Magnetic homogeneity of colossal-magnetoresistance thin films determined by alternating current magnetic susceptibility

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We report measurements of the alternating current (ac) magnetic susceptibility, $\chi_{ac}=\chi'+i\chi''$, performed on colossal-magnetoresistance (CMR) materials. We have studied thin film samples of $La_{0.67}Ca_{0.33}MnO_3$ and $Nd_{0.7}Sr_{0.3}MnO_3$. For homogeneous samples, the temperature of the peak observed in $\chi''(T)$ is in agreement with the temperature of peak resistivity (T_P) obtained from transport measurements. This agreement is not found for inhomogeneous samples, where $\chi''(T)$ shows multiple peaks. The analysis of $\chi''(T)$ enables one to determine the quality of the CMR materials. The results obtained in thin films of $La_{0.67}Ca_{0.33}MnO_3$ and $Nd_{0.7}Sr_{0.3}MnO_3$, are consistent with those obtained from an homogeneous single crystal of $La_{0.80}Sr_{0.20}MnO_3$. We show that the contactless ac magnetic susceptibility technique is a quick method to reveal inhomogeneities which are not directly evident in direct current transport measurements. © *1998 American Institute of Physics.* [S0003-6951(98)01049-3]

The study of perovskite oxides of the form $R_{1-x}A_xMnO_3$ (R=La, Pr, Nd; A=Ca, Ba, Sr) has been renewed after the discovery of colossal magnetoresistance (CMR) in thin films of these materials.[1,2] They are being pursued both for their potential applications as magnetic field sensors[3] and infrared detectors[4] and for understanding the fundamental mechanisms governing their properties.[5–7] The CMR materials exhibit a very large negative magnetoresistance at temperatures close to T_C, where they undergo a ferromagnetic–paramagnetic transition. The resistivity peaks at $T=T_P$ in most cases close to the magnetic transition (T_C), indicate a correlation between transport and magnetic properties. Transport measurements of very homogeneous samples show values of T_P close to the value of T_C determined by direct current (dc) magnetization.[8] In addition to this correlation there is evidence that lattice polarons play an important role in these materials,[9] however, the mechanism responsible for the magnetoresistance is not yet understood.[9,10]

One of the major concerns, both in terms of basic physics and applications, has been the indication of microscopic inhomogeneities in these materials as evidenced by a large ferromagnetic resonance (FMR) line width and other anomalies in several measurements.[11,12] In this work, we show that the contactless ac magnetic susceptibility technique is a quick method which can unambiguously reveal the presence of inhomogeneities.

We measured the ac magnetic susceptibility, χ_{ac}, of thin films of the CMR oxides $La_{0.67}Ca_{0.33}MnO_3$ (samples LCMO-1 and LCMO-2) and $Nd_{0.7}Sr_{0.3}MnO_3$ (samples NSMO-1, NSMO-2, and NSMO-3). We also measured a bulk single crystal of $La_{0.80}Sr_{0.20}MnO_3$ grown by the floating zone technique.[13] Thin film samples were prepared from stoichiometric targets on (001) oriented $LaAlO_3$ substrates using pulsed laser deposition. The deposition conditions are shown in Table I. We controlled the quality of samples LCMO-1, NSMO-1, and NSMO-2 by annealing, according to the conditions shown in Table I, to observe the effect on χ_{ac}.

We used the conventional ac technique[14] to measure the bulk sample. To measure the thin films, we used the screening technique in the reflection configuration.[15] Since the resistivity is large, even for $T\ll T_P$,[16] $\chi'(T)$ and $\chi''(T)$ are proportional to the magnetic moment and the ac losses of the sample, respectively.[17] For conventional ferromagnets in small external magnetic field, $\chi'(T)$ decreases sharply at the Curie temperature, T_C, when going from low to higher temperatures. Also, $\chi''(T)$ peaks at T_C and it is typically 100 times smaller than $\chi'(T)$.[18,19]

We measured $\chi_{ac}(T)$ in the range $50\,K<T<330\,K$, with an amplitude of the ac field $h_{ac}=5.0$ Oe. The bulk single crystal was measured with an ac frequency $f=37.4$ Hz and thin film samples with $f=10$ kHz. We did not

TABLE I. Values of T_C and T_P obtained from $\chi_{ac}(T)$, compared with those obtained from dc magnetization and transport experiments, and processing parameters T_{sub} and P [temperature of the substrate, and pressure of the atmosphere in the periodic lattice distortion (PLD) chamber, respectively].

Sample	T_C(SQUID)	$T_C(\chi')$	T_P (transp.)	$T_P(\chi'')$	T_{ann} (°C)	t_{ann} (h)
LSMO-1	300 K	300 K	318 K	305 K	···	···
LCMO-1	250 K	250 K	270 K	271 K	900	10.0
LCMO-2	250 K	···	250 K	249 K	as dep.	as dep.
NSMO-1	225 K	226 K	227 K	226 K	900	2.0
NSMO-2	223 K	218 K	225 K	218 K	850	1.0
NSMO-3	205 K	203 K	205 K	211 K	as dep.	as dep.

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observe any dependence of $\chi_{ac}(T)$ on *f*. For the thin films we used a higher frequency to increase the resolution of the susceptometer.[14]

In Table I we also compare the results of T_C and T_P obtained from our measurements with those obtained from dc magnetization, using a superconducting quantum interference device (SQUID) magnetometer, and dc resistivity, respectively. We have defined T_C as the temperature where $\chi'(T)$ starts to increase, when going from high to lower temperatures.[20] Also, T_P was determined as the value of the temperature where $\chi''(T)$ peaks. The values of T_C obtained from the $\chi'(T)$ data for the $Nd_{0.7}Sr_{0.3}MnO_3$ and $La_{0.67}Ca_{0.33}MnO_3$ thin films agree with those determined by dc SQUID magnetization measurements. By contrast, the values of T_P obtained from $\chi''(T)$ and from dc transport measurements agree only for high-quality samples.

Since $\chi''(T)$ measures the dissipated power, which should correlate with dc resistivity, this comparison is of interest from the point of view of materials characterization. Previous work has shown that the relation between T_C and *Tp* depends on the material quality.[21] In bulk, as well as in thin films, lower quality samples with small grain size show values of T_C well above the resistive *Tp*. For bulk samples and thin films with large grain size or improved crystallinity and oxygen stoichiometry, the resistive T_P is observed to be close or even higher than T_C.[21] Our results indicate that since $\chi'(T)$ and $\chi''(T)$ correlate with T_C and T_P, respectively, complex $\chi_{ac}(T)$ measurements can serve as a quick and contact-free characterization method to assess sample quality by examining the relation between T_C and T_P.

It has been observed previously[22] that as-grown $Nd_{0.7}Sr_{0.3}MnO_3$ films are oxygen deficient and that extensive postdeposition annealing is required to obtain T_C and T_P close to bulk values. In as-grown films, the value of the saturation magnetization is smaller than the value expected for complete Mn spin alignment. In this case, ferromagnetic resonance (FMR) lines are very broad, indicating significant magnetic inhomogeneities in the samples.[11] With progressive annealing in oxygen it is observed that T_C, T_P and the saturation magnetization increase, while FMR line widths decrease.

We observe features in the $\chi_{ac}(T)$ measurements that clearly correlate with these changes. In Fig. 1 we show the $\chi'(T)$ and $\chi''(T)$ data for an as-grown film (NSMO-3) and two oxygen annealed films (NSMO-1 and NSMO-2) of $Nd_{0.7}Sr_{0.3}MnO_3$. As shown in Table I, T_C values obtained from $\chi'(T)$ for this set of samples agree with those from SQUID magnetization measurements, indicating a progressive increase in T_C as the samples are annealed. More noteworthy is the fact that features in $\chi''(T)$ clearly distinguish annealed samples from as-grown samples. We observe that peaks in $\chi''(T)$ correlate reasonably well with the values of T_P obtained from dc resistivity measurements. In addition, the as-grown film shows an additional broad peak in $\chi''(T)$ at a lower temperature ($\simeq$100 K). When annealed at 850 °C for 1 h (NSMO-2), this second peak shifts to a higher temperature. When annealed at 900 °C for 2 h (NSMO-1), the second peak disappears and we see only a single narrower peak corresponding to the T_P from resistivity measurements. These results correlate well with FMR measurements on the

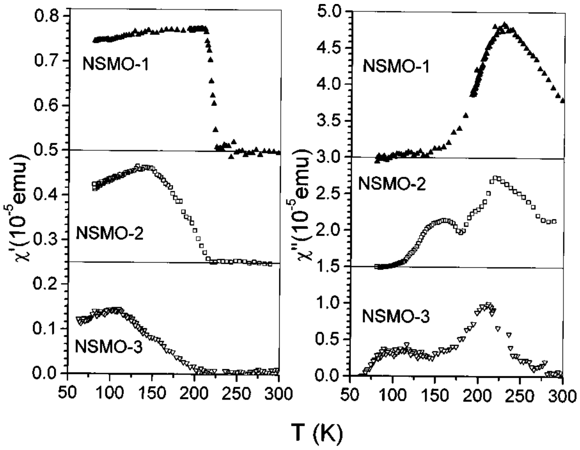

FIG. 1. Evolution of $\chi'(T)$ and $\chi''(T)$ for the thin films of $Nd_{0.7}Sr_{0.3}MnO_3$ according to the annealing conditions. For clarity, $\chi'(T)$ and $\chi''(T)$ are vertically shifted by 0.25×10^{-5} and 1.5×10^{-5} emu, respectively.

same samples. The FMR linewidths decrease with increasing time and temperature of the annealing conditions, which indicate that the magnetic homogeneity improves. The additional low temperature peaks observed in $\chi''(T)$ are thus indicative of sample inhomogeneity which is *not* directly evident in the dc resistivity data. It is worth mentioning, however, that the presence of such inhomogeneities tend to broaden the resistivity drop below T_P. We observe that the resistive transition in dc measurements becomes sharper as the samples are annealed.[22]

In Fig. 2, we observe that this correlation between the features in $\chi''(T)$ is also followed by the films of $La_{0.67}Ca_{0.33}MnO_3$ (samples LCMO-1 and LCMO-2). In this case, sample LCMO-2 was measured as deposited, and sample LCMO-1 was measured after annealing. We have also verified this correlation in bulk samples of both $La_{0.67}Ba_{0.33}MnO_3$ and $La_{0.67}Ca_{0.33}MnO_3$, and also in thin films of $La_{0.67}Ca_{0.33}MnO_3$ with low oxygen content.

We have measured $\chi_{ac}(T)$ for a bulk single crystal of $La_{0.80}Sr_{0.20}MnO_3$ (sample LSMO-1). This sample exhibits a sharp transition in both χ_{ac} components at $T=300$ K, in agreement with its high compositional homogeneity. The sharp peak in $\chi''(T)$ confirms that it is a reliable indicator of

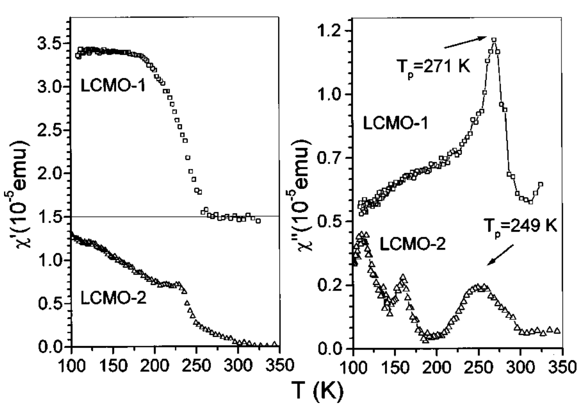

FIG. 2. Evolution of $\chi'(T)$ and $\chi''(T)$ for the thin films of $La_{0.67}Ca_{0.33}MnO_3$ according to the annealing conditions. For clarity, $\chi'(T)$ and $\chi''(T)$ are vertically shifted by 1.5×10^{-5} and 0.5×10^{-5} emu, respectively.

sample homogeneity. However, for this sample, the values of T_P obtained from transport measurement and from $\chi''(T)$, do not agree with each other. This result shows that, even for a sample compositionally homogeneous, magnetic and transport measurements give different values of T_P. This can be explained in terms of magnetic inhomogeneities (magnetic clusters) in the sample.[8]

In summary, from a single experiment of $\chi_{ac}(T)$ it is possible to assess the sample quality, and to obtain simultaneously both parameters T_C and T_P. We have established a correspondence between the peak observed in $\chi''(T)$ and the value of T_P obtained from dc resistivity. This agreement is clear for those samples exhibiting just one peak in $\chi''(T)$ but is not directly valid for low quality samples. In the latter case, we observe multiple peaks in $\chi''(T)$ which are a clear indication of inhomogeneities. This feature is not directly evident in dc transport measurements and thus $\chi''(T)$ is a better indicator of magnetic inhomogeneity than resistivity. Also, it correlates with FMR but χ_{ac} is much easier to use and gives extra information (values of T_C and T_P). Since χ_{ac} is a low-field technique, it explains that T_P obtained from $\chi''(T)$ is lower than the value of T_P obtained from transport measurements. Thus, the use of the ratio between T_C and T_P to infer the quality of the sample is more appropriate using the χ_{ac} technique. Also, besides being contact-free, this technique is more representative of the sample properties since it measures the region of the sample close to the secondary coils, instead of just the percolation path between the electrical contacts. The results presented on $Nd_{0.7}Sr_{0.3}MnO_3$ and $La_{0.67}Ca_{0.33}MnO_3$ thin film samples further illustrate the value of the χ_{ac} method.

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