Low-Temperature Glassy Response of Ultrathin Manganite Films to Electric and Magnetic Fields

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The glassy response of thin films of La$_{0.8}$Ca$_{0.2}$MnO$_3$ to external magnetic and gated electrostatic fields in a field-effect geometry has been studied at low temperatures. A hierarchical response with irreversible memory effects, non-ergodic time evolution, aging and annealing behavior of the resistance suggest that the dynamics are governed by strain relaxation for both electronic and magnetic perturbations. Cross-coupling of charge, spin and strain have been exploited to tune the coercivity of an ultrathin manganite film by electrostatic gating.

Manganites, known for their ‘colossal’ magnetoresistance (CMR), possess a diversity of phases driven by correlations between the spin, charge and orbital degrees of freedom of the electrons and their strong coupling to the lattice [1]. Localized electrons on Mn$^{3+}$ sites create large lattice distortions via the Jahn-Teller effect, causing strong strain fields to develop [2]. When these electrons are delocalized, for example by the double exchange mechanism between aligned Mn core spins, the local strain is relieved. Under appropriate circumstances, manganites have an admixture of phases of very different electronic, magnetic and structural properties, but nearly equal free energies [3]. Consequently, the properties of these systems may be strongly susceptible to external perturbations that lead to phase conversion within the admixture [4], giving rise to ‘colossal’ effects. The presence of competing strain fields, Coulomb interactions, magnetic correlations and defects may frustrate this process, giving rise to a complex free energy landscape with many nearly degenerate minima and hierarchical barriers. This naturally gives rise to glass like dynamics [5,6], at low temperatures. Our understanding of the response of such a system to external forces is complicated by the cross-couplings between the different degrees of freedom. However, if the hierarchy of barriers being crossed can be attributed to just one degree of freedom (e.g. spin or strain), then that ‘rate limiting’ property governs the dynamics on large time scales, simplifying the analysis. Conversely, cross-couplings present the opportunity to influence one kind of order with a force that couples to a different variable.

In this letter we investigate the response of ultrathin films of La$_{0.8}$Ca$_{0.2}$MnO$_3$ (LCMO) to electric and magnetic fields. This composition is close to the phase boundary between a ferromagnetic metal (FM) at higher Ca doping and a ferromagnetic charge ordered insulator (FCOI) at lower doping. Bulk single crystals of similar composition are believed to exist in a mixed phase with co-existing regions of insulating and metallic properties [7], with the transport properties at low temperatures arising from percolation of metallic regions. The samples are typically 21 u.c ($\sim$82Å) thick films of La$_{0.8}$Ca$_{0.2}$MnO$_3$ grown using ozone-assisted molecular beam epitaxy on surface treated SrTiO$_3$(STO) substrates locally thinned to 35-50µm [8], permitting a field-effect geometry. A Pt electrode (1000Å thick) on the back of this thinned region serves as the gate. The manganite film is patterned into a wire 100µm wide, with tabs for carrying out four terminal measurements, which were performed using standard DC techniques. The gate-drain current was always monitored, and remained below 0.6nA, while the source-drain measurement current was 100nA.

We observe a magnetic transition at about 150K, and an accompanying resistive transition, from an activated insulating state to a nominally metallic state near the Curie temperature, along with CMR [Fig.1]. However, at the lowest temperatures ($<36K$) there is a reentrant insulating phase [9]. Near the resulting minimum, the resistance has a large susceptibility to gate and magnetic fields. We observe clear signatures of hierarchical energy barriers, glassy dynamics and aging in the response. We argue that the dynamics are governed by structural relaxation. Cross-coupling has been exploited to effect a measurable change in the magnetic coercivity of a sample upon application of a gate electric field.

The details of the gate effect at low temperatures will be discussed elsewhere [10]. For the present purpose, it suffices to note that the gate electric field couples to the charge degrees of freedom, while the magnetic field couples to spin. The applied gate voltage is always negative, inducing ‘hole’ like charge carriers. The electrostriction in STO at low temperatures is known to saturate at electric fields of approximately 15kV/cm [8], well below 85kV/cm, the maximum field applied here. Thus, the effects that we observe are not due to biaxial substrate strain.

Within a mixed phase scenario, measurements of resistance are particularly sensitive to changes in the percolative metallic path. Upon applying an external field that favors the growth of one phase with respect to the other, the change in resistance depends on the motion of domain boundaries separating the two. In this context,
the presence of hierarchical energy barriers was graphically demonstrated [11] in resistivity measurements of \textit{La}_{0.5}\textit{Ca}_{0.5}\textit{Mn}_{0.95}\textit{Fe}_{0.05}\textit{O}_3. We have measured a similar hierarchical response to both applied electric and magnetic fields at 30K. A succession of external magnetic/gate electric field pulses of different values and duration were turned on and off for times of 0.5-1.5hr and 1hr, respectively. When a field was turned on, the resistance decreased to a value \( R_{ON} \), with a large ‘fast’ change and a smaller ‘slow’ part of that evolved with a logarithmic dependence on time. On turning off the field, the resistance relaxed to an intermediate value \( R_{TR} \) (thermo-remnant resistance), indicating that the sample resistance undergoes an irreversible change, analogous to thermo-remnant magnetization in spin glasses [12]. On subsequent pulses, if the value of the field exceeded that of the maximum field previously applied, \( R_{TR} \) decreased further, but otherwise the response was reversible and \( R_{TR} \) did not change [Fig.2(a,b)]. Thus, the \( R_{TR} \) has memory of the previous highest field applied. Furthermore, the \( R_{TR} \) does not discriminate between the application of an electric or magnetic field. This was demonstrated by first turning on a large gate electric field, turning it off, and then applying a series of increasing magnetic field pulses [Fig.2(c)]. The hierarchy of barriers for the lowering of resistance due to an applied magnetic field seems to ‘respect’ the barriers already crossed by application of the gate electric field, regardless that they couple to spin and charge respectively.

We interpret the hierarchical barriers in terms of the dynamics of pinned domain walls that separate the insulating and metallic regimes. The mutual equivalence of barriers can be explained if they are primarily due to strain in the insulating patches. Competing strain fields can cause frustration and pinning of the domain walls [13]. On application of an external force, pinning sites up to a certain threshold are overcome and the walls move irreversibly. The strain field acquires a new configuration and can now relax in a reversible manner in response to external forces until a pinning site of the next higher strength is encountered. A greater external force is required to bring about the next irreversible change. If the hierarchy of pinning is determined by the strain fields alone, it does not matter that the force is applied via aligning spins or inducing charge at the domain walls since they cross-couple to the same strain field.

We also observe thermally assisted crossing of hierarchical barriers, or ‘annealing’. Upon warming the film from the lowest temperature up a temperature \( T_{anneal} \), with the gate/magnetic field on, and cooling back down, the resistance of the film changes irreversibly. On subsequent thermal cycles, the resistance varies reversibly so long as \( T_{anneal} \) of the last cycle is not exceeded. The qualitative similarity between the annealing curves in electrostatic and magnetic fields again suggests a common mechanism. This also bears a striking resemblance to the evolution of the resistance seen upon structural annealing of amorphous quench-condensed films [Fig. 3(c)] [14]. This is due to crystallization at ever increasing length scales as the film is progressively annealed at higher temperatures, resulting in a ‘mixed phase of amorphous and crystalline material’.

We now turn to the dynamics of the response. On turning on a gate electric field or magnetic field, a small part of the response evolves logarithmically in time [Fig.4(a)], typical of glasses. We also observe wait time dependence or aging of the relaxation in a magnetic field. After cooling the sample in zero field to 30K, a large magnetic field of 2.5T was turned on at 30K for about 1hr. The field was then set to zero and the sample allowed to relax for 1hr to define an appropriate base line value for the resistance. Subsequently, a smaller field of 1.5T was turned on for different wait times \( t_W \) [Fig.4(c)] and then turned off, and the sample was allowed to relax for approximately 3\( t_W \). The slow logarithmic relaxation that occurs after this field is turned off depends inversely upon \( t_W \). The curves for wait times of up to 120min collapse when the relaxation times are scaled by \( t_W \) [Fig.4(d)]. This is consistent with ideas about aging in the context of spin and structural glasses [12], where \( t_W \) determines the height of the largest energy barrier crossed by the system, and consequently the rate limiting relaxation time scale when the field is turned off. The rate of relaxation was observed to slow down to the point of saturation between wait times of 120min and 240min, shown by the fact that these relaxation curves fall on top of each other within the spread of our data. This may indicate that the phase space for barriers of incrementally higher value is very limited for the 1.5T magnetic field applied. We have also measured wait time dependence with a gate electric field. With the application of the highest fields available (300V = 85kV/cm), aging was not observed within the uncertainty of our data, and the relaxation traces seem to lie on top of each other [Fig.4(b)]. This is not merely due to the size of the gate electric field, since we do observe aging in a magnetic field with the same wait times and equivalent strength (1T). This is also in contrast to the aging observed on gating charge glasses [15] and may be due to the fundamentally different ways that gate and magnetic fields affect the film. In the insulating regions, the gate electric field is not screened, and goes right through the film. In metallic regions, it is strongly screened and only affects the first few unit cells at the dielectric-film interface. The strongest effects are likely to be felt near the insulator/metal boundaries, where the electric field would couple maximally to the film [16]. In contrast, an applied magnetic field would influence all the spins in the film equivalently. The relaxation of strain occurs throughout the insulating regions, as opposed to just at the boundaries for the gate effect. Thus, during \( t_W \), the system is able to sample a greater phase space in the hierarchy of higher energy barriers during the application of a magnetic field, producing a more pronounced slowing down or aging effect. However, since the barriers being crossed just at the boundaries are the same in magnitude, the hierarchy is preserved in re-
sistance measurements.

As a further example of strong cross-couplings, we have measured the effect of a gate electric field on the magnetic moment of a film, motivated by recent work on magnetic semiconductors [17]. In manganite films below a certain thickness, \( H_C \) is enhanced both by decreasing thickness and lowering temperature [18], similar to the behavior found in AuFe cluster glasses [19]. This is attributed to the pinning of magnetic domain walls in a metastable energy landscape, due to defects caused by strain or other microstructure [20].

We used an unpatterned film (21 u.c.) with a large area gate (12 mm\(^2\)) to allow detection of small changes in the magnetic moment of the film in a SQUID magnetometer. The coercivity at 2K was 484 Oe, significantly higher than that of thicker films of the same composition. The sample was cooled in zero field and then saturated by applying +5000 Oe. The field was then reversed to +450 Oe, a gate voltage of –200V (-30kV/cm) was applied across the dielectric in 100V steps, and the moment was measured as a function of time [Fig.5]. The sign of the total moment reversed, indicating that \( H_C \) was crossed. Considering that the effective gated area was only about 55% of the total film area, the change in magnetic moment of the gated area was about 36% of the saturation value. Furthermore, upon cooling the film in a 5.5T field from above \( T_c \) to 2K, \( H_C \) was reduced by about 120 Oe compared to the ZFC value. Since application of either a gate or magnetic field serves to lower the resistance, our measurements indicate that the pinning of magnetic domain walls is correlated to the fraction of insulating material, much as inclusions and strain do in other systems. The reduction in \( H_C \) is then related to the lowering of the number and strength of pinning sites upon reducing the fraction of the insulating phase.

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FIG. 4. Glassy dynamics and aging at 30K: (a) The response $R(t)$ after turning on a magnetic field of 2.5T (200 Oe/s) and gate voltage of –300V, after cooling in zero field to 30K. In the aging experiments, initially a field of 2.5T was turned on for 1hr, then off for 1hr to make the subsequent response reversible at lower fields. (b) $G(t)$ with gate field pulses of -300V turned on for different $t_W$, and measured upon turning off, showing no discernable signs of aging. (c) $G(t)$ with magnetic field pulses of 1.5T of different $t_W$. (d) Wait time scaling of $G(t/t_W)$ from (c).

FIG. 5. Gate induced change in magnetic moment. A magnetic field of –450 Oe was applied at $t=0$ after saturating at 5000 Oe. The gate voltage was changed in two steps. Inset (i) indicates section of hysteresis loop where the gate was turned on, and (ii) is a zoomed in view of the change in magnetic moment. The effect of the gate is equivalent to an abrupt increase in magnetic field of 50 Oe.
FIG. 2. A. Bhattacharya et al.

(a) $V_g(V)$, $R(\Omega)$, $H(T)$ vs. $t$ (min)

(b) $V_g(V)$, $R(\Omega)$, $H(T)$ vs. $t$ (min)

(c) $V_g(V)$, $R(\Omega)$, $H(T)$ vs. $t$ (min)
FIG. 3. A. Bhattacharya et al.
FIG. 4. A. Bhattacharya et al.
FIG. 5. A. Bhattacharya et al.

$V_G = 0$

$V_G = -100V$

$V_G = -200V$