Ferromagnetic resonance and magnetic homogeneity in a giant-magnetoresistance material $La_{2/3}Ba_{1/3}MnO_3$

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Systematic magnetization, resistivity, and ferromagnetic resonance measurements have been done on bulk as well as thin-film samples of $La_{2/3}Ba_{1/3}MnO_3$. Bulk specimens and as-grown films show broad lines whose width increases to nearly 1 kOe as T is reduced to 77 K. At low T, the bulk magnetization is as expected for fully aligned spins [$4\pi M(0)=7.2$ kOe]. As-grown films, however, show somewhat smaller values. The main finding is that films which have been annealed for several days at 1000 °C in an atmosphere of O_2 exhibit narrow (~200 Oe at 10 GHz) linewidths which are effectively independent of temperature. These are, to our knowledge, the narrowest lines observed in giant magnetoresistance materials, a strong indication of homogeneity. The low-T magnetization is near the expected value, and its temperature dependence is highly suggestive of low-lying spin-wave excitations.

Mixed manganites of the type $A_xB_{1-x}MnO_{3-y}$ where A is typically a trivalent cation such as La, Nd, etc., and B a divalent cation such as Ba, Ca, Sr, etc., are attracting considerable attention as some of them have been shown to exhibit giant magnetoresonance (GMR). Although their magnetic and transport properties have been studied for over 40 years[1] and many explanations have been proposed, it is fair to say that none of the existing models are totally satisfactory. The often-used "double exchange" (DE) model proposed by Zener has been repeatedly found to be wanting.[2]

The magnetic state of these materials is complex and is known to be strongly influenced by both x and y. Clearly, inhomogeneity and nonuniformity are serious concerns. It seems crucial to obtain a prototypical manganite sample whose *magnetic* homogeneity is unequivocal. Once available, it can be expected to form the basis for not only obtaining a thorough understanding of both the magnetic and transport phenomena in these interesting systems, but also for developing materials with optimal GMR. One of the most powerful methods for exploring magnetic homogeneity is via ferromagnetic resonance (FMR). Surprisingly, there have been very few previous FMR studies on the manganites.[3] Using "single crystals" a rather broad (>2 kOe at 100 K) resonance whose width increased rapidly as the temperature T dropped below the Curie temperature T_C was observed. *This is not symptomatic of a uniform d-state ferromagnet.*[4] Thus even the properties of single crystals must be interpreted with great care.

We undertook a systematic study of $La_{2/3}Ba_{1/3}MnO_3$, supplementing the usual transport and magnetic measurements with magnetic resonance studies. As we shall see, using well-annealed single-crystal films of $La_{2/3}Ba_{1/3}MnO_3$ one obtains a FMR line whose width is quite small (~0.25 kOe at 77 K and 10 GHz), nearly independent of T for 77 K $<T<0.9T_C$ and increases linearly with microwave frequency. All of these features would be expected of a uniform, homogeneous ferromagnet.[4]

Ceramic samples of $La_{2/3}Ba_{1/3}MnO_3$ were made by the usual heat-and-grind method. X-ray-diffraction patterns indicated a single-phase material. Superconducting quantum interference device (SQUID) measurements of dc magnetization ($4\pi M$) showed that the low-T result was near the theoretical value of 7.2 kOe for spin-only magnetism.[1] The ac susceptibility was measured at low (<2 Oe) fields to determine T_C. Each of these measurements showed behavior expected of a "homogeneous" material. The bulk samples were next used as targets to produce films by pulsed-laser deposition (PLD) onto $LaAlO_3$ (LAO) substrates. After deposition, some of the films (~4000 Å thick) were "annealed," at 1000 °C in an atmosphere of O_2 with a flow rate of about 40 cm^3/min for several days, and some were left as grown. Rutherford backscattering (RBS), ion channeling, and x-ray diffraction[5] showed that the films had very good crystallinity. dc magnetization was measured with a SQUID magnetometer in fields of 0–10 kOe applied parallel to the film plane. The dc resistivity ρ and magnetoresistance $MR(H)=\{[\rho(T,0)-\rho(T,H)]/\rho(T,0)\}$ were measured using four-probe techniques.

FMR measurements were performed at 3.5, 10, 22, and 36 GHz, using conventional modulation and lock-in detection techniques[4] over a temperature range of 77–360 K. For the bulk samples, we used parallelpipeds (1.5 mm×1.5 mm×6 mm) with the applied field $H \parallel$ long axis of the sample. Data for the films were taken in both the parallel ($H \parallel$ film plane) and perpendicular ($H \perp$ film plane) geometries.

It is well known that ferromagnetic resonance lines are well described by the Landau-Lifshitz-Gilbert equation.[4] For the narrow lines observed here, it is justified to use the Kittel resonance equations:

$$\frac{\omega}{\gamma}=[H_\parallel(H_\parallel+4\pi M_{\rm eff})]^{1/2}, \tag{1a}$$

$$\frac{\omega}{\gamma}=H_\perp-4\pi M_{\rm eff}, \tag{1b}$$

where ω is the microwave frequency, $\gamma=(g\mu_B/\hbar)$ the gyromagnetic ratio, $H_\parallel$ and $H_\perp$ the resonance fields in the parallel and perpendicular geometries, respectively, and $M_{\rm eff}$ the effective magnetization.

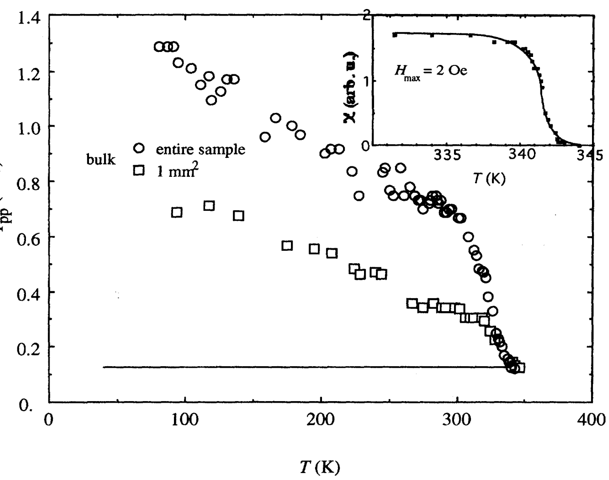

FIG. 1. Measured linewidth $\Gamma_{p.p.}$ vs T at 10 GHz. For the squares, the entire sample, and for the circles, a small ($\sim$1 mm^2) area was exposed. The solid line represents the expected T dependence of $\Gamma_{p.p.}$ for a uniform ferromagnet. The inset displays the ac susceptibility, marking a sharp transition, $T_C \sim 343$ K.

The bulk ceramic samples exhibit a sharp magnetic transition as revealed by low-field ac susceptibility χ (inset Fig. 1). The T_C values span the range 330–343 K.

The first FMR measurements used samples whose T_C is $\sim$330 K. The entire sample was placed within the microwave cavity. Using Eq. (1a) and data at several frequencies, it was found that $g=2.00$, $4\pi M_{\rm eff}=4\pi M$, and it is not necessary to invoke any anisotropy fields. The peak-to-peak linewidth $\Gamma_{p.p.}$ as a function of T is shown in Fig. 1 (circles) for 10 GHz. Note that, near T_C, $\Gamma_{p.p.} \sim 150$ Oe, which is quite narrow. However, as in Ref. 3, it increases rapidly as T drops below T_C, a sign of magnetic inhomogeneity. To reduce the effects of inhomogeneity, the sample was placed outside the cavity with only a small (<1 mm^2) central area of the surface exposed to the microwaves. Although the linewidths reduced significantly (squares, Fig. 1), they still continue to increase with decreasing T.

FMR data from as-grown films are also problematic. At 300 K, the resonance is quite narrow ($\Gamma_{p.p.} \sim 0.2$ kOe), but at lower T several additional lines appear, especially in the perpendicular geometry. This is a clear indication of inhomogeneity. For the parallel geometry, $\Gamma_{p.p.}$ of the main resonance (Fig. 2) increases rapidly when T is lowered, but becomes effectively constant at $\sim$1.3 kOe for $T \leqslant 200$ K. Although the x-ray and RBS data point to a homogeneous material, the FMR clearly suggests otherwise. Figure 2 also shows $4\pi M_{\rm eff}(T)$ obtained from Eq. (1a) using $g=2.00$. At 77 K, $4\pi M_{\rm eff}=2.5$ kOe, which is significantly smaller than the value of $4\pi M=4.5$ kOe determined by dc magnetization. The difference, presumably, arises from strains or other disorder in the film.

It is useful to note that, in all the above cases, the increase in $\Gamma_{p.p.}$ follows closely that of M, thereby suggesting that the observed M is an average value and that a ripple in M values could account for the data.

The FMR linewidth in highly annealed films, shown in Fig. 3 for 10 GHz, is effectively independent of T, as expected for a soft ferromagnet.[6] As a further check, it is noted (Fig. 4) that $\Gamma_{p.p.}$ increases linearly with frequency f. However, there is a small additional contribution presumably due to a residual ripple in M. The linear term in $\Gamma_{p.p.}$ should be interpreted in terms of Landau-Gilbert damping, namely,

$$\Gamma_{p.p.}=1.45\alpha\,\frac{\omega}{\gamma}, \tag{2}$$

where α is the Landau-Gilbert damping coefficient. We get $\alpha=0.02$, comparable[4] to that of pure Ni. α is usually attributed to spin-orbit coupling. This value of α is, therefore, surprisingly large. One would have expected a smaller value for α from a material with $g=2.00$.

It is interesting to note that for the highly annealed film, $4\pi M(T)$ follows the Bloch $T^{3/2}$ law at $T<100$ K and $4\pi M(0)$ is equal to the fully aligned value.[1] The net variation being small, the precision is far from satisfactory. However, as shown in Fig. 5 the data are consistent with $[M(0)-M(T)]/[M(0)]=BT^{3/2}$ with $B=(6\pm1)\times10^{-5}$ K$^{-3/2}$. Using spin-wave theory,

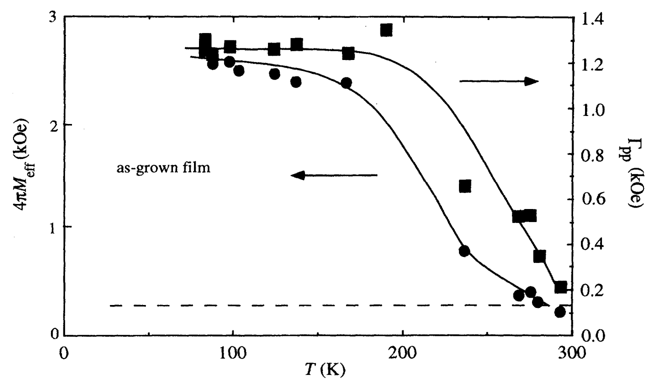

FIG. 2. Measured linewidth $\Gamma_{p.p.}$ (squares) vs T for an as-grown film. The solid line is a guide to the eye. The dashed line represents the expected T dependence of $\Gamma_{p.p.}$ for a uniform ferromagnet. $4\pi M_{\rm eff}$ (circles) vs T for an as-grown film from 10-GHz data.

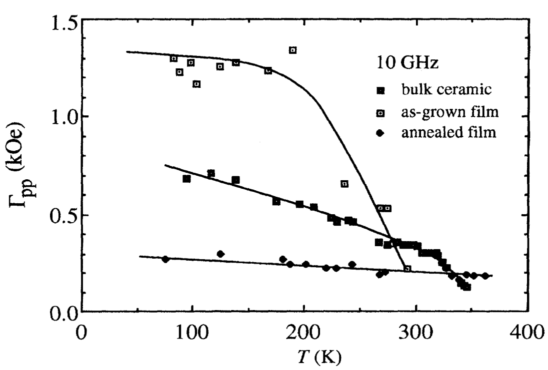

FIG. 3. $\Gamma_{p.p.}$ vs T for a highly annealed film, an as-grown film, and a bulk sample at 10 GHz. The lines are guides to the eye. For the annealed film $\Gamma_{p.p.}$ is nearly independent of T, as expected for a homogeneous ferromagnet.

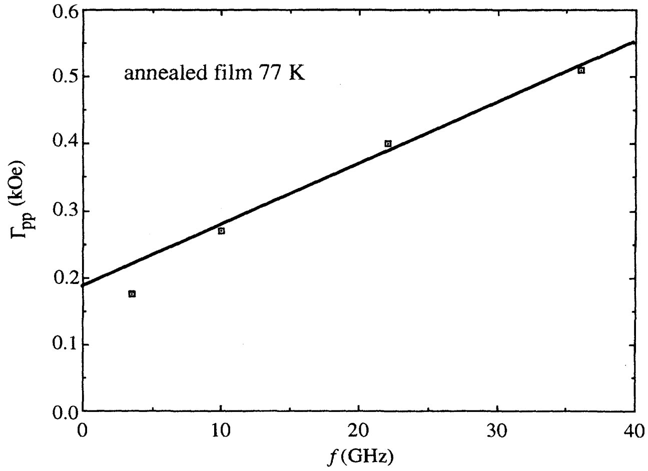

FIG. 4. $\Gamma_{p.p.}$ vs f for a highly annealed film. The linear dependence of $\Gamma_{p.p.}$ is as expected of a uniform ferromagnet [Eq. (2)].

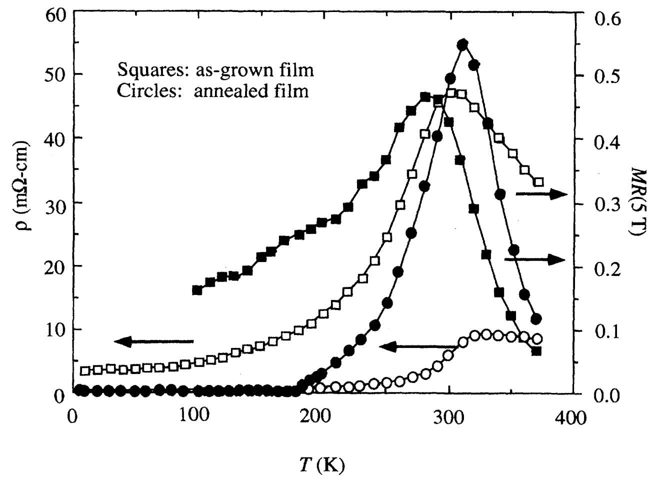

FIG. 6. Zero-field ρ and MR(5T) vs T for an as-grown (squares) and an annealed film (circles).

$$B=2.61\,\frac{g\mu_B}{M(0)}\left(\frac{k_B}{4\pi D}\right)^{3/2},\tag{3}$$

where D is the stiffness coefficient ($\epsilon=Dq^2$) and the other symbols have their usual meanings. The present results give $D\sim(100\pm20)$ meV Å^2. This is significantly smaller than the value estimated by Millis *et al.*[2]

Now consider the transport data. For the unannealed case, the sample being inhomogeneous, one can only define an effective resistivity and obtain $\rho(T_p,0)\sim50$ mΩ cm (open squares, Fig. 6) at the peak temperature T_p, and MR (solid squares, Fig. 6) has a maximum value of $\sim50\%$. This is qualitatively similar to the data of von Helmolt *et al.*[7] However, in Ref. 7, $T_p\sim250$ K, which is much lower than the present value, presumably, reflecting sample quality. Annealing leads to a dramatic (5 times) reduction (open circles, Fig. 6) in the magnitude of $\rho(T_p,0)$, but has only a slight effect on T_p and MR (solid circles, Fig. 6). $\rho(T_p,0)\sim10$ mΩ cm, so that $\rho(T_p,5T)\sim5$ mΩ cm.

Although no complete theory of electrical conductivity[8] is available, many authors[2,9] have developed the DE ideas to account for the sharp drop in $\rho(T,0)$ at $T<T_p$, where T_p is identified with T_C, although some experiments indicate T_p values well away from T_C. Kubo and Ohata[9] predicted that for $T\ll T_C$, a DE ferromagnet should exhibit $\rho(T)$ varying as $T^{9/2}$. In this connection it is important to note that in the annealed (homogeneous) film $\rho(T)=[A_0-B_0T+C_0T^2]$ for $T\leqslant100$ K, with the A_0, B_0, and C_0 values[10] given in Fig. 7.

One possible explanation for the T^2 dependence is spin-wave scattering. In typical ferromagnetic metals this term amounts to $C_0\sim10^{-8}$ mΩ cm K^{-2}. However, it is useful to note that the spin-wave scattering resistivity[11]

$$\rho_{\rm spin}\propto\frac{m^{*2}}{ND^2},\tag{4}$$

where m^* is the carrier mass and N the carrier density. First, D here is roughly one-fifth that of Fe. Further, if there is sizable mass enhancement and the carrier density is rather low, $\rho_{\rm spin}$ could become large enough to account for the present observations in the annealed film. However, it must

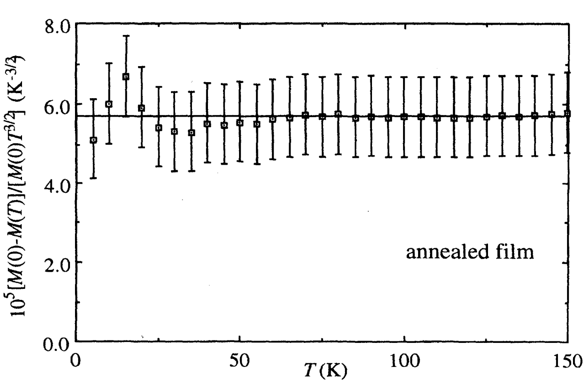

FIG. 5. Test of the Bloch $T^{3/2}$ law for the magnetization of an annealed film.

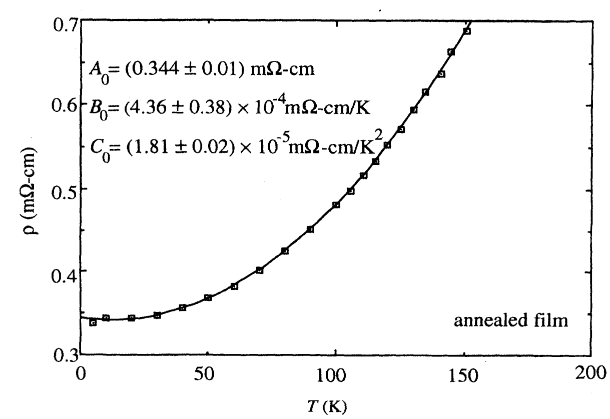

FIG. 7. Zero-field ρ vs T at low T for an annealed (homogeneous) film. The solid line represents $A_0-B_0T+C_0T^2$.

be pointed out that recent measurements[12] on other nonmagnetic perovskites give T^2 dependences of like magnitude.

The (negative) linear T dependence is interesting and suggests a richer behavior at low T than envisaged by previous transport studies on manganites. Measurements are being extended to lower T to improve the precision in this term and further discussion will be presented elsewhere.

In conclusion, it has been found that bulk and as-grown thin-film samples of $La_{2/3}Ba_{1/3}MnO_3$, which appear to be quite uniform by other techniques, show wide FMR lines, suggestive of sizable magnetic inhomogeneity. Using a proper annealing treatment of thin films, behavior symptomatic of a uniform, homogeneous ferromagnet was observed in both the frequency and temperature dependence of the FMR linewidths. The present FMR linewidths are the narrowest observed in any GMR manganite system. The as-grown samples have a resistivity maximum of 50 mΩ cm at 300 K with a change of about 25 mΩ cm on application of a field of 5 T. Both the maximal resistivity (at 330 K) and its change on application of a field in an annealed film are about one-fifth of that in the as-grown films. At $T \leqslant 100$ K, both the magnetization and resistivity show T dependences consistent with having spin waves as low-lying excitations. It is worth mentioning that the highly annealed films still show MR $\sim 50\%$ while having a low resistivity, a necessity for device applications. It seems reasonable to claim that the heat treatment used here, although not fully optimized, yields the most homogeneous manganite films studied so far. This can be expected to become a benchmark for further work on these interesting systems. In particular, plans are underway to introduce well-controlled defects and inhomogeneities in the samples and correlate them with the magnitude of ρ, MR, etc.

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