Anomalous anisotropic ac susceptibility response of $La_{1-x}Sr_xMnO_3$ ($x \approx 1/8$) crystals: Relevance to phase separation

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The dynamic response of $La_{1-x}Sr_xMnO_3$ crystals ($x=0.1$ and 0.125) has been studied by ac susceptibility. A strongly frequency- and field-dependent susceptibility anomaly was observed along *a* and *b* axes in the intermediate temperature range between the onset of magnetic order and the orthorhombic–''pseudocubic,'' O′-O″, structural transition. No anomaly was present if the ac field was applied along the *c* axis. This unusual response, reminiscent of cluster-glass behavior, is attributed to a strongly anisotropic, magnetically nonuniform state. This observation would constitute a clear indication of phase separation in low-doped manganites.

The hole doped manganite perovskites $La_{1-x}Sr_xMnO_3$ are of interest not only for the practical importance of their ''colossal'' magnetoresistance effect but also for the underlying physics ruling their unusual magnetic and transport properties.[1] The region of $x \approx 0.1$–0.15, usually denoted as ''lightly doped'' regime, which bounds the commensurate fraction of charge carriers $x=1/8$, is of special interest as the intermediate state between the antiferromagnetic-insulating ($x \sim 0$) and the ferromagnetic-metallic ($x \geqslant 0.15$) behavior.[2] The complex magnetic and transport properties of the lightly doped regime were originally interpreted as representative of canted antiferromagnetic (CA) order, resulting from the competition between the antiferromagnetic superexchange and the ferromagnetic double exchange interactions.[3] More recent physical models invoked to explain these properties have been, so far, based on an homogeneous description of the ground state.[4–10] However, it has been proposed that this homogeneous canted state is thermodynamically unstable[11] and that there is a strong tendency towards a phase separation in hole-rich (ferromagnetic) and hole-poor (antiferromagnetic) regions. This phase separation is receiving great attention for its implications in the understanding of the ground state of strongly correlated electronic systems.[12]

From the experimental point of view, direct evidences of phase separation, particularly at low-doping levels, are scarce. However, recent low-temperature data from elastic neutron scattering[13] and nuclear magnetic resonance[14] have provided some indications of the formation of distinguishable ferromagnetic dropletlike regions having a magnetic moment slightly larger than the matrix. If confirmed, the phase separation in the double exchange model will imply that many experimental results should be reconsidered in the light of the magnetic and electronic inhomogeneity of the ground state.

The temperature, frequency, and field dependence of the complex ac susceptibility has proven to be a versatile and powerful tool to identify magnetic transitions and to study the dynamic response of different spin systems. Recently, ac susceptibility of $LaMnO_3$ single crystals has been reported, revealing a small canting moment of the *A*-type antiferromagnetic structure.[15] However, ac-susceptibility studies in $La_{1-x}Sr_xMnO_3$ close to the commensurate fraction $x=1/8$ are scarce and nonsystematic.[16,17]

In this paper we present ac-susceptibility measurements of $La_{1-x}Sr_xMnO_3$ ($x=0.1, 0.125$) single crystals with doping level close to the commensurate fraction $x=1/8$. The results suggest the presence of distinguishable anisotropic magnetic clusters, between the onset of magnetic order and the O′-O″ transition, in agreement with ''phase-separation'' models.

Single crystals of $La_{1-x}Sr_xMnO_3$ ($x=0.1, 0.125$) were grown by floating zone method with radiation heating without crucible. The $x=0.125$ crystal was oriented using a Laue camera and cut along the main crystallographic axes ($d_{a\text{-}axis}=1$ mm, $d_{b\text{-}axis}=2.5$ mm, and $d_{c\text{-}axis}=0.7$ mm). The $x=0.1$ crystal was not oriented and had an irregular shape with dimensions $d \sim 2\times2\times1$ mm^3. The susceptibility measurements were carried out by a mutual impedance bridge. The in-phase, χ', and quadrature, χ'', components of the complex ac susceptibility, $\chi=\chi'-j\chi''$, were measured at different frequencies ($f=10$–1000 Hz) at fixed ac fields ($h_{ac}=8-800$ A/m) in warming runs stabilizing the temperature within 0.1 K at each measuring point. Occasional cooling and warming scans, in sweep mode, were also carried out. The external susceptibilities (not corrected for demagnetizing effects) were calculated from the mass and x-ray densities of the crystals.

The $\chi'(T)$ and $\chi''(T)$ components of the ac susceptibility for the $x=0.125$ crystal measured along different crystallo-

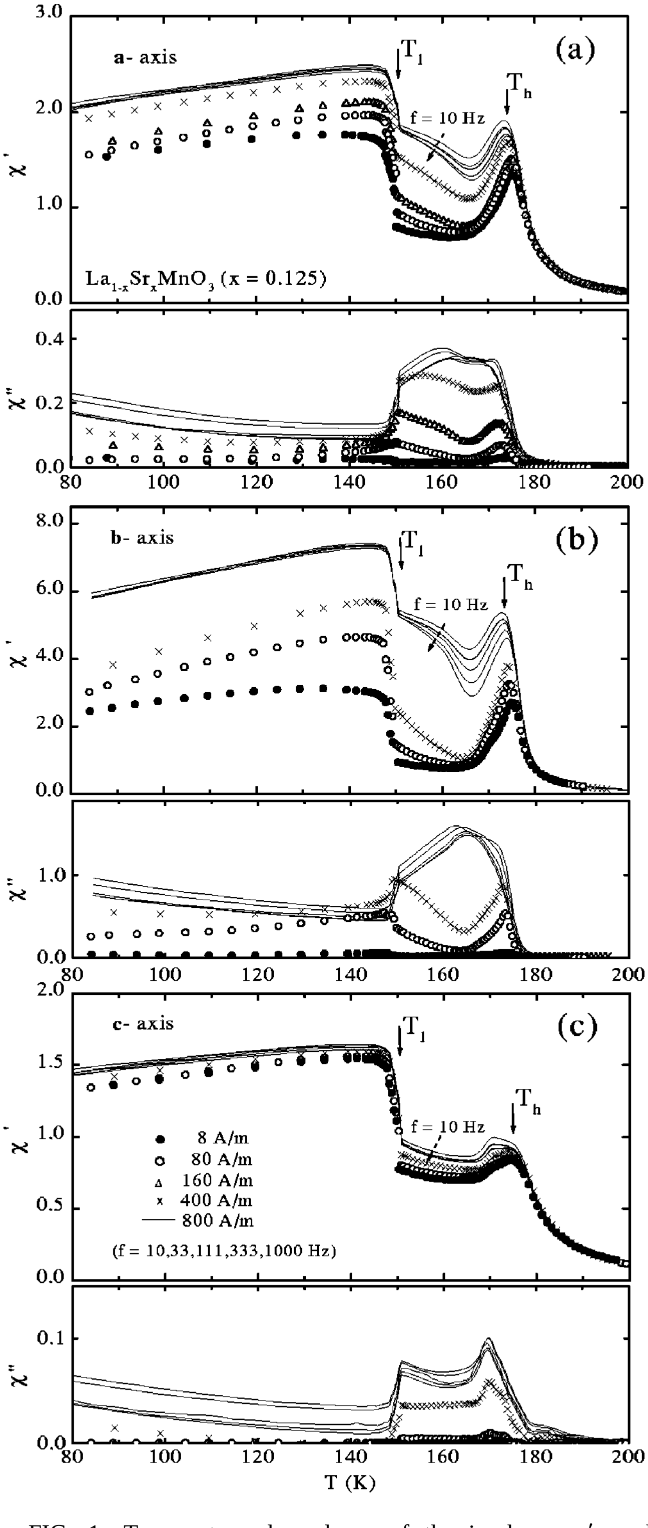

FIG. 1. Temperature dependence of the in-phase, χ', and quadrature, χ'', external susceptibilities (dimensionless, in SI units) for $La_{1-x}Sr_xMnO_3$ ($x=0.125$) for different ac fields and frequencies applied along the (a) *a* axis, (b) *b* axis, and (c) *c* axis.

graphic directions are given in Fig. 1. The results for the field applied along the *a* or *b* axes are rather similar. At relatively low fields ($h_{ac}<80$ A/m), when the temperature is lowered from room temperature, $\chi'(T)$ exhibits a maximum at $T_h=175$ K, after which $\chi'(T)$ changes only slightly in the temperature range $T=149$–165 K. At $T_l=149$ K, $\chi'(T)$ shows a discontinuity, with a subsequent broad maximum on $\chi'(T)$ at lower temperatures. Two peaks in $\chi''(T)$ accompany the T_h maximum and the T_l discontinuity.

It is natural to attribute the discontinuity in $\chi'(T)$ at $T_l=149$ K to the recently found ferromagnetic-metallic to ferromagnetic-insulator transition which is related to the orthorhombic pseudocubic, O′-O″, charge ordering structural transformation[2,8–10] and the maximum at $T_h=175$ K to the onset of a magnetically ordered state, or more precisely to the temperature at which the applied field equals the coercive field. Furthermore, cooling and warming runs with similar cooling-heating rates indicate that the discontinuity of $\chi'(T)$ at T_l is hysteretic in temperature, with $\Delta T\sim 4$ K, for a cooling-warming rate of $\beta\sim 2$ K/min, indicating the first-order nature of the O′-O″ transition.

Application of larger driving fields leads to significant variations in the shape of $\chi'(T)$ and $\chi''(T)$. As shown in Fig. 1, applied ac fields above $h_{ac}=80$ A/m promote an increase in $\chi'(T)$ and $\chi''(T)$, being the main change that $\chi'(T)$ is no longer constant in the T_l–T_h($T=149$–165 K) range but increases sharply with decreasing temperature. In addition, a strong frequency dependence of the susceptibility is observed in this temperature interval.

It can be observed in Fig. 1(a) and 1(b) that the structural and magnetic changes occurring at T_l appear to suppress the features observed in $\chi'(T)$ [and $\chi''(T)$] in the T_l–T_h temperature range. This key observation, together with the strong frequency and field dependence, suggest that the dome in $\chi'(149<T<165$ K) could be a fraction of a developing maximum in $\chi'(T)$, which is overcome by the sharp rise of susceptibility at the low-temperature transition T_l.

The susceptibility response along the *c* axis [Fig. 1(c)], is remarkably different from the one observed along *a* and *b* axes. First, the field dependence is much weaker. Of the greatest relevance is the fact that the strong increase in susceptibility with decreasing temperature in the T_l–T_h range is no longer observed. Similarly, the frequency dependence in the same intermediate temperature range is drastically reduced. It is worth noting that for the smallest applied ac field ($h_{ac}=8$ A/m), $\chi'(T)$ is the same along the three different axes in the intermediate T_l–T_h range if demagnetizing effects are taken into account (demagnetizing factors are $N\approx 0.38, 0.1, 0.46$ for *a*, *b*, and *c* axes.[18])

It is well known that the O′-O″ transition occurring at T_l can be pushed to lower temperatures by reducing the hole doping in $La_{1-x}Sr_xMnO_3$ manganites.[4,5] Thus reducing *x* to $x=0.1$, with $T_l\approx 95$ K, should allow us to study if the dome observed in $\chi'(T)$ in the $x=0.125$ crystal is indeed a truncated maximum. Hence the nonoriented $x=0.1$ crystal was measured along a number of different directions until systematic results were found. Three orthogonal directions were identified. Similar to what was obtained for the $x=0.125$ crystal two of the directions exhibited the same behavior, whereas the third direction showed different results. When applying the ac field along the ''third'' direction [Fig. 2(b)], $\chi'(T)$ shows first a maximum at about $T_h=145$ K, followed by a plateau before a broad maximum around $T_l=95$ K. These features correspond to the onset of magnetic order and to the O′-O″ structural transition. Correspondingly, $\chi''(T)$ shows two maxima at $T_h=145$ K and $T_l=95$ K, respectively. The dependence of $\chi'(T)$ and $\chi''(T)$ on the ac-field

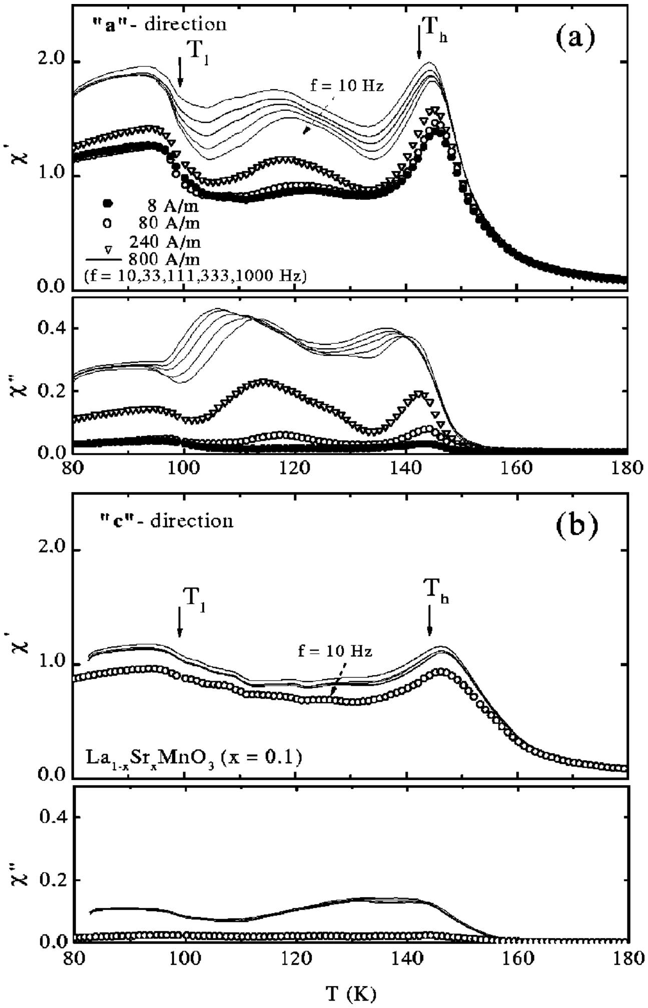

FIG. 2. Temperature dependence of the in-phase, χ', and quadrature, χ'', external susceptibilities (dimensionless, in SI units) for $La_{1-x}Sr_xMnO_3$ ($x=0.1$) for different ac fields and frequencies applied along the (a) ''a''-''b''-like direction and (b) ''c''-like direction. See text for the meaning of ''a''-, ''b''-, ''c''-like direction.

amplitude and frequency is rather weak. The behavior in this direction is analogous to that observed for the c-axis measurements on the oriented $x=0.125$ crystal. As expected, the T_h-T_l temperature interval has broadened almost twice when going from $x=0.125$ to $x=0.1$. Thus the dome, that was emerging in the susceptibility of the $x=0.125$ crystal for h_{ac} applied within the a-b plane, should be fully visible in the $x=0.1$ crystal. Indeed this is the observed behavior. As shown in Fig. 2(a), when the ac field is applied along either of the other two directions, the susceptibility $\chi'(T)$ shows a clear broad maximum at T_m, between T_l and T_h. While the maximum is almost field independent for ac fields smaller than $h_{ac}=80$ A/m, it strongly increases for larger ac-field amplitudes. The new maximum in $\chi'(T)$ at T_m is accompanied by a maximum in $\chi''(T)$. As the ac-field amplitude is increased, the maxima in $\chi'(T)$ and $\chi''(T)$ at T_m shift to lower temperatures. Moreover, a strong frequency dependence of the ac susceptibility is observed, where T_m rises with increasing frequency. These results are quite similar to those observed in the a and b axes of the $x=0.125$ crystal if we assume that in the $x=0.125$ crystal the peak at T_m is truncated by the appearance of the low-temperature O$''$ phase at T_l.

In summary, the susceptibility data for $x=0.1$ and 0.125 crystals in the temperature interval between the T_h and T_l, display a strong field- and frequency-dependent maximum (or truncated maximum) along the a and b axes. No maximum is observed along the c axis.

The strong frequency dependence of the ac susceptibility along a and b axes observed between the two characteristic temperatures T_l and T_h and the maximum (or truncated maximum) of $\chi'(T)$ when decreasing T from T_h, indicate that the observed behavior may be due to the proximity of some kind of blocking temperature. The results are consistent with effects expected from freezing of magnetic clusters, i.e., cluster glass.[19] At T_m, freezing of the clusters appears through the probability of each cluster to overcome the energy barrier E, created by the local anisotropy, expressed in terms of relaxation time $\tau=\tau_0\exp(E/kT)$. An anomaly on the ac susceptibility will appear when τ becomes comparable with the characteristic measuring time, i.e., when τ is of the order of $1/2\pi f$. Hence T_m is expected to decrease with decreasing frequency, as observed experimentally. The change of the temperature at which $\chi''(T)$ exhibits a maximum, T_m, for decade of frequency leads to $K=\Delta T_m/(T_m\Delta\ln f)=0.04$, which is consistent with cluster glass freezing.[19] From the ac-field dependence of $\chi'(T)$, the clusters appear to ''grow'' or become more ''susceptible'' as the ac field is increased above a certain value. The results resemble those found in electron doped polycrystalline perovskite compounds $Ca_{1-x}Sm_xMnO_3$ ($x\sim0.12$).[20] This indicates that clustering effects may occur at both ends (hole-rich and hole-poor) of the manganites phase diagram.

It is noteworthy that the described anomalies in the intermediate temperature range for $x=0.125$ and $x=0.1$ remain present even for cooling experiments (not shown).

The existence of magnetic clusters in the intermediate temperature range ($T_l<T<T_h$) implies a nonhomogeneous magnetic state and thus reflects a phase separation.

The presence of freezing phenomena in the $T_l<T<T_h$ temperature region is in agreement with the observation of hysteresis in the zero-field-cooled/field-cooled magnetization and the relaxing resistivity[8] and consistent with structural inhomogeneities inferred from x-ray-diffraction analysis.[21,22] Moreover, detailed inspection of recent specific-heat measurements in $La_{1-x}Sr_xMnO_3$ (Ref. 9) also reveals an extra maximum in the intermediate temperature range, suggesting that some sort of additional ordering takes place, which could be in agreement with our proposal of a ''blocking temperature'' of a secondary magnetic phase. An important aspect of our experimental results is the anisotropic magnetic response of the magnetic clusters: (i) they display a large field- and frequency-dependent susceptibility within the a-b plane and (ii) the blocking temperature T_m is no longer visible for h_{ac} applied along the c axis. These results indicate that with increasing field the clusters can be more easily magnetized within the a-b plane, which is probably related to the layered nature of the manganite perovskites. Moreover, these results are also compatible with pancake-shaped ferromagnetic droplets as suggested by some recent neutron-

diffraction data.[23] Note that orientation dependent results have also been found in dielectric permeability and dynamic conductivity studies.[17]

Thus the experimental results are in agreement with the proposed phase-separation models, although the exact nature of the phases involved is difficult to elucidate from the obtained experimental results. It has been argued that electronic phase separation may be an intrinsic property of low-doped double exchange oxides.[11,12] However, the first-order nature of the O′-O″ transition taking place at T_l implies that fractions of the high- and low-temperature phases can coexist in a certain temperature range, thus leading to a phase separation which is not of primary electronic origin. Nevertheless, the existence of the $\chi'(T)$ maximum at T_m in both cooling and warming experiments imply that the observed effects are not related to the O′-O″ transition. An electronically driven phase separation seems to be an appropriate mechanism to account for the experimental data. However, it has been pointed out (see, for instance, Ref. 2) that below the Curie temperature the antiferrodistortsive orthorhombicity—reminiscent of the static Jahn-Teller distortion—vanishes only gradually, thus suggesting that locally distorted regions could be present in that temperature range.

Finally, we note that ac susceptibility has proven to be a very sensitive tool to study phase separation. Moreover, it has revealed rather unconventional aspects of the magnetic response of La-Sr manganites, such as the presence of a shoulder at the T_h maximum [Fig. 1(c)], the tail in $\chi''(T)$ at high temperatures [Fig. 1(c)], or the non-purely ferromagnetic nature of the transition at T_h. Complete discussion of these results will be presented elsewhere.

In conclusion, the frequency and field dependence of the ac susceptibility for $La_{1-x}Sr_xMnO_3$ ($x=0.1,0.125$) crystals have been studied. We have argued that the presence of a frequency and field-dependent anomaly at temperatures between the O′-O″ transition (T_l) and the onset of magnetic order (T_h), indicates the existence of distinguishable and anisotropic magnetic clusters in this temperature range. These clusters are probably created by an electronically driven phase separation. The anisotropic nature of the clusters imposes important constrains for the driving mechanisms of phase separation. Thus our results should be useful for any theoretical microscopic understanding of the origin of phase separation in manganites.

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