al.*[7] (see Fig. 1). Initial magnetization curves were measured using a vibrating sample magnetometer (VSM) from 0 to 12 kG between 240 and 400 K ($\Delta T = 2$ K). The magnetization values to fit the ESR data were taken at $H = H_r$, where $H_r = \omega/\gamma$ is the resonance field ($\omega = 2\pi\nu$ and $\gamma = g|e|/2mc$).

In Fig. 2 we present the experimental linewidth for $La_{0.67}Sr_{0.33}MnO_3$ (a) and $Pr_{0.67}Sr_{0.33}MnO_3$ (b) single crystals at 9.4 GHz, as a function of polishing. The linewidth for polycrystalline samples is also shown for comparison. Powder ceramic samples show a minimum linewidth of ≈ 130 and ≈ 260 G for La- and Pr-based compounds, respectively, at $T_{\min}(\approx 1.05T_C)$. Below this temperature $\Delta H(T)$ suddenly increases, reaching values of 1300 G at 300 K ($\approx 0.79T_{\min}$) for $La_{0.67}Sr_{0.33}MnO_3$ and 2000 G at 280 K ($\approx 0.87T_{\min}$) for $Pr_{0.67}Sr_{0.33}MnO_3$. On the other hand, as was expected, the linewidth of a small flat single crystal ($1 \times 1 \times 0.1\ mm^3$) remains nearly constant below T_C at about 70 G for $La_{0.67}Sr_{0.33}MnO_3$ and 200 G for $Pr_{0.67}Sr_{0.33}MnO_3$. However, when these single crystals are spherical-shaped polished (0.5–1 mm in diameter), they show a minimum value of

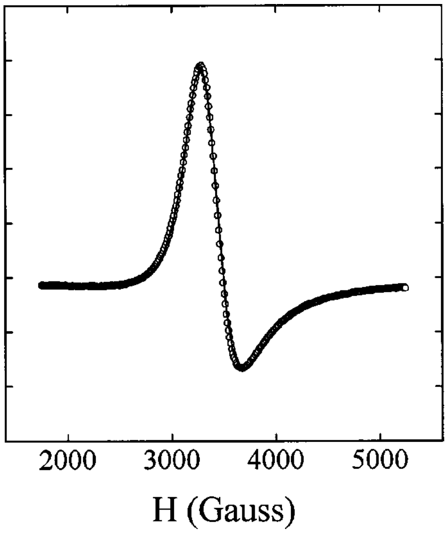

FIG. 1. Experimental line (circles) of $La_{0.67}Sr_{0.33}MnO_3$ (X band, 365 K) and absorption-dispersion combination function (solid line) that better fits the data. The difference between the experiment and the fit is always lower than 5%.

ΔH, which increases below this temperature, as ceramic samples do. Moreover, this increase below $T_{\min}$ is strongly dependent on the size of the surface pits caused during the polishing process as can be seen in Fig. 2.

Two sources of line broadening in polycrystalline samples (or polished single crystals) not present in single crystals are (a) the random orientation of the anisotropy energy axes from grain to grain and (b) the demagnetizing fields arising from nonmagnetic inclusions, pores between grains, or surface pits in polished single crystals, etc.

Lofland *et al.*[8] recently determined the crystalline anisotropy field H_A in a single crystal of $La_{0.7}Sr_{0.3}MnO_3$ by FMR, yielding $H_A \approx 230\,\mathrm{G}$. In view of the much larger ΔH observed, it is clear that mechanism (a) is not the main case for the observed increase of the linewidth. Let us now consider the effect of porosity in our samples. As is shown in Fig. 3, the excess linewidth [ΔH(ceramic)-ΔH(single crystal)] for $La_{0.67}Sr_{0.33}MnO_3$ and $Pr_{0.67}Sr_{0.33}MnO_3$ is well fitted by the following phenomenological equation:

$$\Delta H(T < T_{\min}) = 4\pi M \Phi, \tag{1}$$

where M is the measured magnetization at $H = H_r$ and Φ is a fitting factor.

Following the theory developed by Sparks,[9] $\Phi = p\beta$, where p is the porosity and β is a factor related to some geometrical parameters such as the shape of the pores. The excess linewidth depends linearly on the fraction of the sample occupied by pores and is proportional to M. This result is similar to a demagnetization effect. As is clear from Fig. 3, successful fits are obtained considering porosity broadening only and neglecting the anisotropy term. This agrees with the results of Seiden and Grunberg for polycrystalline ferrites.[10] They obtained a porosity contribution to the linewidth 90% larger than the anisotropy one, even in high-density ($p < 1\%$) materials. We have calculated experimentally the porosity of the ceramic samples as the difference between x-ray and macroscopic densities. Typical values for porosity between 8% and 9% were obtained. The $\beta = 3.95(3)$ value derived for $La_{0.67}Sr_{0.33}MnO_3$ is slightly higher than typical values applying Schlömann and Sparks theories ($\beta \approx 1.5$).[9] However, as this approach was developed for ideal spherical pores in low magnetization ferrites ($4\pi M \ll H$), similar values for β are not expected for FM manganites ($4\pi M \approx H$).

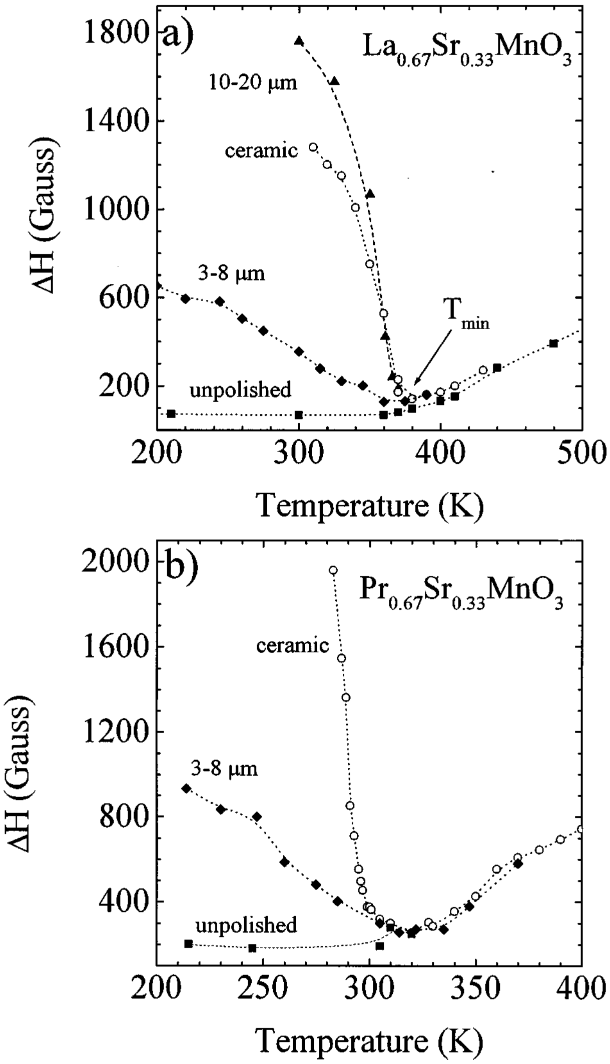

FIG. 2. ΔH vs T for single crystals (solid symbols) and ceramic (open symbols) of $La_{0.67}Sr_{0.33}MnO_3$ (a) and $Pr_{0.67}Sr_{0.33}MnO_3$ (b). ESR data were taken at 9.5 GHz (X band). The size of the surface craters induced by polishing in the single crystals (indicated in the figure) was determined by SEM.

The high value of $\Delta H(T < T_{\min})$ for $Pr_{0.67}Sr_{0.33}MnO_3$, near the twice of those for the other ceramic and single-crystal samples measured at the same frequency, is also noticeable. The Pr^{3+} ion acts as a strong relaxing ion species and contributes to $\Delta H(T < T_{\min})$ with an additional term, giving rise to a large linewidth broadening.[11] These additional contributions to $\Delta H(T < T_{\min})$, apart from that of the porosity, are also the reason for the large value of $\beta \approx 10$ here obtained. Although we know that some additional contributions to the intrinsic linewidth have not been considered, these constitute only a very small percentage of the observed line broadening in our samples, and their omission does not

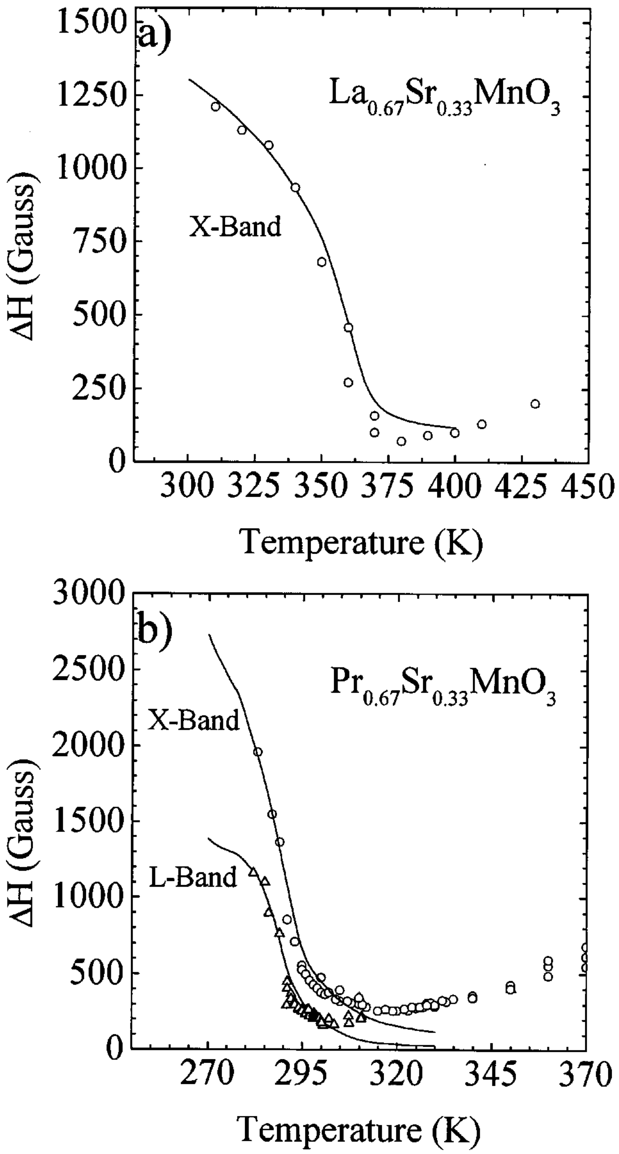

FIG. 3. Excess linewidth (ceramic minus single crystals) vs T for ceramic samples of $La_{0.67}Sr_{0.33}MnO_3$ (a) and $Pr_{0.67}Sr_{0.33}MnO_3$ (b) at different frequencies. The solid line corresponds to Eq. (1) with M measured at 3300 G (X band) and 400 G (L band). Equation (1) fits very well the experimental excess linewidth (ceramic minus single crystal) in both $Pr_{0.67}Sr_{0.33}MnO_3$ and $La_{0.67}Sr_{0.33}MnO_3$.

affect the main conclusions of the paper. These mechanisms of relaxation can lead to non-negligible contributions to the linewidth in the case of ferrimagnetic resonance, where some materials have exceptionally narrow lines.

Good correlation between experimental $\Delta H(T<T_{\min})$ and $M(H_r)$ through Eq. (1) was also obtained for $La_{0.67}Ca_{0.33}MnO_3$ ceramic samples at different frequencies. In Fig. 4 we show Q-band data along with the fit to Eq. (1).

The usual FMR linewidth is the relaxation frequency of the uniform precession spin wave (i.e., $k=0$, $\lambda=\infty$). But the demagnetizing energy introduced by the pores produces the relaxation of the uniform precession into other spin-wave modes ($\lambda\neq\infty$). This gives rise to the nonintrinsic porosity contribution to the linewidth. The presence of nonmagnetic impurities or surface craters in single crystals induces similar linewidth spread near T_C. Dionne[12] reported a surface contribution to the linewidth of ferrite and garnets single crystals proportional to $4\pi M\delta$, where δ is the surface/volume ratio. Surface demagnetization effects penetrate effectively to a depth which in high conductive samples is similar to the skin depth, and only the surface contribution to the linewidth is observed. That is the reason why two lines (one from the bulk, unaffected by temperature and polishing, and another from the surface) are not observable. Residual surface strains that cause field-dependent losses exist in polished single crystals. To the best of our knowledge, the modelization of this contribution does not exist, although in Ref. 11 an experimental estimation was made in YIG samples. These authors found that the strain contribution is always negligible in the presence of the main porosity contribution.

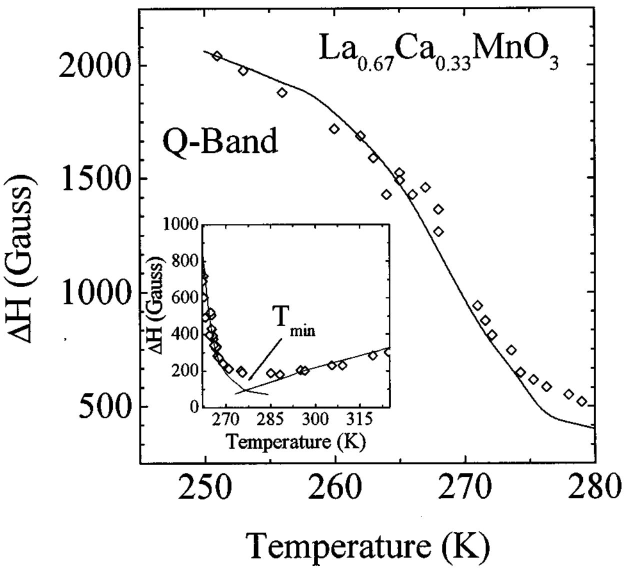

FIG. 4. Q-band (35 GHz, $H_r=12$ kG) data of $\Delta H(T<T_{\min})$ for $La_{0.67}Ca_{0.33}MnO_3$ (triangles) and theoretical prediction (solid line). Note how the $T=T_{\min}$ can be accurately predicted (inset).

The difference in the $4\pi M$ proportionality factor for ceramic ($p\beta$) and single crystals (δ) explains the apparent contradiction of how 1.5 μm pores can produce a linewidth broadening higher than those caused by 3–8 μm surface craters in single crystals (see Fig. 2).

In view of these results, plots of the linewidth of different-sized spheres as a function of the reciprocal diameters and extrapolation to the intercept should be made to extract the intrinsic linewidth (especially in high magnetization materials).

Also, a strong frequency dependence of $T_{\min}$ has been observed [see Fig. 3(b)] as a consequence of the larger fields necessary for resonance ($H_r=\omega/\gamma$).

Finally, we would like to mention that fitting the high-temperature data $[\Delta H(T>T_{\min})]$ to the expression derived by Causa *et al.* in Ref. 2 and $\Delta H(T<T_{\min})$ to Eq. (1), $T_{\min}$ can be accurately predicted and the whole temperature range ESR linewidth successfully reproduced (Fig. 4, inset).

However, it must be noted that the linewidth we have calculated to be due to porosity could arise from structural defects, inclusion of second-phase grains, and changes in the composition, as well as air pores or any other effect that changes the magnetization due to variations in the composition. However, we have experimentally measured the porosity and proved that in our case this is equivalent to the effective magnetic porosity (which accounts for the experimental temperature dependence of the linewidth below $T_{\rm min}$).

In summary, we have shown that relaxation of the uniform precession magnons into other spin-wave modes is the most important relaxation pathway in polycrystalline samples of CMR manganites, near below T_C. The linewidths $\Delta H(T<T_{\rm min})$ in all the cases studied have their origin in demagnetizing fields arising from pores between grains in polycrystalline materials or surface irregularities in single crystals, and it is proportional to the magnetization measured at $H=H_r$. Without including any magnetocrystalline anisotropy energy term or the presence of any kind of local chemical inhomogeneities, we have fitted the experimental $\Delta H(T<T_{\rm min})$ satisfactorily.

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