Domain-wall dynamics in the disordered ferromagnet $LaMnO_{3.075}$

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Low-field ac susceptibility measurements have been made on the cation-deficient perovskite manganite $LaMnO_{3.075}$. As the temperature is increased toward T_C (122 K), the real part of the ac susceptibility (χ') exhibits discontinuous jumps at roughly regular intervals, followed by gradual decays on the high-temperature side, resulting in a series of spikes in the χ' vs temperature plot. It is argued that the spikes appear as a consequence of disaccommodation, combined with periodic, spontaneous domain-wall jumps.

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I. INTRODUCTION

Domain walls in ferromagnets have a strong influence on the magnetic properties. For instance, the coercivity and the initial permeability, two important parameters in the application of magnetic materials, vary over many orders of magnitude, depending on the mobility of the domain walls.[1] In mixed-valence perovskite manganites,[2–10] a group of materials extensively studied for the colossal magnetoresistance effect, the domain walls affect not only the magnetic properties but also the transport properties. Recent studies[2,3] on $La_{0.7}D_{0.3}MnO_3$ thin films ($D=$Ca or Sr) have shown that the domain-wall resistance is higher by orders of magnitude than expected from a simple model based on the double-exchange mechanism, indicating that the domain walls play a significant role in the low-field magnetoresistance.

Along with direct observation of magnetic domains by various techniques, such as magnetic force microscopy[3] and Kerr microscopy,[4] ac susceptibility measurements have been employed to study domain-wall dynamics in mixed-valence manganites.[5,6] Wang *et al.*[5] have measured the ac susceptibility ($\chi=\chi'+\chi''$) of $La_{0.7}Ca_{0.3}MnO_3$ as a function of temperature (T) and observed a number of steps in the χ' vs T curves. They interpret the discontinuous jumps of χ' as resulting from domain-wall jumps activated by thermal energy and the magnetic field.[5] We have recently studied the time dependence of χ in $LaMnO_{3.075}$ and discovered disaccommodation or a decrease in $|\chi|$ with time after demagnetization which has been ascribed to the coupling of local moments in the domain walls with electronic transitions of various types.[6]

In this work, we have measured the ac susceptibility of $LaMnO_{3.075}$ as a function of temperature and found a series of spikes, similar to the steps reported in Ref. 5, in the χ' vs T curves. We discuss these spikes in terms of spontaneous domain-wall jumps combined with disaccommodation.

II. EXPERIMENTAL PROCEDURE

The sample used in this study was a sintered pellet (4.5 mm in diameter and 3.0 mm in thickness) of $LaMnO_{3+\delta}$ ($La_{1-\delta/(3+\delta)}Mn_{1-\delta/(3+\delta)}O_3$), identical to the one used in a previous study.[6] It was prepared by standard ceramic processing, described in detail in Ref. 7. The final heat treatment in air at 1000 °C, followed by quench into liquid nitrogen, resulted in a cation-deficient composition $LaMnO_{3.075}$ ($La_{0.976}Mn_{0.976}O_3$).[7] The sample was about 85% dense with the grain size ranging between 2 and 4 μm. X-ray diffraction analysis has indicated that the sample is single phase and has a quasicubic perovskite structure with a slight rhombohedral distortion.[7] Measurements of magnetization were made using a superconducting quantum interference device (SQUID) magnetometer, while those of ac susceptibility were made using a mutual inductance bridge with a lock-in amplifier for signal detection. The field was applied along the symmetry axis of the pellet in the measurements of both types.

III. RESULTS AND DISCUSSION

In Fig. 1, the magnetizations (M) measured in fields (H) of 100 Oe and 70 kOe are plotted as functions of temperature (T). The measurements were made with increasing temperature after the sample was cooled in the field. For $H=100$ Oe,

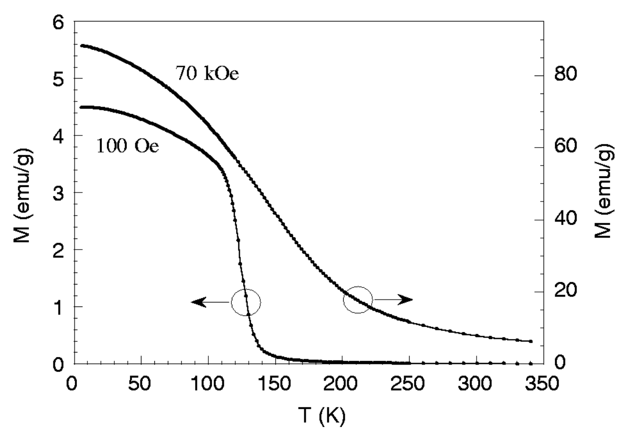

FIG. 1. Temperature dependence of magnetization (M) measured in $H=100$ Oe and 70 kOe (field cooled).

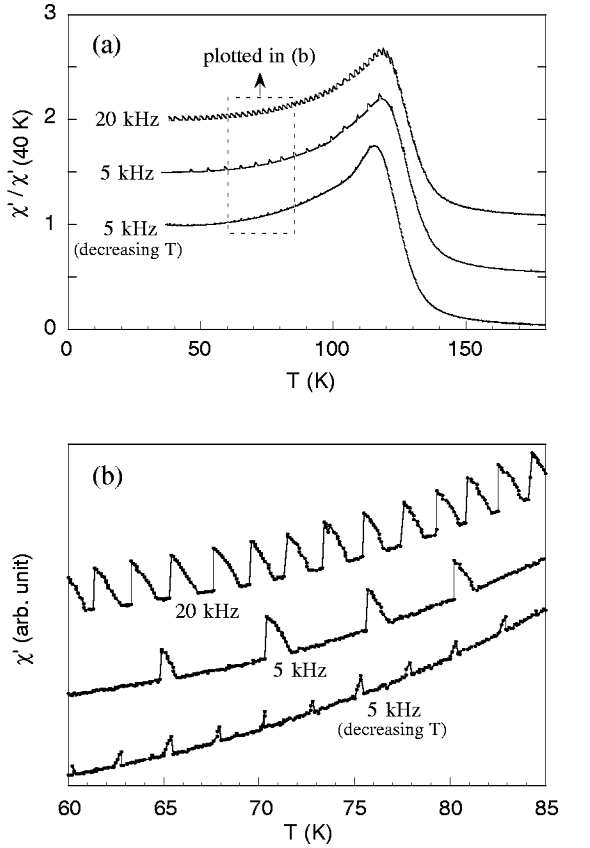

FIG. 2. (a) Temperature dependence of χ', the real part of ac susceptibility, measured in $H_{ac}=350$ mOe. The top two plots were obtained from measurements at different ac-field frequencies with increasing temperature, and the bottom plot from a measurement at 5 kHz with decreasing temperature. The curves are normalized to the values at 40 K, and the top two plots are displaced vertically. Parts of the plots are magnified in the inset and (b).

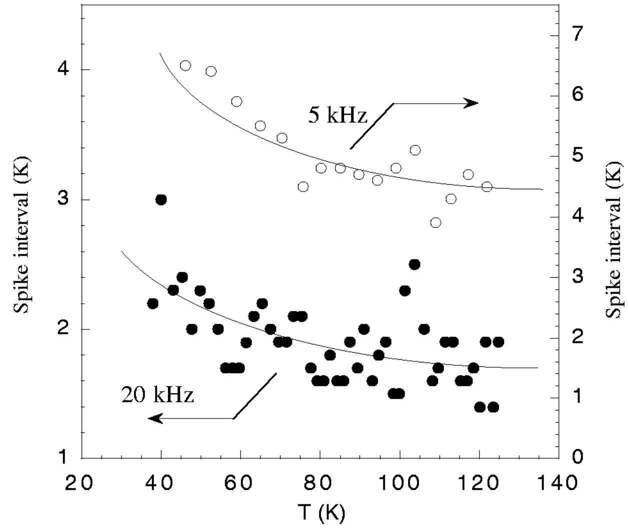

FIG. 3. Intervals between spikes in the χ' vs T curves (Fig. 2) plotted as functions of temperature.

a relatively sharp ferromagnetic transition is observed below 150 K, with a T_C (defined as the temperature corresponding to the inflection point of the M vs T curve) of 122 K. For $H=70$ kOe, on the other hand, the ferromagnetic transition is much broader with significant tailing of the M vs T curve on the high-T side. Tailing of the M vs T curve in a high field has also been observed in other manganites[8] and is consistent with the increase in the magnetic correlation length under a high field over a wide temperature range above T_C.[9] The low-temperature saturation magnetization is $3.70\mu_B$/Mn site, a value slightly smaller than, but close to, the spin-only value expected for a mixture of 85% Mn^{3+} and 15% Mn^{4+}, $3.85\mu_B$/Mn site.[7]

In Fig. 2(a), the real part of the ac susceptibility (χ') measured in an ac field (H_{ac}) of 350 mOe is plotted as a function of temperature. The top two curves were obtained from measurements at two different frequencies (f) with increasing temperature and the bottom curve from a measurement at $f=5$ kHz with decreasing temperature. (The temperature was swept at a constant rate of 1.3 K/min in all measurements.) The curves are normalized to the values at 40 K and for clarity the top two curves are displaced vertically. The overall temperature dependence of χ' is similar to that observed in $LaMnO_{3.07}$,[10] and characterized by a smooth asymmetric curve having a peak near T_C and a steeper decrease on the high-temperature side. Superimposed on it is a series of spikes, which persists up to a temperature near T_C. The spikes are asymmetric, as can be seen more clearly in Fig. 2(b), where parts of the χ' vs T curves are magnified. In the χ' vs T curves measured with increasing temperature, the low-temperature side of the spikes is almost vertical, while the high-temperature side is more gradual. The temperature interval between spikes is smaller for $f=20$ kHz than for $f=5$ kHz, and tends to decrease with increasing temperature as can be seen in Fig. 3, where the temperature intervals between spikes are plotted as functions of temperature. In the χ' vs T curve measured with decreasing temperature, the asymmetry is reversed; that is, the high-temperature side is steeper. However, the spikes are much smaller and irregular than in the case of increasing temperature. This is probably due to significant undershooting of temperature, which was difficult to avoid when the temperature was swept downward. (Temperature overshooting was negligible in the case of upward sweep.)

We interpret the appearance of spikes in the χ' vs T curve as resulting from periodic domain-wall jumps, combined with disaccommodation, or a decrease in χ' with time, observed recently in $LaMnO_{3.075}$.[6] Below T_C, a ferromagnet, unless it is small enough to be in the single-domain regime, is divided into magnetic domains to reduce the magnetostatic energy associated with free poles appearing on the surface. At a given temperature, the equilibrium positions of the domain walls are determined so as to minimize the sum of the wall energy and the magnetostatic energy, the magnetocrystalline anisotropy energy or the magnetostrictive elastic energy, depending on the type of the domains.[1] Because of inhomogeneity, always present in real materials, the domain-wall distribution, in general, is not in equilibrium; rather, the domain walls are located in positions corresponding to local potential minima and oscillate around these metastable positions in response to a small ac field. The amplitude of this oscillation and hence χ' decrease with time as the potential well becomes deeper.[6] This time decay of χ', or disaccommodation, corresponds to the gradual side of the spikes, which naturally appears on the high- (low-) temperature side when the temperature is swept upward (downward). The equilibrium domain-wall positions change with temperature, since the saturation magnetization, magnetocrystalline anisotropy constant, and magnetostriction constant are all temperature dependent. Thus, as the temperature increases (or decreases), the domain-wall distribution deviates more from equilibrium, and the magnetic pressure on the domain walls increases. This, on the one hand, lowers the potential barrier that keeps the domain walls in metastable positions and, on the other, decreases the curvature at the bottom of the potential well. The latter effect counteracts the increase in the curvature due to disaccommodation; this accounts for the flat sections between spikes in the χ' vs T curve. The potential barrier eventually becomes comparable to the thermal energy, and the domain walls jump to establish a new metastable distribution closer to equilibrium. This accompanies a sudden increase in χ', since the newly created domain walls oscillate at a larger amplitude. The repetition of the above process results in a series of spikes in the χ' vs T curve.

From the above model, it is expected that domain-wall jumps, and hence discontinuous increases in χ', occur more frequently in a range where the magnetization depends more strongly on temperature, since the domain-wall jumps are induced by magnetic pressure arising from changes in the magnetostatic energy, which is proportional to M^2.[1] Figures 1 and 3 indeed show that the temperature interval between spikes decreases as the temperature dependence of magnetization becomes stronger.

The f dependence of the temperature interval between spikes is consistent with the f dependence of disaccommodation observed in Fig. 4, where the variations of χ' with time measured at various temperatures are shown for $f=5$ and 20 kHz. (χ' was recorded for 180 s after the sample was demagnetized by reducing the amplitude of an additional ac field of 100 Hz from 50 Oe to zero in 1 s; these conditions are the same as those adopted in a previous study.[6]) It can be seen that the decrease in χ' is roughly proportional to ln t and faster for $f=5$ kHz than for $f=20$ kHz at any temperature below T_C, 122 K. This means that the domain walls stabilize themselves more (i.e., the potential well becomes deeper) in a given time for a lower f than for a higher f. Thus, for a lower f the magnetic pressure (plus the thermal energy) needs to be increased more to induce the next domain wall jumps, consistent with the larger temperature interval between spikes in the χ' vs T curve for $f=5$ kHz than for $f=20$ kHz.

The f dependence of disaccommodation may be explained as follows. Let us consider the region occupied by a domain wall of width W in $H_{ac}=0$. As the domain wall oscillates with an amplitude of A in response to H_{ac}, only part of the region (region I), having a total width of $W-2A$, is within the domain wall at all times. The remaining region (region II), having a total width of $2A$, stays within the domain wall only for periods varying between $\tau/2$ and τ at a time, where $\tau(=1/f)$ is the period of the domain-wall oscillation. As we

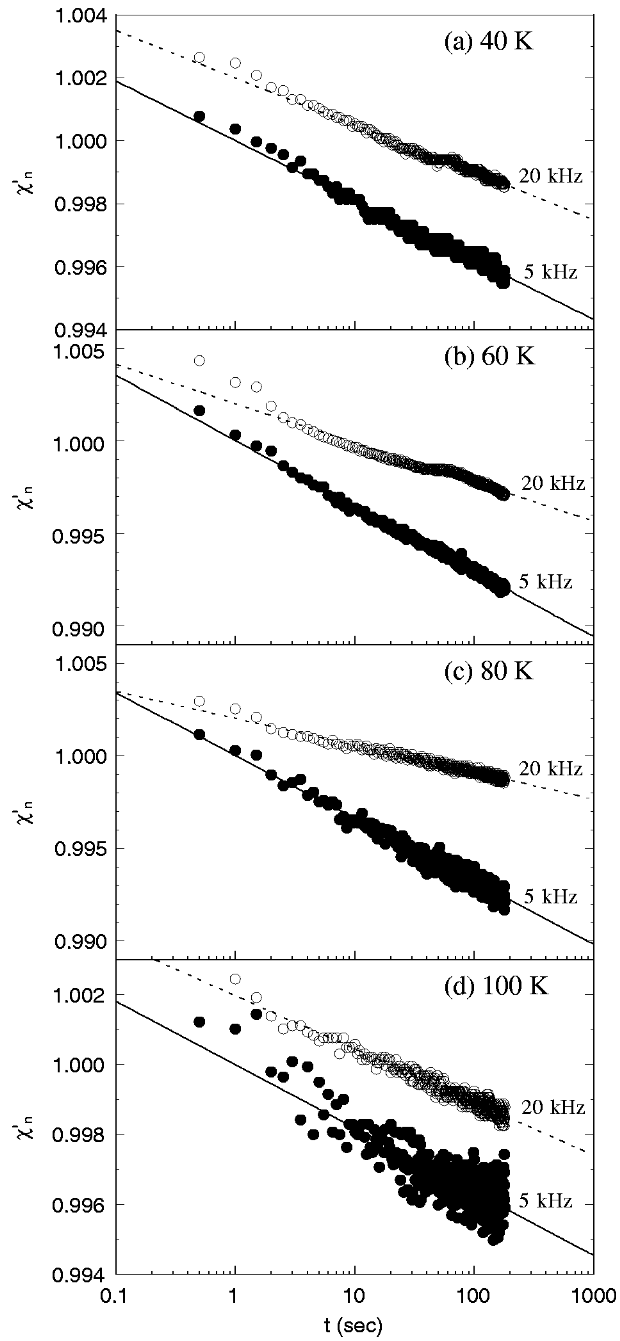

FIG. 4. Real part of ac susceptibility (χ') measured at various temperatures as a function of time after demagnetization. The plots are normalized to the values at $t=1$ s, and for clarity the plots for $f=20$ kHz are displaced vertically by 0.002. The straight lines are the best fits of the data points to the equation $\chi'_n=\chi'_{n0}-S\ \ln t$.

have argued in a previous paper,[6] the disaccommodation in $LaMnO_{3.075}$ results from interactions of the domain walls with electronic transitions of the following three types, which induce favorable exchange interactions and magnetocrystalline anisotropy, thereby stabilizing the domain walls: (i) e_g-electron hopping from a Mn^{3+} ion to a Mn^{4+} ion, which changes the charge distribution; (ii) e_g-electron hopping within a Mn^{3+} ion, which changes the orientation of the occupied e_g orbital; and (iii) localization or delocalization of

e_g electrons, which converts Mn ions in the mixed-valence state into Mn^{3+} and Mn^{4+} ions or vice versa. Since region II remains in the domain wall only for periods less than τ, those transitions that take times longer than τ cannot take place and do not contribute to the relaxation process in that region. Thus, in region II the transitions that take times between 1/20 000 and 1/5000 s contribute to disaccommodation for 5 kHz but not for 20 kHz, resulting in a faster decay of χ' for the lower *f*.

There is an apparent inconsistency between the data presented in Fig. 2 of Ref. 6 and those in Fig. 2: the former show that the disaccommodation becomes negligibly small as the temperature increases toward $T_C(=122\ \mathrm{K})$, whereas the latter show that the spikes persist up to about 140 K, although the height of the spikes decreases quickly with increasing temperature above T_C. This discrepancy is explained as follows. In standard disaccommodation measurements, χ' is recorded at a constant temperature as a function of time after the sample is demagnetized by applying an additional ac field, greater in amplitude than the ac field used for the measurement of χ', for a short time. At low temperatures, this procedure will place a domain wall in a new metastable position as intended, since the thermal energy is unlikely to be high enough to overcome all the energy barriers associated with minor potential wells in the vicinity of the original domain-wall position. At higher temperatures, however, minor energy barriers are overcome by the thermal energy, and there is a significant probability that a domain wall returns to the original position where the potential energy has already been lowered through disaccommodation prior to the ac demagnetization procedure. The subsequent decrease in χ' with time is small, as a result. In measurements of χ' as a function of temperature, by contrast, most of the domain walls, after spontaneous jumps, will settle in new positions regardless of temperature, since the domain-wall jumps in this case are induced by changes in the equilibrium domain-wall configuration with temperature and the resultant magnetic pressure. Time dependence of χ' and hence spikes in the χ' vs T curve are therefore observed as long as domain walls are present and the mechanisms of their stabilization with time are operative. [It is reasonable to expect that domain walls are present in the temperature range of up to about 150 K, considering that the ferromagnetic transition is not sharp and M remains significant in that temperature range even in $H=100$ Oe (Fig. 1), and that T_C was defined as the temperature corresponding to the inflection point of the M vs T curve measured in 100 Oe on a sample having a relatively large demagnetization factor.]

The above argument is supported by the data presented in Fig. 5, where the time dependence of χ' is shown for two types of measurement: one in which the sample was demagnetized by applying an ac field of 50 Oe (100 Hz) and decreasing the amplitude to zero in 1 s, a standard procedure employed in the experiments described above and in Ref. 6 (ac demagnetization), and the other in which the sample was demagnetized by applying a dc field of 1 kOe (parallel to the ac field used for the measurement of χ') and then reducing it to zero in 2.5 s (dc demagnetization). The coercivities are essentially zero at these temperatures, and the dc demagnetization procedure ensures that all the domain walls are newly created. It can be seen that in the case of dc demagnetization the disaccommodation is significant at 120 K ($\approx T_C$), decreases with increasing temperature, and becomes negligibly small at 150 K, while in the case of ac demagnetization the disaccommodation is negligibly small already at 120 K, fully consistent with the above argument. It is noted that the decrease in χ' with time cannot be ascribed to magnetic viscosity, because at these temperatures χ' decreases with increasing dc field (and hence M), reflecting the concave-downward M vs H curve ($H \geqslant 0$),[7] and a decrease in M with time after dc demagnetization (magnetic viscosity) would result in an *increase* in χ' with time.

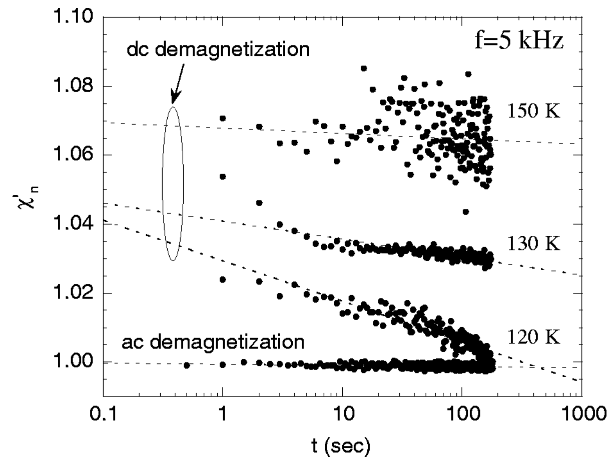

FIG. 5. Real part of ac susceptibility measured at various temperatures as a function of time after demagnetization. The bottom plot corresponds to the case where the sample was demagnetized by applying an additional ac field of 50 Oe (100 Hz) and reducing the amplitude to zero in 1 s (ac demagnetization), while the top three plots correspond to the cases where the sample was demagnetized by applying a dc field of 1 kOe and reducing it to zero in 2.5 s (dc demagnetization). The plots are normalized to the values at 180 s, and the top two plots are displaced vertically for clarity.

We next discuss the model proposed by Wang *et al.*[5] to explain the steps observed in the χ' vs T curves of $La_{0.7}Ca_{0.3}MnO_3$. In their model, it is assumed that the domain walls are released periodically from the pinning centers by the combined action of the dc field, the ac field and the thermal energy, and the discontinuous jumps of χ' are ascribed to the smaller magnetic pressure exerted on the domain walls in new metastable positions. We do not think this model provides a reasonable explanation of the appearance of spikes in the χ' vs T curves of $LaMnO_{3.075}$ (Fig. 2) for the following reasons. (1) Since no dc biasing field was applied in our measurements of χ, there was no driving force to change the magnetization of the sample. Domain-wall jumps and the resultant discontinuous jumps of χ' were nevertheless observed. (2) The amplitude of domain-wall oscillations, to which χ' is proportional, is determined by the curvature at the bottom of the potential well that characterizes the pinning center and is not influenced by the magnetic pressure itself. This is because the Zeeman energy term $E_z = -\alpha H_{dc} x$, where α is a constant and x is the displacement of the domain wall from an equilibrium position in $H_{dc}=0$, is linear

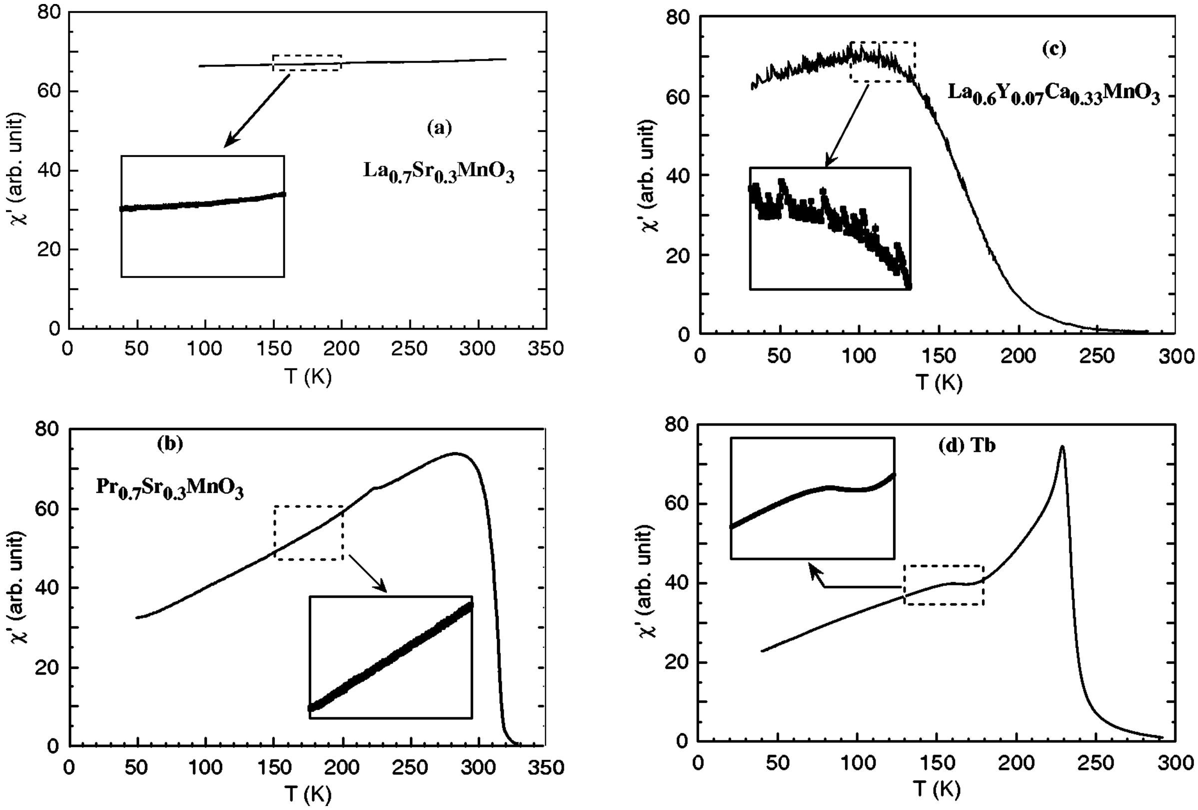

FIG. 6. Temperature dependence of χ', the real part of ac susceptibility, measured in $H_{ac}=350$ mOe (5 kHz) with increasing temperature for (a) $La_{0.7}Sr_{0.3}MnO_3$, (b) $Pr_{0.7}Sr_{0.3}MnO_3$, (c) $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$, and (d) Tb (99.99%). Part of the plot is magnified in the inset in each graph.

in x and hence $d^2E_z/dx^2=0$. (The magnetic pressure does change the position of the potential minimum, which could result in either an increase or a decrease in χ' depending on the shape of the potential well.[11]) Thus, domain-wall jumps by themselves do not account for a discontinuous increase in χ'. (This is consistent with the fact that not all ferromagnetic materials exhibit spikes and steps in the χ' vs T curves; see below.) (3) Without disaccommodation the decreases in χ' between spikes and steps (in both Fig. 2 and the χ' vs T curves presented in Ref. 5) should not occur. (4) The physical meaning of the f^2 dependence of the excitation energy, assumed in Ref. 5 to explain the f dependence of the temperatures at which discontinuous jumps of χ' occur, is not clear. We believe our model involving periodic domain-wall jumps and disaccommodation provides more reasonable, consistent explanations of the observations described in this paper, as well as in Ref. 5.

Finally, we discuss the conditions under which spikes are observed in the χ' vs T curve. From the foregoing arguments, the appearance of spikes is expected only when the following two conditions are satisfied: (1) domain walls jump periodically as the temperature is swept and (2) the material exhibits disaccommodation over a wide range of temperature. (As explained above, condition 1 is *not* a sufficient condition for the appearance of spikes.) Condition 1 is satisfied in most ferro (ferri) magnetic materials, which normally contain impurities and/or inhomogeneities that work as pinning centers and prevent the domain walls from establishing an equilibrium configuration; only in those specially prepared materials which are of high purity and free from inhomogeneities would condition (1) not be satisfied. Condition (2), on the other hand, is not satisfied in most ferro (ferri) magnetic materials. Pure magnetic materials in general do not exhibit disaccommodation. Crystalline materials such as Fe_3O_4, $Nd_2Fe_{14}B$, and $Y_3Fe_5O_{12}$ show disaccommodation,[12–14] which, however, is limited in certain temperature ranges, because of narrow distributions of the activation energies associated with relaxation processes. Some amorphous ferromagnets exhibit disaccommodation over a wide temperature range,[15] and spikes in the χ' vs T curve may be observed for these materials. In manganites having a high T_C, such as $La_{0.7}Sr_{0.3}MnO_3$, disaccommodation is small because of the dominance of double-exchange interactions over superexchange interactions.[6] Large disaccommodation and hence spikes in the χ' vs T curve are thus expected for lower-T_C manganites, in which double-exchange and superexchange interactions are in competition.

The validity of the above predictions is demonstrated in Fig. 6, where χ' vs T curves are presented for the following materials: (a) $La_{0.7}Sr_{0.3}MnO_3$ ($T_C=365$ K), (b) $Pr_{0.7}Sr_{0.3}MnO_3$ ($T_C=312$ K), (c) $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$ ($T_C=152$ K), and (d) Tb (99.99%, $T_C=229$ K). Spikes, similar to those in Fig. 2, are observed in the χ' vs T curve for $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$,[16] in which T_C is significantly suppressed by partial substitution of much smaller Y ions for La ions, but not for the higher-T_C manganites or Tb, consistent with the predictions.

IV. CONCLUSIONS

A series of asymmetric spikes has been observed in the real part of ac susceptibility (χ') vs temperature (T) curves of the cation-deficient perovskite manganite $LaMnO_{3.075}$. It is shown that the occurrence of spikes, the dependence of the shape of the spikes on the temperature-sweep direction, and the dependence of the interval between spikes on the ac-filed frequency are consistently explained in terms of periodic, spontaneous domain-wall jumps combined with disaccommodation. It is argued that domain-wall jumps by themselves do not result in a discontinuous change in χ'; and therefore that spikes in the χ' vs T curve are observed only for limited classes of materials, such as perovskite manganites having a lower T_C and presumably some amorphous ferromagnets, which exhibit disaccommodation over a wide range of temperature.

This work highlights unique features of perovskite manganites, namely, intrinsically inhomogeneous magnetic and electronic structures and strong coupling between the spin, charge, and orbital degrees of freedom, which we argue are the origin of the weakly temperature dependent disaccommodation, a property not expected in usual crystalline materials, and of the spikes in the χ' vs T curves.

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[11] In the simple case where the potential well is represented by a quadratic function $U(x)=\beta x^2$ ($\beta>0$), the curvature $d^2U(x)/dx^2=2\beta$ and hence χ' are independent of the domain-wall position x. However, as the domain wall is moved far enough from the original equilibrium position by magnetic pressure, χ' will eventually increase because the height of the potential well is finite and $d^2U(x)/dx^2$ starts to decrease at some point.

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[16] Spikes occur much less regularly for $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$ [Fig. 6(c)] than for $LaMnO_{3.075}$ (Fig. 2) probably because the former is less homogeneous on a macroscopic scale. $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$ has three different A-site cations (La, Y, and Ca), while $LaMnO_{3.075}$ has only one (La); accordingly, macroscopic inhomogeneity, extrinsic in origin, is more difficult to eliminate in $La_{0.6}Y_{0.07}Ca_{0.33}MnO_3$ than in $LaMnO_{3.075}$.