Microwave absorption studies of Mn-based perovskites

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We review recent studies of microwave absorption in a few prototypical manganites which exhibit colossal magnetoresistance. Ferromagnetic resonance measurements show that most bulk samples are far from homogeneous. Careful control of deposition parameters yields thin films with greatly improved homogeneity. The best films were used to observe spin wave resonances and obtain the spin wave stiffness parameter. Surface impedance measurements in zero field and applied fields show quite unexpected cross-overs from normal ($\text{Re}Z \propto \sqrt{p}$ or $\rho$) to inverted ($\text{Re}Z \propto 1/\sqrt{p}$ or $\rho$) behavior. The magnetoresistance at 10 GHz is even larger than that in the dc studies. Ferromagnetic antiresonance signals are used to get colossal magnetoimpedance (60% in 60 mT) as well as demonstrate that the ferromagnetic transition is continuous (second order).

Key words: magnetoresistance, microwave absorption, Mn-perovskites.

Estudios de Absorción en Microondas en Perovskitas basadas en Mn.

Se revisan los estudios recientes de absorción en microondas de algunas manganitas que presentan efecto de magnetoresistencia gigante. Las medidas de resonancia ferromagnética muestran que la mayoría de las muestras masivas están lejos de ser homogéneas. Un cuidadoso control de los parámetros de deposición de películas delgadas permite su obtención con una gran homogeneidad. Las mejores películas fueron utilizadas para observar la resonancia de la onda de spin y obtener los parámetros de dureza de la onda de spin. Las medidas de impedancia en superficie a campo cero y bajo campo aplicado muestran un inesperado cruce desde la conducta normal ($\text{Re}Z \propto \sqrt{p}$ o $\rho$) hacia la invertida ($\text{Re}Z \propto 1/\sqrt{p}$ o $\rho$). La magnetoresistencia a 10 GHz es aún mayor que en los estudios de dc. Las señales de antirresonancia ferromagnética son usadas para obtener magnetoimpedancia gigante (60% en 60 mT) así como demostrar que la transición ferromagnética es continua (segundo orden).

Palabras clave: magnetoresistencia, absorción en microondas, magnanitas.

1. INTRODUCTION

The Mn perovskites $R_{1-y}D_yMnO_3$, where R is a trivalent rare earth such as La, Y, or Nd and D a divalent alkaline earth such as Sr, Ca, or Ba, although known for a long time, (1) have become the focus of very intense studies in the recent past. (2) Much of the excitement is driven by the observation of very large changes in the dc resistivity on application of a magnetic field of ~ 5 T. Further, for $0.2 < x < 0.4$, the materials exhibit a transition to the ferromagnetic state when the temperature $T$ is lowered, and this is often accompanied by a large drop in the dc resistivity $\rho_{dc}$. This observation led Zener (3) to propose a novel exchange mechanism, the so-called double exchange (DE), which fundamentally ties spin alignment to enhanced conductivity. That is, in order for an electron to get de-localized it is essential to have parallel spins at the two sites between which the hopping takes place. Although DE is quite successful in explaining some of the transport phenomena, it is clear that it is not the whole story, especially since in the paramagnetic state, the resistivity often appears to be activated (4) and polaronic, and one must invoke Jahn-Teller and other lattice effects to complete the picture.(5)

A vast majority of the research on the manganites is concentrated on dc magnetotransport studies using polycrystalline and thin-film samples. The Maryland group has done its share of such researches. (6) However, realizing that in a doped material the local chemistry is difficult to control but can be rather important in determining the proper properties of interest, we initiated studies on the magnetic resonance in the ferromagnetic phase of the perovskite manganites. Ferromagnetic resonance (FMR) is very demanding of magnetic homogeneity and uniformity since both the position and width of the resonance are strongly influenced by the fields «seen» by the spins. That is, any variations in the internal fields caused by departure from perfection would be directly revealed by FMR even if other structural studies suggested that the sample was of «high quality.» As we shall see, by combining FMR data with other investigations, our group has managed to produce some of the most uniform thin films available at this time. Starting with large values such as ~ 0.1 T, the FMR linewidths have been reduced to 2 mT.(7) In turn, this has allowed us to observe spin wave resonances (SWR) and effect the first determination of the spin wave stiffness in these systems.(8) The FMR technique also enables one to explore the effects of strains consequent upon mismatch with the substrate (9) as well as those arising from differential thermal expansion.(10) We have obtained...
direct signatures of the distribution of Curie temperatures in the specimen and by using a microwave "microscope" scanned a sample for gross inhomogeneity.

It was also felt that measurements of the surface impedance at high frequencies, both in zero field and applied magnetic fields, would shed further light on the transport mechanisms as well as demonstrate the utility of these materials for possible microwave device construction. These investigations have led to several novel results.(11) First we studied the conduction electron response. That is, the absorption of microwaves as well as demonstrate the utility of these materials for possible microwave device construction. Second, we studied the microwave absorption arising from the layer by layer permeability µ, well away from the FMR regime. As we shall see, (i) in thin films, the surface resistance (R) changes from the normal film electron response. That is, the absorption of microwaves

In bulk, this gives /c \( \approx \gamma \), and with a judicious choice of \( \omega/\gamma \) to trace out the ferromagnetic antiresonance (FMAR) (sharp dip in absorption when \( \omega/\gamma = \mu_0 M(T) \) where \( M \) is the magnetization) by varying \( T \) in the neighborhood of the Curie temperature \( T_C \). This effect has been exploited to yield a colossal low-field magneto-impedance (50\% for \( \mu_0 H \approx 30 \) mT) as well as to show that the ferromagnetic transition in single crystal \( \text{La}_0.7\text{Sr}_{0.3}\text{MnO}_3 \) (LSMO) is indeed second order.

Here we will briefly review some of the highlights of our investigations while full details can be found in other publications from this laboratory.

2. SAMPLES AND EXPERIMENTAL METHODS

The thin film samples used in the present investigation were prepared at Maryland in the laboratories led by Profs. R. Ramesh and T. Venkatesan. The method employed is pulsed-laser deposition onto a variety of substrates. In order to obtain the most homogeneous films, it is necessary to control the deposition parameters very carefully. Complete details can be sought in Ref. 14. In addition to the investigations reported here, the films were characterized by x-ray diffraction, Rutherford back-scattering, ion-channeling, and atomic force microscopy.

The single crystal specimens come from Dr. Mukovskii's group in Moscow. For the FMR studies, they were cut to yield thin (0.5 mm) slices and polished with diamond paste.

The target materials have been purchased from SSC where they were made by a proprietary process.

The FMR was studied using conventional microwave techniques.(7) Measurements were made with the applied field \( H \) in the sample plane (parallel geometry) or rotated out of the plane. The perpendicular geometry refers to \( H \) being normal to the sample surface. The ac susceptibility \( \chi_{ac} \) was measured using a locally built two-secondary counterwound transformer(15) which allows for not only the measurement of \( \chi_{ac} \) but also direct monitoring of the field derivative of the ferromagnetic hysteresis loop with maximal applied fields \( \pm 5 \) mT. The microwave absorption studies were done using the cavity perturbation technique, (11) the sample being located at the site of the maximum of the microwave magnetic field \( b \) which is parallel to the surface.

3. RESULTS AND DISCUSSION

3.1 Ferromagnetic Resonance

In a high quality ferromagnetic metal one should expect (12) to observe an FMR linewidth which is sensibly independent of \( T \) when \( T < 0.9 T_C \) but rises rapidly for \( T > T_C \). Any deviation from such a dependence at low \( T \) is a direct indicator of magnetic inhomogeneity. Fig. 1 shows the observed temperature dependence of the parallel geometry FMR width \( \Gamma \) in an as-grown film of \( \text{La}_{0.67}\text{Ba}_{0.33}\text{MnO}_3 \) (LBMO) as well as the same film after it had been heat treated for 3 days at 1000° C in an \( O_2 \)-rich atmosphere. The reduction in the low \( T \) value of \( \Gamma \) is truly dramatic. However, since \( g \sim 2 \) in these materials, it was felt that even this width was too large. A systematic study (17) involving variation of deposition temperature, oxygen pressure, etc. finally led to the perpendicular geometry linewidth \( \Gamma \) variation shown in Fig. 2 for LBMO and LSMO films.
barring single crystals, all bulk samples of manganites have quite sizable widths in their $T_C$ distribution. Quite often, attempts are made to identify $T_C$ with the temperature at which the zero-field resistivity has a peak. Such identification must be treated with care.

### 3.2. Spin wave resonance

Once the FMR in the perpendicular geometry became sufficiently narrow, it became possible to resolve several SWR modes. In a perfect ferromagnetic thin film of thickness $t$ with identical spin pinning on both surfaces one should expect to observe a series of SWR modes whose field positions $H_n$ satisfy

$$\mu_0 H_n = \frac{\omega}{\gamma} + \mu_0 M - \frac{D(n\pi)^2}{\gamma t}$$

with $n$, the mode number, being only odd. In most films, however, slight deviations from homogeneity and/or asymmetric spin pinning yield SWR spectra in which both odd and even modes occur. This is indeed the case in the present LSMO-on-Si and LBMO films (Figs. 4 a,b). The slope of the lines gives a spin wave stiffness $D$ around 100 meVÅ$^2$ at room temperature. In the LBMO case one could follow the SWR over a wide range of $T$ and check that the $T$ dependence of $D$ was in accord with conventional theory (Fig. 5c). Unfortunately, the behavior of the LSMO film was strongly influenced (10) by the large difference in the thermal expansion coefficients of LSMO and Si. The SWR was measurable only for $280 < T < 310$ K.

### 3.3 Zero-field surface resistance

The surface impedance $Z$ of a sample of thickness $t$ and resistivity $\rho$ immersed in a rf $b$ field should be written as

$$Z = \alpha^2 \kappa p \coth(\kappa t) + (1 - \alpha) \kappa p \tanh(\kappa t / 2)$$

where $k = (-\mu_0 \omega p / \rho)^{1/2}$ and $\alpha$ is a measure of the difference between the $b$ field at the two surfaces. $\alpha = 0$ implies symmetric excitation while for $\alpha = 1$, the $b$ field is non-zero at only one surface. It has been shown severally (19) that for studying the contribution from the conduction electrons (i.e. $\mu = 1$, dependence of $Z$ on $\rho$) one should neglect the symmetric term. One then gets for the real part of the surface impedance

$$R_s = (\mu_0 \omega p)^{1/2}$$

for bulk samples, i.e. $t >> \delta = (2p / \mu_0 \omega)^{1/2}$ the electromagnetic skin depth, and

$$R_s = \rho / t$$


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**Fig. 3.** $T$ dependence of the FMR linewidth in LSMO single crystal. The inset shows a sharp transition, but the low-$T$ increase in $\Gamma_{11}$ is symptomatic of residual inhomogeneity.

**Fig. 4.** FMR linewidth in bulk NSMO at $T$ close to $T_C$. The peak [18] arises because the sample does not have a single $T_C$ value.
10 GHz
LSMO Film
300 K
\( \perp \) Geometry

\[ dR_s / dH \]

0.58
\( \mu_0 H (T) \)

Fig. 5. a. SWR in LSMO film. Inset shows \( n^2 \) dependence, Eq. [1]. The slope yields the indicated D value. b. Same as a. but for LBMO film. c. \( T \) variation of the spin wave stiffness. The full line represents \( T^2/2 \) as expected from spin wave theory.

10 GHz
LBMO film
228 K
\( \perp \) Geometry

\[ dR_s / dH \]

0.67
\( \mu_0 H (T) \)

Fig. 6. a. Temperature dependence of the surface resistance in an a-axis-oriented YBCO film. b. dc resistivity of an a-axis-oriented YBCO film. Note that \( R_s^c \) is normal (\( \propto \rho \)), designated N, while \( R_s^\alpha \) is inverted (\( \propto \rho^2 \)) and marked I.

hold in all cases. Figs. 6 through 8 show the effect in a straightforward manner. Figs. 6 a,b show the observed \( R_s \) and the corresponding \( \rho_{dc} \) for an a-axis-oriented film of \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) (YBCO). Note that \( R_s^\alpha \) (rf currents flowing along the b axis) scales with \( \rho_{dc}^B \) while \( R_s^\alpha \) varies as \( \rho_{dc}^{-1} \). This phenomenon occurs when the sample is rotated in situ so that the only change is with the direction of the microwave currents. Figs. 7 a-c compare the \( R_s \) vs. \( T \) behavior of \( \text{La}_{0.7}\text{Sr}_{0.3}\text{CuO}_3 \) (LSCO) and NSMO with the dependences exhibited by the respective \( \rho_{dc}s \). Again, LSCO is normal (\( R_s \propto \rho_{dc} \)) while NSMO is inverted (\( R_s \propto \rho_{dc}^{-1} \)). Systematic studies lead us to suggest that the crossover occurs at \( \rho_{dc} \sim 0.1 \) \( \Omega \cdot \text{m} \). This was totally unanticipated. However, the surprise becomes even more dramatic when one compares the \( R_s \) of a high-density (\( \sim 80\% \)) NSMO 1-mm-thick sintered sample (max \( \rho_{dc} \sim 220 \text{ m}\Omega \cdot \text{cm} \)) with that of a low-density (50%) NSMO target (max \( \rho_{dc} \sim 23 \text{ m}\Omega \cdot \text{cm} \) slice of thickness 0.5 mm. Whereas the former is normal the latter is inverted (Fig. 8a,b). In fact, Fig. 8a shows the microwave resistivity \( \rho_{MW} \) using \( R_s \propto 1 / \rho_{dc} \). Once \( \rho_{MW} \) is scaled to \( \rho_{dc} \) at 300 K the \( T \) dependences are identical except below \( T_C \) (\( \sim 215 \) K) when the microwave resistivity is strongly suppressed. This is most probably a consequence of the granularity and poor connectivity of a low-density specimen.

It should be noted that the switch over from normal to inver-
Fig. 7. T-dependence of a. the surface resistance in LSCO and NSMO films, b. the dc resistivity of LSCO film, and c. the dc resistivity of NSMO film. The surface resistance of the LSCO film is normal ($\rho_s \propto T$), while that of the NSMO film is inverted ($\rho_s \propto T^{-1}$).

Fig. 8. T-dependence of a. the surface resistance b. dc resistivity in two NSMO bulk samples. Here the sintered sample shows normal response ($R_s \propto 1/\rho_{dc}$) while the target has $R_s \propto 1/(\rho_{dc}^2)$. It is to be noted that for the target $\rho_{dc}$ at low $T$ is much smaller than $\rho_{dc}$.

3.4. Microwave giant magnetoresistance (MGMR)

Our laboratory was the first to report a giant magnetoresistance at microwave frequencies. As an example, Fig. 10 shows the observation of MGMR $= \mu_0 M(0) \rho_{dc} - \rho_{dc}(H)/\rho_{dc}(0)$.
3.5. Low-field giant magneto-impedance (13)

Here we consider the field dependence of \( R_e \), arising from the field variation of the dynamic permeability \( \mu \) far from the FMR regime. For a bulk disk-shaped sample, in the parallel geometry, it has been known for a long time that \( R_e \) being proportional to \( \rho_e \mu \) one should observe a sharp dip in \( R_e \) when just below \( T_C \), on the bulk NSMO target slice. A 70% effect at 1 T is among the largest reported so far. The initial slope is much higher so that the low-field GMR yields \( (d\ln \rho_{\mu \nu}/d\mu) = 1.5 \, T^{-1} \).

\[
\frac{\omega}{\gamma} = \mu_0 (H + M). \quad [5]
\]

Technically, this is the so-called ferromagnetic antiresonance (FMAR). From Eq. [5] it is clear that for \( H = 0 \) and \( \omega \) fixed one could «tune» the system by varying \( M \). This is most conveniently accomplished by varying \( T \) in the neighborhood of \( T_C \) because in that regime \( M \) varies rapidly with \( T \). Fig. 11a shows \( R_e \) vs. \( T \) for three microwave frequencies. Indeed one observes a clear minimum whose position is fixed by \( \omega/\gamma = \mu_0 M \). Alternately, one can keep \( \omega \) fixed, apply a field \( H \) and trace out the FMAR dip as a function of \( T \). This is shown in Fig. 11b. Such data were used recently to show that in an LSMO single crystal \( M \) varies as \( (T_C - T)^{\beta} \) with \( \beta = 0.45 \pm 0.05 \).

The FMAR phenomenon also provides the possibility of appreciably varying \( R_e \) at low \( H \). Fig. 12 shows \( M_{\mu \nu} = [R_e(H_{||}) - R_e(H_{\perp})]/R_e(H_{||}) \) at \( \mu_0 H = 60 \, mT \). Here \( H_{||} \) and \( H_{\perp} \) refer to the configuration wherein \( H \perp b \) (coupling to spins) or \( H \parallel b \) (no coupling to spins), respectively. It is clear that one can get a truly giant effect at rather modest fields. \( R_e \) changes by nearly 70% while a 60 mT field is rotated from the parallel to the perpendicular geometry. The full line in Fig. 12 was derived from the \( \mu \) obtained using the Landau-Gilbert equations. Further details are in Ref. 13.

To conclude, microwave absorption, especially magnetic resonance, measurements on a variety of bulk and thin film manganite samples show that most of the samples studied are far from being the uniform, homogeneous materials that are assumed for obtaining credible agreements with proposed models. Considerable systematic effort will be needed to obtain intrinsic results. In particular, generalizations claimed in some recent reports on these systems should be treated with healthy skepticism. However, it is encouraging that by careful tuning of the parameters, one can expect to obtain highly field-sensitive materials at ambient temperatures for use in the next generation of microwave devices.

ACKNOWLEDGEMENTS

We thank Profs. R. Ramesh and T. Venkatesan and their groups for providing thin film samples; Ya. Mukovskii, S. G. Karabashev, and A. M. Balbashov for providing the LSMO crystal; J. F. Mitchell for supplying the \( La_{2}Sr_{2}Mn_{2}O_{7} \) crystal; and R. P. Sharma for ion-channeling and RBS studies. S. M. B. thanks the organizing committee for the invitation to speak and financial support. •
Fig. 11 Surface resistance vs. T showing FMAR at H = 0 and different frequencies.

Fig. 12 Surface resistance vs. T showing FMAR at 10 GHz and indicated applied field values.

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20. This sample was kindly provided by J. F. Mitchell of Argonne National Laboratory, Argonne, Illinois, USA.