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# Phase-segregated glass formation linked to freezing of structural interface motion

P. A. Sharma,[1,*] S. El-Khatib,[2] I. Mihut,[3] J. B. Betts,[3] A. Migliori,[3] S. B. Kim,[4] S. Guha,[4] and S.-W. Cheong[4]
[1]*Department of Material Physics, Sandia National Laboratories, Livermore, California 94551, USA*
[2]*Los Alamos Neutron Science Center, Los Alamos National Laboratory, Los Alamos, New Mexico 87544, USA*
[3]*National High Magnetic Field Laboratory, Los Alamos National Laboratory, Los Alamos, New Mexico 87544, USA*
[4]*Department of Physics and Astronomy and Rutgers Center for Emergent Materials, Rutgers University, Piscataway, New Jersey 08544, USA*

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A potentially new kind of glass transition may exist among phase-separated regions in $La_{0.215}Pr_{0.41}Ca_{3/8}MnO_3$. We have observed a very large damping of ultrasonic waves in the dynamically phase-segregated state of this material. This damping is connected to the motion of structural interfaces at megahertz frequencies, which is a much faster time scale than that of magnetic relaxation effects. At lower temperatures, the dynamics of the phase-separated state freeze at the glass transition. Our observations link the onset of this freezing to a sudden decrease in mobility of interfaces between structurally dissimilar phase-segregated regions.

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## I. INTRODUCTION

"Window glass" is an example of an everyday material that still defies understanding. Despite being a homogeneous and otherwise inert substance, heavily disordered silicon oxide possesses time dependence in its physical properties without any apparent approach to equilibrium on cosmological time scales.[1] How such disordered systems fall out of equilibrium is fundamentally not understood; but interestingly, this glass transition has found analogs in systems with other degrees of freedom. For example, disordered magnetic materials appear to undergo a sort of glass transition with a very similar phenomenology (thus the well-known designation "spin glass").[2] Disordered systems with other unusual degrees of freedom might be more easily studied (e.g., by allowing another more convenient knob with which to turn, as magnetic field is in a spin glass). In this sense, "glass formation" realized with different degrees of freedom is of great interest in understanding disordered systems.

The perovskite manganese oxide $La_{215}Pr_{0.41}Ca_{3/8}MnO_3$ (LPCMO) exhibits many nonequilibrium properties that are reminiscent of a glass yet distinct from known glassy systems.[3–6] Does this system exhibit a glass transition with new degrees of freedom?[3–6] The magnetic properties of LPCMO are similar to a spin or cluster glass. LPCMO displays a frequency-dependent cusp in the magnetic susceptibility as well as an associated change in magnetic relaxation from above to below a well-defined transition temperature ($T_G \sim 30$ K).[3,4] Cooling in zero magnetic field (ZFC) results in a magnetization ($M$) that is substantially reduced compared to field cooling (FC) below $T_G$ (Ref. 5); a phenomenon named thermomagnetic irreversibility. For many years, these observations were interpreted as evidence for a conventional spin or cluster glass ground state in this and related perovskite manganites.

This "magnetic glass"[6] state is not a simple spin or cluster glass because as the glass transition is crossed the ferromagnetic volume fraction of the sample changes markedly and contributes to the magnetic relaxation.[3,4,7] LPCMO is composed of coexisting ferromagnetic metallic (FM) and charge-ordered (CO) insulating regions of up to several microns in size at low $T$.[8,9] The glass transition occurs in the midst of this FM/CO phase segregation. Magnetic force microscopy observations show that as $T_G$ is crossed, the FM volume fraction changes,[6] a conclusion also supported by the percolation-dominated $T$-dependent resistivity ($\rho$) (Ref. 4) above and below $T_G$. In the spin or cluster glass picture, individual spins or large clusters of spins freeze in their orientation without exhibiting any long-range order. In LPCMO, in addition to the possible freezing of the spin orientation of individual FM regions, the FM volume fraction also changes as $T_G$ is crossed at fixed $H$. Relaxation of the magnetic moment is due predominantly to time-dependent changes in the FM volume fraction, with some contribution from domain reorientation and coarsening within FM regions.[4] As the magnetic relaxation drops markedly in the glass phase, phase separation has been termed "dynamic" above and "static" below $T_G$.[3] The thermomagnetic irreversibility also has a contribution from the $T$-dependent changes in FM volume fraction associated with the glass transition. The large change in FM volume fraction that accompanies freezing is what distinguishes this and many other materials that share the same phenomenology[6,10,11] from spin and/or cluster glasses. However, a precise idea of what is "freezing" that is also associated with changes in the FM volume fraction has not been provided. In order to establish this phenomenon as a new kind of glass transition and to provide a step toward understanding the mechanism of freezing, the answer to this question must be provided.

In the present work, we experimentally link this unusual glass formation in LPCMO to the dynamics of interfaces between coexisting phases using resonant ultrasound spectroscopy (RUS). The RUS technique is a way of measuring the elastic constants and the attenuation of ultrasound (internal friction) in the megahertz regime.[12] The internal friction is highly dependent upon the static and dynamic microstructures of a sample. We are able to systematically associate the internal friction with structural interface motion. The internal friction becomes large in the region of dynamic phase segre-

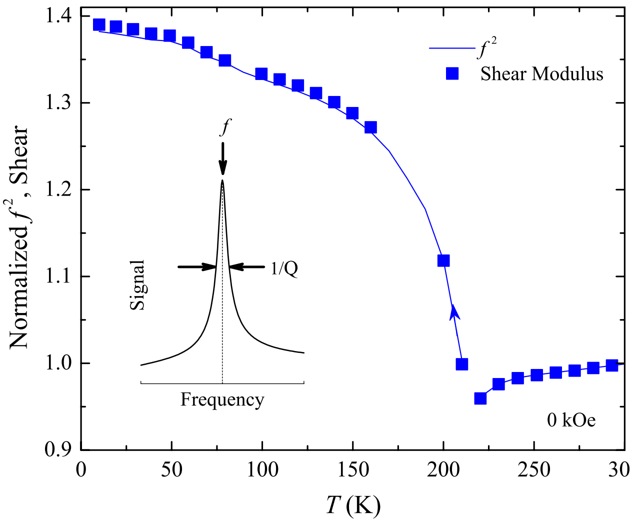

FIG. 1. (Color online) The quantity $f^2$ closely tracks the shear modulus, which was fit using the entire RUS spectrum. In this work, $f^2$ is considered to be proportional to the shear modulus. The definition of $1/Q$ and $f$ are shown in the inset.

gation while suddenly decreasing in the frozen phase-separated state. The most important finding of this work is that the drop in internal friction at $T_G$ can be linked to a drop in the motion of structural interfaces. The time scale for structural interface motion ($1/\text{MHz} \sim \mu\text{s}$) is widely separated from that of magnetic relaxation effects. It is proposed that these observations support the idea that structural interface motion constitutes a new degree of freedom undergoing a glass transition. The shear modulus also appears to track nonequilibrium properties observed in $M$ measurements.[5] If freezing of interface motion underlies this unusual glass transition, a mechanism for freezing based on elastic interactions could be proposed.

## II. RESONANT ULTRASOUND SPECTROSCOPY

RUS is used to extract the elastic moduli and ultrasonic attenuation of a material by measuring its mechanical resonant frequencies ($f$=0.2–2 MHz in our experiments), the mass density, and dimensions of a parallelepiped-shaped sample.[12] The LPCMO sample under study was polycrystalline,[13] and the lack of preferred grain orientation allows us to describe the elasticity of the sample in terms of constants $c_{11}$ and $c_{44}$ (a shear modulus) only. More than 20 resonances were collected at each $T$ so as to produce a fit to the $c_{11}$ and $c_{44}$ elastic constants at 0 kOe.[14] A great majority of resonances are associated with more than 85% shear, typical of RUS. This fact allows us to take detailed measurements of certain resonance frequencies dominated by the shear without the need of a lengthy fitting process. The resonances shown in this work are all composed of more than 90% shear and should be understood to be directly proportional to the shear modulus according to the relation $f^2 \sim c_{44}$.[12]

We display the correspondence between $f^2$ and $c_{44}$ in Fig. 1 where the shear modulus and the resonance are compared, each normalized at 300 K. It is clear that $f^2$ faithfully reproduces the $T$ dependence of the fitted $c_{44}$ over the entire $T$ range of interest for our work.[15] The ultrasonic attenuation or internal friction at each $f$ is given by $1/Q = \Delta f/f$, where $\Delta f$ is the width at half maximum of a resonance (Fig. 1 inset). Since the physical properties of LPCMO are highly $T$ and $H$ dependents, we recorded the RUS spectrum from 5–300 K and 0–50 kOe. $\rho(T)$ and $M(T)$ measurements from a specimen of the same batch were compared to the RUS measurements in the same $T$ and $H$ ranges and under the same cooling ($C$) and warming ($W$) conditions. In addition, the sample was measured under consistent $H$ treatment conditions, in particular cooling under zero field (ZFC) and cooling in $H$ (FC). For example, ZFC-$W$ at 10 kOe means that the sample was cooled down to ~5 K in 0 kOe, then subjected to 10 kOe, and finally measured as a function of increasing $T$.

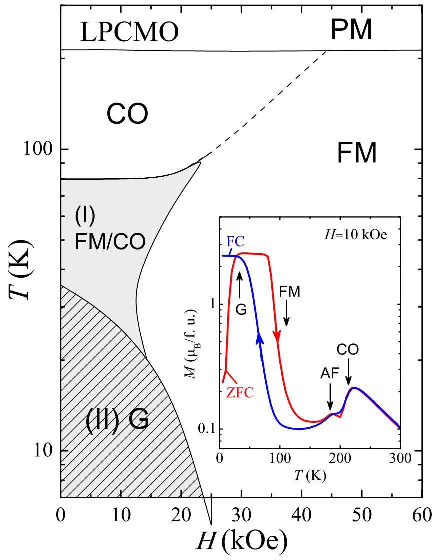

FIG. 2. (Color online) The magnetic phase diagram of LPCMO indicates the $T$ and $H$ regimes of phase separation into FM/CO regions and $g$ formation. The boundaries were drawn with a combination of $\rho(T)$ and $M(T)$ measurements taken at fixed $H$ under ZFC-W conditions. There are two regions of phase separation: (i) dynamic and (II) static; the latter corresponding to the glass state. (Inset) One pronounced signature of the glass transition is the thermomagnetic irreversibility ($M_{\text{FC}} > M_{\text{ZFC}}$) below $T_G$.

## III. EXPERIMENTAL RESULTS

The glass transition temperature and the phase-separation regime are both highly $T$ and $H$ dependent in LPCMO, as outlined schematically in the magnetic phase diagram (Fig. 2). The phase boundaries were defined using a combination of $M(T)$ and $\rho(T)$ measurements taken upon warming at various fixed $H$ under ZFC conditions.[5] An $M(T)$ curve recorded at 10 kOe displays all the phase transitions that are observed in this sample (Fig. 2 inset). CO sets in at ~210 K from a high $T$ paramagnetic (PM) state indicated by a dip in $M(T)$. Further cooling the sample leads to an antiferromagnetic transition (~190 K). At still lower $T$, a rise in $M(T)$ signals the formation of FM regions. $T_{\text{FM}}$ is hysteretic in a wide $T$ range being nearly 40 K lower for cooling versus heating and thus indicating the first-order nature of the FM/CO phase transition.

At $H<25$ kOe, this FM state is significantly inhomogeneous.[8,9] The microstructure of the phase-separated state indicated in Fig. 2 consists of large micron scale CO and FM regions.[9] The FM regions are metallic, while the CO regions are insulating. The CO and FM phases are both formally orthorhombic but have different lattice parameters. The most important structural difference is that the CO phase has a higher tetragonality ($c<b\sim a$) than the pseudocubic ($c\sim b\sim a$) FM phase. The phase-separated state described here is therefore electrically, magnetically, and structurally heterogeneous. At ~30 K, $T_G$ is characterized by the appearance of thermomagnetic irreversibility ($M_{\text{ZFC}}<M_{\text{FC}}$; inset of Fig. 2) within the phase-separated state.[16] The phase-separated state shown in Fig. 2 extends from the appearance of FM down to at least the lowest $T$ measured (5 K). This type of large-scale phase separation always occurs in manganites close to a first-order metal-insulator/structural transition in the presence of disorder.

There are two regimes of phase separation: (I) $T_G<T<T_{\text{FM}}$ and (II) $T<T_G$ (labeled accordingly in Fig. 2). Both regimes vanish at high enough $H$, at which point the sample is a homogeneous FM. Region (I) is dynamic in that the relative CO/FM fractions are highly time dependent, while in region (II) this relaxation becomes much slower.[3] The transition from (I) to (II) defines $T_G$. Our RUS experiments show that the internal friction is large in the dynamic phase-separated region and then becomes sharply reduced in the static phase-separated region. We also show that certain nonequilibrium features observed in $M(T)$ experiments associated with the metastability of the FM volume fraction are also reflected by changes in the shear modulus.

The elasticity and internal friction correlate with the transport and magnetic signatures of phase transitions in LPCMO (Fig. 3). The CO transition is indicated by an upturn in the resistivity ($\rho$) and a kink in $M(T)$. A representative ultrasonic resonance ($f^2$) exhibits a clear dip at the CO transition ($H=0$ kOe) accompanied by a peak in $1/Q$. This resonance also appears to exhibit a kink at the FM $T_C$ although this feature is relatively weak such that the cooling/warming hysteresis evident in $M(T)$ and $\rho(T)$ is less pronounced in $f^2(T)$. The drop in the absolute value of $\rho(T)$ and the fact that $d\rho/dT>0$ signifies the metallic nature of the FM state. A dip in $f^2(T)$ and a sharp peak in $1/Q(T)$ are expected at structural transitions, notably those exhibiting phonon mode softening. A diffusionless structural phase transition separates the PM and CO phases as well as the CO and FM phases.

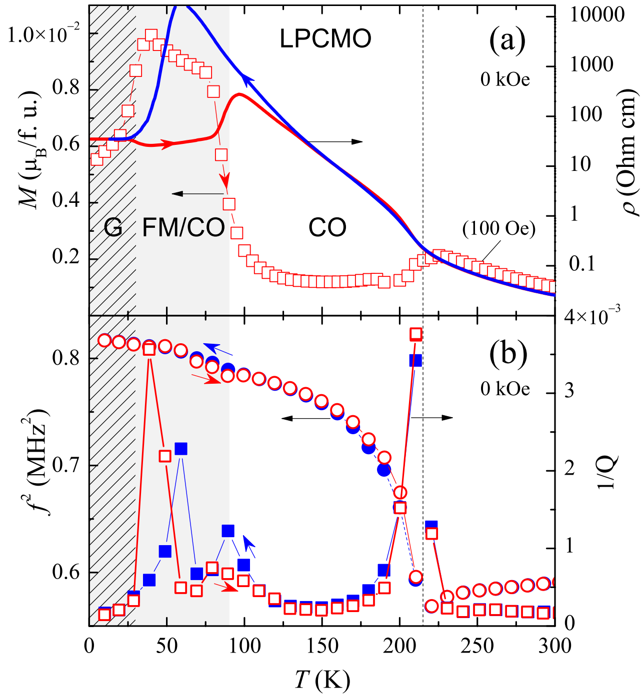

FIG. 3. (Color online) (a) $\rho(T)$ at 0 kOe and $M(T)$ at 100 Oe. (b) Elastic properties at 0 kOe for both heating and cooling. The left scale shows a representative ultrasound resonance ($f^2$), while the right scale shows the corresponding internal friction ($1/Q$) for this resonance. Upon the appearance of FM regions, indicated by a rise in $M(T)$ and a drop in $\rho(T)$ at ~90 K, $Q^{-1}$ rises to large values. As the sample is cooled toward and through the glass transition (~30 K), $1/Q$ drops, reaching nearly the 300 K value.

$1/Q$ changes in an unusual way at low $T$ that is associated with the phase-separated state [Fig. 3(b)]. Instead of exhibiting a sharp peak at the appearance of FM, as is the case for the CO transition, $1/Q$ is large in a wide $T$ range that closely matches the phase-segregated region of the phase diagram for $T_G<T<T_{\text{FM}}$ at $H=0$ kOe. Large "spikes" in the $1/Q$ values occurred only in the phase-separated regime above $T_G$ and were highly variable. However, the broad $T$ dependence of $1/Q$ was always observed from run to run as well as being $f$ independent. $1/Q$ starts to increase at ~125 K, at a somewhat higher $T$ than the features in bulk $\rho(T)$ and $M(T)$ measurements. In addition, $1/Q$ lacks the cooling/warming hysteresis observed in $\rho(T)$ and $M(T)$. The increase in $1/Q$ at ~130 K could be due to the appearance of small FM regions. FM transitions have been observed in LPCMO as high as ~150 K depending upon sample preparation conditions.[17] The presence of small FM regions would not be obvious in the low $H$ $\rho(T)$ and $M(T)$ data. Therefore, the large increase in $1/Q(T)$ at low $T$ is closely related to the appearance of FM/CO phase separation in LPCMO at 0 kOe.

Upon entering the phase-separated glass transition regime, $1/Q$ gradually decreases but then falls abruptly at $T_G\sim30$ K. Figure 3(b) shows the initial decrease in $1/Q$ as the glass regime is approached, and a closer scan around $T_G$ reveals that the internal friction suddenly drops (Fig. 4) at the glass transition where $T_G$ is defined by $M(T)$ and $\rho(T)$ measurements. This sudden drop in $1/Q$ is reversible upon cooling and heating, consistent with the $M(T)$ and $\rho(T)$ signatures of $T_G$. The ~5 K value of $1/Q$ is very nearly that of the sample at 300 K, above the phase-separation regime. Unlike $1/Q$, a very subtle change in the shear modulus is observed, but it is noteworthy that the modulus stiffens upon entering the glass state and also displays no cooling/warming hysteresis consistent with $M(T)$ and $\rho(T)$. In some cases, this weak feature in $f^2(T)$ was slightly broadened for different resonances. The abrupt drop of $1/Q$ at $T_G\sim30$ K occurred for all frequencies measured.

Features in the internal friction and elasticity track the presence of phase separation as a function of $H$ in addition to

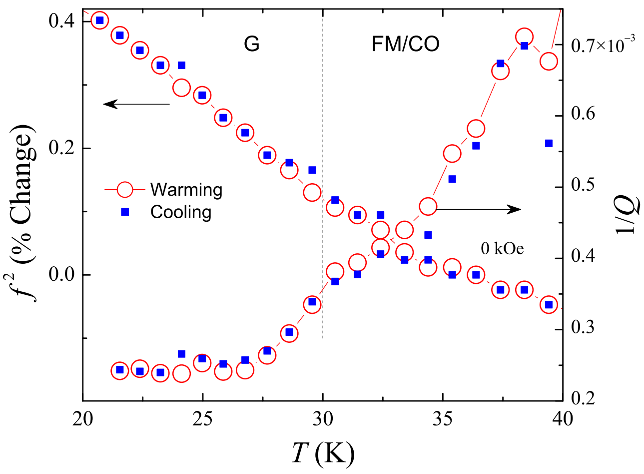

FIG. 4. (Color online) $f^2$ and $1/Q$ show fine-scale features at the ~30 K glass transition $T$ in 0 kOe. $f^2$ displays a very subtle increase at $T_G$, but $1/Q$ exhibits a clear and noticeable drop.

$T$. In Fig. 5, we repeat our experiments upon various field-cooling conditions at 10 kOe. The quantity $f^2$ [Fig. 5(a)] tracks $M(T)$ measured under the same conditions. The different $T$ regimes of phase separation are similar to those in 0 kOe, but a larger FM volume fraction exists in the sample at 10 kOe. At $T_{\mathrm{FM}}$, the shear modulus appears to dip more noticeably at features in $M(T)$ upon both cooling and warming, in contrast to the weak features at 0 kOe. At $T_G$, a pronounced FC/ZFC thermomagnetic irreversibility appears in $f^2(T)$, consistent with $M(T)$. In LPCMO, $M_{\mathrm{FC}} > M_{\mathrm{ZFC}}$ indicates that FC conditions result in a larger FM volume fraction in the sample. The FC shear appears to be smaller than that for ZFC at the lowest $T$ measured: $f^2_{\mathrm{FC}} < f^2_{\mathrm{ZFC}}$. $1/Q$ at 10 kOe [Fig. 5(b)] shows the same general features as the 0 kOe data in Fig. 3(b). A high $1/Q$ value appears in the phase-separated regime ($T > T_G$ and $H=10$ kOe) and does not possess the $T$ hysteresis seen in $f^2(T)$ or $M(T)$. Upon entering the glass transition phase-separated regime, $1/Q$ undergoes a sudden drop at ~30 K, consistent with the magnetic phase diagram (Fig. 2). The shear modulus exhibits a more pronounced increase at $T_G$ for 10 kOe compared to 0 kOe. Features in $1/Q$ and $f^2$ are significantly broadened in $H$ at $T_G$.

The presence of phase separation can be progressively removed with $H$ so that the concurrent disappearance of the low $T$ hump in $1/Q(T)$ with increasing $H$ unambiguously links a large internal friction with the dynamic phase-segregated state. Figure 6(a) displays $1/Q(T)$ at various fixed $H$. The values of $1/Q$ displayed have been averaged over 20 frequencies across the entire RUS spectrum for each $T$. The magnitude of the hump in $1/Q(T)$ is largest at 0 kOe and then progressively decreases in magnitude. In addition, $1/Q$ becomes much less $T$ dependent at higher $H$. At 50 kOe, a nearly featureless $1/Q(T)$ is observed. $M$(5 K) yields the full Mn ordered moment expected from the stoichiometry at $H=50$ kOe. As $H$ is increased and the sample becomes more homogeneous, this peak in $1/Q(T)$ is lost.

While $1/Q$ is very sensitive to the dynamic phase-separated regime, the shear modulus is sensitive to nonequilibrium changes in the FM volume fraction. One of the unique features of metastability[3] due to the glass state in LPCMO is that $T$-cycling the sample above and below $T_G$ creates progressively more FM regions that can be tracked using $M(T)$ measurements. This effect occurs because the magnetic relaxation rate peaks sharply near $T_G$.[3] $M$ increases as a function of time so that a peak in relaxation leads to an increase in the FM volume fraction of the phase-segregated state. The magnetic relaxation should not change appreciably upon repeated $T$ cycling, but the FM volume fraction will continuously increase. Therefore, this procedure allows us to separate out the effects of magnetic relaxation versus a change in FM volume fraction on the elastic properties.

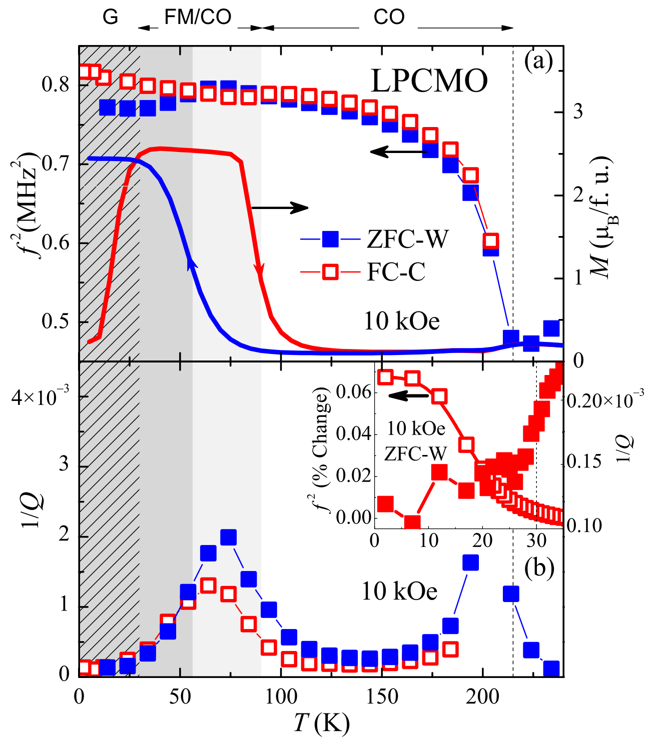

FIG. 5. (Color online) (a) $M(T)$ compared to $f^2(T)$ at 10 kOe. $f^2$ appears to decrease at the FM transition signaled by the increase in $M$ for both heating and cooling. The thermomagnetic irreversibility in $M$ is partly reflected in the $f^2$ data. (b) $1/Q(T)$ is large in the high-temperature phase-separated regime (Fig. 2) and does not display a large hysteresis. $1/Q$ is always lowered in the phase-segregated glass regime. Inset: $f^2$ and $1/Q$ show fine-scale features at ~30 K in 10 kOe. $f^2$ increases more noticeably at $T_G$ in higher $H$ but is significantly broadened. The decrease in $1/Q$ in the glass state is evident but also broadened in $H$. The elasticity measurements agree with the magnetic phase diagram in Fig. 2.

As seen in Fig. 6(a), we carried out the aforementioned procedure by performing a FC in 19 kOe to 4 K, then measuring the sample upon warming to ~50 K, and cooling down again. $T$ cycling above and below the glass transition in the presence of $H$ reduces the $T$ dependence and magnitude of $f^2$. This $T$-cycled 19 kOe $f^2(T)$ nearly approaches that of the 50 kOe state, which is completely homogeneous. An increased FM volume fraction appears to be associated with a smaller $T$ dependence and magnitude of the shear modulus; a conclusion also supported by both the dip in $f^2(T)$ at $T_{\mathrm{FM}}$ at 10 kOe and the thermomagnetic irreversibility of the shear [Fig. 5(a)]. Unlike the shear, $1/Q$ does not change with $T$

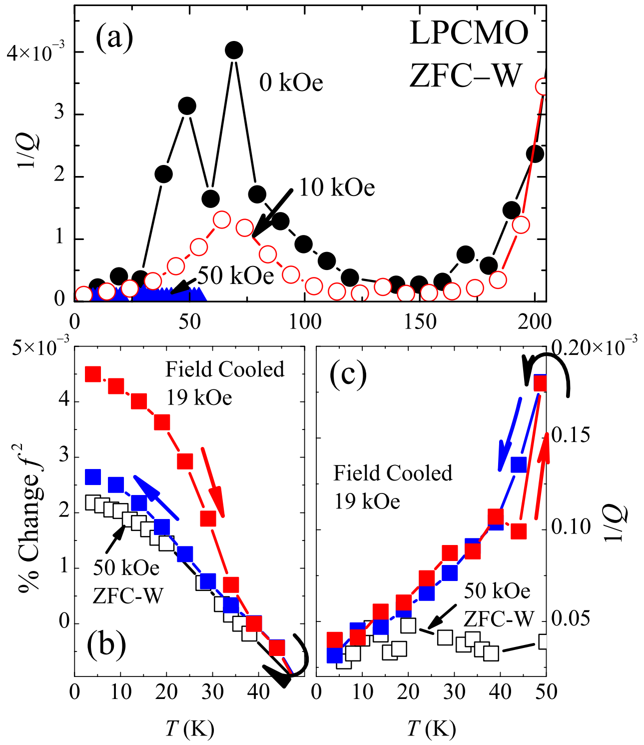

FIG. 6. (Color online) (a) The low $T$ "hump" in $1/Q$, which corresponds to the dynamic phase-separated regime, is progressively reduced with increasing $H$. In the 50 kOe homogeneous FM state, $1/Q$ is small and nearly $T$ independent. (b) At a fixed $H = 19$ kOe, repeated cycling of the sample $T$ above the glass transition (up to 50 K) results in an $f^2(T)$ (normalized to 40 K) approaching that of the (fully homogeneous) ZFC 50 kOe FM state. A $T$ cycling of the sample in this way has been shown to induce a larger fraction of FM domains (Refs. 3 and 6). $1/Q$ is insensitive to $T$ cycling at 19 kOe but disappears in the homogeneous 50 kOe state.

cycling [Fig. 6(b)] and possesses no thermomagnetic irreversibility [Fig. 5(b)]. Thus, the internal friction does not seem to depend on the absolute FM volume fraction and is most sensitive to the presence or absence of dynamic phase separation.

## IV. INTERNAL FRICTION LINKED TO DYNAMIC PHASE SEPARATION

Our experiments show that the internal friction displays a large magnitude and $T$ dependence in the dynamically phase-segregated state, which suddenly falls at the glass transition. According to Figs. 3(b) and 5(b), $1/Q$ takes on relatively small values ($\sim 10^{-4}$) in the room $T$, homogeneous state of this system. The appearance of the dynamic FM/CO phase-separated state at low $T$ results in an order of magnitude larger $1/Q$ ($\sim 10^{-3}$). As $T$ is lowered further, $1/Q$ gradually decreases but undergoes an abrupt drop at the glass transition as it is defined by $M(T)$ and $\rho(T)$ measurements. As a function of increasing $H$, $1/Q$ progressively decreases in a fixed $T$ range as the sample becomes more homogeneous [Fig. 5(a)]. The drop in $1/Q$ at $T_G$ is observable at intermediate $H$ although somewhat broadened [Fig. 5(b) inset]. Judging from the lack of thermomagnetic irreversibility [e.g., Fig. 5(b)] and metastability near $T_G$ [Fig. 6(c)], $1/Q$ does not depend on the absolute FM volume fraction. As a function of $T$ and $H$, a large $1/Q$ is linked to the fluctuating nature of the dynamic phase-segregated state.

## V. INTERNAL FRICTION LINKED TO STRUCTURAL INTERFACE MOTION

The "loss" or internal friction $1/Q$ reveals sources of energy dissipation due to defects in materials: a mobile defect will move with the application of stress and cause a time delay between applied stress and the strain, manifested by the width of an RUS peak and may also result in a lower shear modulus. The motion of a defect at the time scale of a resonant frequency will cause attenuation of ultrasound at that frequency. There are also intrinsic sources for $1/Q$. Our goal is to identify the source of the large "hump" in $1/Q(T)$ that is linked to the presence of dynamic phase separation.

Our measurements as a function of $T$ and $H$ allow us to eliminate many potential contributions to $1/Q$. Intrinsic (i.e., unrelated to defects) sources for the internal friction hump can be eliminated since $1/Q$ is an order of magnitude smaller and $T$ independent in the homogeneous regions of the magnetic phase diagram. If there were a large intrinsic internal friction in the FM phase (e.g., from the interaction of ultrasonic waves with conduction electrons or spin waves), then $1/Q$ would not only be potentially large at 50 kOe but also would scale with the FM volume fraction, both of which are contrary to our observations. The homogeneous CO phase has a fairly small internal friction in the absence of FM regions, as judged from $1/Q(T)$ [Fig. 3(b)].

Several sources of extrinsic defect-induced internal friction can also be eliminated based on our experimental observations. The dynamically phase-segregated $1/Q(T)$ signature is unusual in that it is largely $f$ independent (in the megahertz range of our experiments) and occurs at low $T$. Grain boundaries, point defects, and other sorts of static imperfections are effectively quenched and immobile in this $T$ range (30–100 K) and have only been observed to contribute to the internal friction near and above room $T$.[18] More exotic point defects with an internal degrees of freedom (such as a two-level system) might have a low $T$ response but possess a highly specific $f$-dependent $1/Q$ in the measured range,[18] which we do not observe. Since the presence and dynamics of quenched defects should not be affected appreciably by $H$, these sources of $1/Q$ are also unexpected from the $H$ dependence of the internal friction. Orthorhombic twin boundaries can scatter ultrasound in a wide $T$ and $f$ ranges; however, the magnetically homogeneous yet potentially twinned CO and FM orthorhombic phases each possesses a small $1/Q$, probably as a result of pinning via grain boundaries.

The source of the large internal friction in the dynamically phase-segregated state can be linked to a very specific kind of defect: the structural interface between the pseudotetragonal CO and pseudocubic FM regions of the sample. The first-order structural transition separating the CO and FM phases is diffusionless as the high- and low-temperature structures are simply related by a shear distortion. Such a structural transition, also known as a martensitic transition, leads to phase coexistence in the hysteretic $T$ regime of supercooling and heating. Interfaces between structurally dissimilar phases produced during the martensitic transformation are known to be highly mobile and lead to a large $1/Q$.[19,20] The internal friction of mobile structural interfaces in martensites does not possess a systematic $f$ dependence and is often $f$ independent.[21] The existence of mobile interfaces is consistent with the observation that phase segregation is dynamic in LPCMO.[3] The hysteretic martensitic transition has already been suggested as the origin of the large-scale phase-separated state in certain manganites.[22] Systematically reducing the phase coexistence through applied $H$ leads to a smaller loss so that mobile structural interfaces are thus a natural explanation for the broad feature in $1/Q(T)$, as exemplified in Fig. 1(b).

The fact that the internal friction occurs in the megahertz range and is also $f$ independent is meaningful. The time scale associated with interface motion must be on the order of microseconds consistent with the high mobility of martensitic interfaces.[19] While glass transitions are often associated with $f$-dependent behavior, this is observed (e.g., in the magnetic relaxation) at a much lower-frequency range ($\sim 1$ Hz) in LPCMO so it is not unexpected that there are no relaxational effects in the internal friction in the megahertz range. Thus, the time scale for fluctuating interfaces is widely separated from the relaxation behavior associated with the glass transition. Relaxation times in spin glasses, for example, are associated with the size of fluctuating correlated collections of electron spins that are widely separated from the very fast fluctuation of individual spins. The microsecond time scale could make the observation of interface motion very difficult with conventional microscopies. Nevertheless, we have identified a separate important time scale in LPCMO that is independent of previously studied relaxation phenomena, which could be interpreted as evidence that interface motion is a new degree of freedom that can undergo freezing.

## VI. DISCUSSION

The glass transition in LPCMO is considered unusual and potentially "new" because the FM volume fraction is time dependent and changes appreciably as $T_G$ is traversed. Therefore, the glass transition cannot only be associated with the freezing of spin orientations as in a spin and/or cluster glass. This conclusion then leads to the question of what degree of freedom is freezing. Our RUS experiments link a large internal friction to fluctuating structural interfaces. While interface motion is a necessary implication from the relaxation of the magnetic volume fraction, the experimental observations establish that this relaxation scatters ultrasound and occurs in the megahertz frequency range. The internal friction and thus structural interface motion continuously decreases and then abruptly drops on approach to and at $T_G$. The time scale for the interface motion is in the microsecond range and is distinct from the time scale for relaxation of the relative FM/CO volume fraction. We propose that this observation means that structural interfaces comprise the degrees of freedom that freeze at this unusual glass transition.

The set of materials that display this unusual glass transition have been classified as possessing a strongly hysteretic first-order magnetostructural transition in the presence of quenched disorder,[5] but a mechanism for freezing has not been formulated. A first-order transition can exhibit a large hysteresis, i.e., the phase transition $T$ is larger for heating than cooling, which can be further broadened in the presence of disorder.[23] This hysteresis is controlled, in part, by the nucleation and growth of new domains. A new sort of "glass" may then be realized by presupposing that there is a sudden arrest in domain formation kinetics[6] at $T_G$. Such a scenario would explain a change in volume fraction as a glass transition is traversed. LPCMO is not unique in exhibiting this glass transition; there are many other magnetic materials that exhibit the same phenomenology.[6,10,11] All of the materials that are suspected to exhibit this unusual glass formation fall within the classification of undergoing a widely hysteretic first-order magnetostructural transition in the presence of quenched disorder. Nevertheless, this successful classification must introduce a freezing mechanism in an *ad hoc* fashion and also does not explicitly imply what degrees of freedom could be freezing.

Changes in magnetic volume fraction at a glass transition are not easily understood in terms of magnetic interactions. The FM exchange interaction lowers the free energy of the FM as opposed to the CO phase in LPCMO at low $T$. This free-energy difference should become gradually more pronounced at still lower $T$; however, it does not lead to glassiness. Since the magnetic relaxation above $T_G$ is associated with a change in the magnetic volume fraction, one cannot invoke a spin-glass freezing independently superimposed on free-energy driven $T$-dependent changes in the FM volume fraction in order to explain the phenomenology of this transition.

The freezing of structural interfaces is an appealing idea with which to further understand this potentially new glass transition in contrast to electron spin. The motion of a structural interface necessarily implies the change in relative volume fraction of each coexisting region. Nonequilibrium glasslike changes in the FM volume fraction, such as relaxation, can be attributed to nonequilibrium changes in regions with different structures. Importantly, by viewing the glass transition as being driven by the freezing of structural interfaces, one can invoke elastic strain as a mechanism for freezing.

Competing elastic interactions can lead to a very complex free-energy landscape that is a necessary ingredient for a glass transition,[24] especially in the presence of quenched disorder. An interface between structurally dissimilar regions necessarily implies an energy barrier that originates from elastic strain. The motion of a structural interface is controlled by the free-energy difference between the CO and FM phases, an elastic energy that results from the different lattice parameters in each phase, and interfacial friction. The mobility of interfaces generated during a martensitic structural transition is particularly high.[18,19] Interfaces interact elastically[25] so that an analogy between the magnetically mediated freezing process in a spin glass or the freezing in structural glass and the present case might be formulated. While many different experiments suggest[3–7,26] that there is a complex free-energy landscape in LPCMO, our results support the idea that elastic strain interactions among interfaces is a reasonable place to begin understanding this complexity. If such energy barriers can be shown to take on a cooperative character—another ingredient of a glass transition—the phenomenon described here may yield a truly new example of glass formation that is mediated by martensitic accommodation strain that ought to apply to a wide range of materials.

This potential mechanism for glass formation is not fundamentally magnetic in nature. The compounds studied to date involve a first-order magnetostructural transition into a FM state, the evolution of which is easy to detect with a magnetometer. Perhaps this glass transition can be realized solely in terms of a first-order structural phase transition, possibly in the presence of disorder. Traditional heavily disordered martensitic alloys (such as the shape memory alloys) share the same characteristics described for LPCMO (Ref. 20) and do not always possess a magnetic phase. There is evidence that a glass transition occurs in the shape memory alloy NiTi (Ref. 27) that is not associated with the freezing of atomic positions. Spin-glass models have previously been applied in order to understand the shape memory effect.[28] Nevertheless, it remains to be seen under what circumstances this glass transition among structural regions can occur given a first-order transition in the presence of quenched chemical disorder.

In summary, measurements of the internal friction in LPCMO link the dynamic phase-segregated state with the presence of fluctuating structural interfaces. Following this interpretation, the glass transition can be associated with a sudden drop in interface motion. Interfaces fluctuate in the megahertz regime, which is widely separated from the time scale for magnetic relaxation. These observations allow us to suggest that structural interfaces are the degrees of freedom that freeze at the transition, in analogy to spins in a spin glass or atomic positions in a structural glass. Interactions among structural interfaces are mediated by elastic strain, which might provide a useful way to formulate this phenomenon as a new glass transition.

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[*] Author to whom correspondence should be addressed: pasharm@sandia.gov

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[14] At 300 K, the shear, bulk, and Young modulus are 51.8, 131.5, and 137.3 GPa, respectively. The Poisson ratio was found to be ~0.326.

[15] We have chosen a few different frequencies with which to display the data in order to faithfully sample the entire RUS spectrum for the reader.

[16] The magnetocrystalline anisotropy of the FM state is very small [see, e.g., L. Ghivelder, R. S. Freitas, M. G. das Virgens, M. A. Continentino, H. Martinho, L. Granja, M. Quintero, G. Leyva, P. Levy, and F. Parisi, Phys. Rev. B **69**, 214414 (2004)] in the FM state of LPCMO so that it does not contribute to the observed thermomagnetic irreversibility.

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