Mesoscopic Thermodynamics of an Inhomogeneous Colossal-Magnetoresistive Phase

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Equilibrium conductivity fluctuations of mesoscopic domains are found in film and bulk single-crystal manganite colossal magnetoresistive material. Temperature and field dependences of the Boltzmann factors for a collection of two-state fluctuators give measures of the magnetic moment and entropy differences between the states, and of the fluctuator volumes. The large resistance step size implies dramatic current inhomogeneities. Occasional anomalous temperature dependences indicate that the film inhomogeneous phase is stabilized by a repulsive interaction between conducting regions.

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The colossal magnetoresistive (CMR) manganites have attracted much attention both because their strongly magnetic-field-dependent resistances may have practical applications and because the fundamental physics of their transitions from semiconducting nonmagnetic states to metallic ferromagnetic states remains unclear [1]. Although theoretical attention for some time focused on models of homogeneous phase transitions, data of various sorts (e.g., muon spin resonance [2], optical absorption [3], magnetothermopower [4], x-ray absorption fine structure [5], and, most recently, imaging by electron microscopy [6] and scanning tunneling microscopy [7]) have shown that in some parts of the phase diagram, the transition between more and less conductive phases occurs inhomogeneously, with the fraction of the material in each of two well-defined states depending strongly on temperature (T) and field (H), leading to a percolationlike conductance transition. Static conductivity contrast has been found on distance scales as small as 20 nm [7], but the dynamics on this length scale have not been studied, and the roles of material inhomogeneities and intrinsic thermodynamic effects in creating the mixed phase have not been definitively sorted out [6,7].

In general, for inhomogeneous metal-insulator transitions, one expects large fluctuations in the resistance (R) in the transition regime, since the regions which switch from conducting to insulating when H or T is changed are ones for which the free energies in the more and less conducting states are nearly equal. Although in principle, such noise could occur via continuous motions of boundaries between phases, in practice, in the presence of disorder, broken-symmetry phases more typically show discrete free energy minima, producing few-state-system equilibrium fluctuations [8]. Large resistance noise has been found in CMR materials, e.g., [9], including discrete steps attributed to the large local current densities appearing on some fluctuating domains due to percolation effects [10], providing a probe of mesoscale CMR dynamics. Very recent measurements have shown sharp increases in noise power near strongly hysteretic phase transitions in some bulk manganite crystals, exhibiting generally the sort of scaling behavior expected near percolation [11].

In this Letter we report noise results on the thermodynamic and transport properties of a collection of discrete two-state systems in single-crystal samples, film and bulk, of $La_{1-x}Ca_xMnO_3$ with $x \approx 0.33$, with nonhysteretic phase transitions as a function of T. (This stoichiometry is the same as that of some imaged material [7].) A characteristic dynamic coherence size will be inferred, very strong current inhomogeneities characteristic of percolation effects will be shown, and evidence for interdomain interactions favoring the mixed phase in the film will be presented.

The materials studied include an epitaxial single-crystal film, 70 nm thick, on a $SrTiO_3$ substrate, prepared by atomic layer-by-layer molecular beam epitaxy [12], and a bulk single crystal of about 1 mm^2 by 100 μm dimensions [13]. Six-probe film samples, with a right-angle bend in the middle, were prepared by lithography, with a total length of 2 mm, width of 100 μm, and lengths of 200 μm between voltage probe pairs on each half of the sample. Four leads were attached to the bulk sample by silver epoxy on evaporated Au pads. All data discussed henceforth will be on a single film sample, except where explicitly noted, but similar data have been obtained on the one other film sample measured.

The dependence of the film R (measured via four-probe methods) on T is illustrated in Fig. 1. As in other similarly prepared films [14], the peak in R and the largest CMR effect are shifted to lower T than in bulk material of similar composition, presumably due to strain effects. Results were virtually identical for the two sample halves, with a shift in the peak of $R(T)$ of less than 0.5 K, indicating that the material was homogeneous on the scale of the sample dimensions. In the bulk sample the maximum R was at about 220 K, more typical for this stoichiometry [13].

Noise was measured simultaneously on each film voltage probe pair, using standard techniques, with current supplied by a 1.5 to 6 V source in series with a quiet 95 kΩ resistor. (For the bulk, a 36 V battery and a 500 Ω

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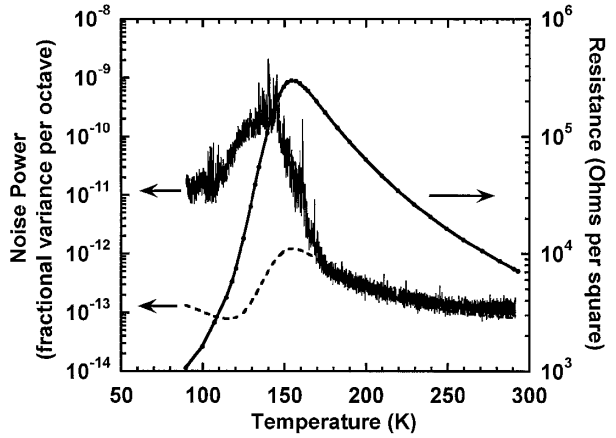

FIG. 1. R (solid line, right-hand scale) and an average normalized noise power per octave, i.e., one third the integral over the three octaves from 12 to 97 Hz of $S(f)/V^2$ vs T. The dashed line indicates the normalized background Johnson noise power. The scatter above 170 K is expected for Gaussian statistics.

resistor were used, with a matching transformer at the preamp input.) The voltage spectral density $S(f)$ was found to be approximately of the $1/f$ form over the range measured, $80 < T < 170$ K. The voltage fluctuations were linear in the applied current over the range (a factor of four, all at low current density) tested. Figure 1 illustrates the T dependence of $S(f)/V^2$. Averaged over any T range, the form of $S(f)$ was close to $1/f$, as in all previous reports [9–11]. Results for the two arms of the sample are similar. The prominent fine structure in the T dependence was due to discrete fluctuators, as illustrated in Fig. 2. In the bulk sample, persistent discrete fluctuators appeared (at $H = 0$) only from 217.4 to 219.9 K.

In any noise measurement, the elimination of contact artifacts is crucial. Here the patterned thin-film geometry allows the complete removal of the voltage sensing contacts from the current-carrying path. Furthermore, simultaneous measurements of voltage fluctuations on the two voltage sensing pairs allow us to locate the fluctuating regions within the sample. Fluctuating R's within the region probed by either voltage pair give large fluctuations in V on that pair accompanied by smaller voltage fluctuations of the opposite sign (due to the finite series resistance) on the other pair. Most of the discrete fluctuations found were of this type, randomly situated in the two voltage probe regions. A few discrete fluctuations appeared with the same sign and magnitude on both probes, as expected for unusually large fluctuations in the large region outside the probes, appearing only due to the finite series resistance. These results are fully consistent with R fluctuations distributed throughout the film, and inconsistent with any contact problems which we can imagine. For the bulk sample, no such compelling geometrical arguments are available, but the qualitative behavior of the discrete fluctuators, in particular, their very strong H and T dependences (to be described), very strongly indicates that they have the same origin as the film noise, and noise power measurements on other bulk materials strongly support that interpretation [11].

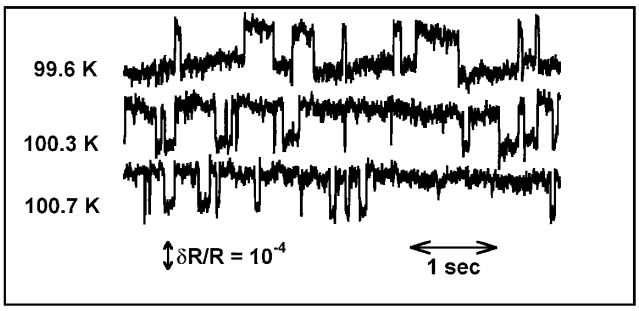

FIG. 2. Some time traces exhibiting discrete fluctuators in the film at different T. The high-R state is favored at higher T.

There are in general two main ways in which transport fluctuations can arise in these CMR materials. The orientation of magnetic domains can fluctuate, with resulting transport effects due to interdomain resistances, or the material can fluctuate between the more or less conductive local states. Distinguishing between them is facilitated by determining coercive fields from R vs H curves, which show dramatic hysteresis only for $|H| < H_C$ [14]. The coercive field H_C is rather sharply defined in the films [14], and ranges from 200 G at 105 K to 100 G at 136 K. Hysteresis effects are much more prominent in the arm parallel to H, indicating the importance of geometrical demagnetizing anisotropy [14]. Above H_C, the nonhysteretic $R(H)$ indicates an equilibrium single-domain structure. This overall magnetization domain structure is not to be confused with the smaller-scale inhomogeneity of the magnetic phase [7]. In the bulk, H_C in the relevant range (near 220 K) was about 10 G, and not sharply defined.

The average statistical properties of the noise are, within the accuracy of our measurements, independent of whether it is measured below or well above H_C, and independent of field cooling vs zero-field cooling. That immediately suggests that magnetic orientation fluctuations are not the main noise source.

For each discrete fluctuator, a Boltzmann factor r can be directly determined from the time traces, simply by taking the ratio of the times spent in the two states. In the film, in 15 of the 17 film cases for which we have unambiguous data, for $|H| > H_C$ the low R state is favored by high $|H|$ and/or by low T (as shown in Fig. 2), as one would expect if the transition from high R to low R were caused by changing ratios of amounts of material in two microphases. Figure 3 illustrates the H dependence of r for typical cases.

The Boltzmann factors for individual fluctuators are, at least approximately, *even* functions of applied H for $|H| > H_C$. Figure 4 illustrates one such case in the bulk sample. In order to track a single fluctuator over a wider range of H than could be followed at fixed T, T was adjusted to keep $r \approx 1$ for each H, and $T(H)$ then recorded.

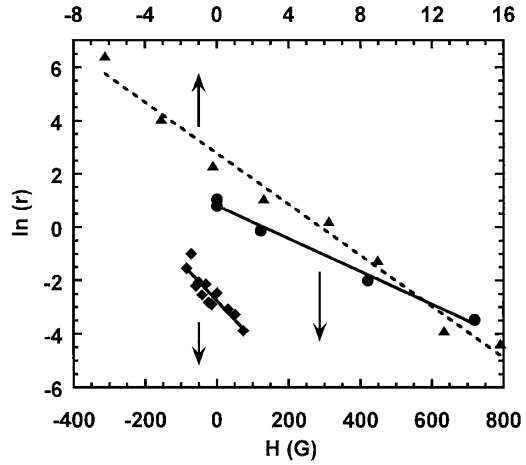

FIG. 3. Boltzmann factors (r) vs H for two-state fluctuators, one from bulk at $T = 218$ K (triangles), one from film at $T = 100$ K (circles), and one from another film sample at $T = 135$ K (diamonds, offset by -6 on the vertical axis for viewing clarity). Large r corresponds to more time in the high-R state. The positive sign of H corresponds to the last prior field above H_C. These results were not dependent on subsequent field history so long as H was kept within the range of the points shown. Note the factor of 50 difference between the two field scales.

For $|H| < H_C$, $\ln(r)$ depended on field history, as seen in a few points in Fig. 4, often with a linear dependence on H for continuous H sweeps, as shown in Fig. 3. At these low fields, the net effective field on the fluctuating region must have been dominated by exchange or dipole effects from neighboring regions with the applied field being a small perturbation on that time-reversal symmetry-breaking local environment. Other data show breaks in the $\ln(r)$ vs H dependences for $|H| < H_C$, including discontinuities and slope changes, indicating effects of the switches of neighboring regions.

All these results are as expected if the fluctuations are not between states with different magnetization orientations but rather between ones with different magnetization magnitudes, with the preferred orientation set by local and applied symmetry-breaking fields. However, they do not logically rule out the possibility that magnetization orientation fluctuations are involved, with the high-R and low-R states of a fluctuator having reversed orientations at $+H$ and $-H$, due to the reversal of all the neighbors.

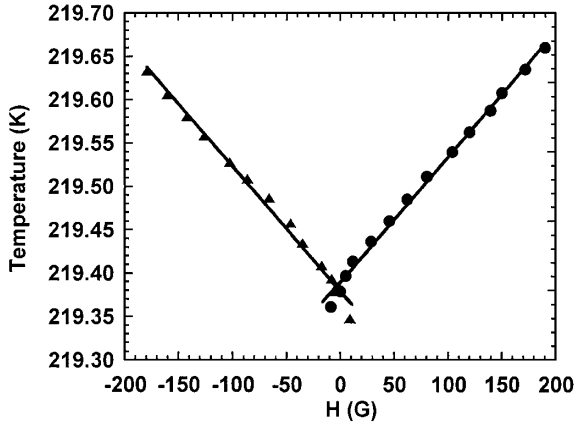

FIG. 4. Approximately even dependence of a fluctuator's Boltzmann factor on H (bulk sample). $T(H)$ is the temperature required to obtain $r = 1$ at each H. The triangles represent data taken with H sweeping from negative to positive, and the circles represent the opposite case.

Assuming that the difference $\Delta\mu$ of the magnetic moment between the two states (along the applied field direction) and their energy difference ΔE are nearly independent of H and T, their values can be obtained from the derivatives of r with respect to H and T:

$$\Delta\mu = kT\,\frac{d\ln(r)}{dH}, \qquad \Delta E = kT^2\,\frac{d\ln(r)}{dT}. \tag{1}$$

All fluctuators observed have Boltzmann factors not too far from unity, requiring that $|\Delta E - kT\Delta\sigma| \leq 5kT$, where σ is the dimensionless entropy difference. Therefore

$$\Delta\sigma \approx \frac{d\ln(r)}{d\ln(T)}. \tag{2}$$

For magnetization differences of about two Bohr magnetons per unit cell typical sizes for the fluctuators are some 1×10^4 unit cells in the film and 5×10^5 in the bulk, each result consistent over the observed fluctuators to within a factor of about 2. The largest dynamical size scale we find is roughly the same as the smallest-scale static structure resolved in images on material with similar composition [7].

In most cases (both in film and bulk) where both H and T dependences were measured, $\Delta\sigma$ was about a factor of 30 (to within a factor of 2) less than the number of Bohr magnetons inferred from the H dependence, strongly suggesting a similarity of the microphases in the two materials. It is not easy to see how such results could arise if the fluctuations were between different magnetic orientations, since in that case the entropy difference would be a domain surface effect and should be significantly smaller (per moment difference) in the larger bulk domains.

The size of the discrete fluctuations in R should be related to the size of the fluctuating regions. If the current distribution were homogeneous, when a roughly spherical region of volume V_D switched to conductivity much greater than the average, in effect a volume of the sample with dimensions comparable to the fluctuating region would be shorted out, reducing R by an amount ΔR of order RV_D/V_S, where V_S is the sample volume. The actual discrete $\Delta R/R$ found are of order 10^{-4}. The approximate V_D/V_S inferred from the thermodynamic properties is 10^{-9}, indicating that a homogeneous current model is not close to being correct.

Near a percolation transition the assumption of homogeneous current density breaks down. Thus one expects a few fluctuators, located along links in the percolating backbone, to have much larger than average current densities and hence to show up disproportionately. Some such

effects were previously invoked to explain non-Gaussian noise in CMR, using an argument that a broad enough distribution of interdomain resistances would maintain a nearly percolating current path over a range of resistances [10]. In the present case, however, in which we see two-state fluctuations of regions between well-defined more and less conducting states, one expects instead a standard sharply defined percolation threshold, although in a weakly conducting background. In view of the irregular large-scale images of the conducting regions found in similar material [6,7], it is not obvious that the statistics of the current distribution can be obtained from formal percolation theory, and we therefore will not attempt such analysis here.

The existence of two fluctuators in the film which spent *less* time in their conducting state as T was reduced has thermodynamic implications. There must be some spatial region for which lower-T favors the less conducting state. Barring some extraordinary intrinsic local reversal of the phase diagram, that means that some region is driven insulating by some neighboring region going conducting. A term in the free energy favoring the mixed phase over the homogeneous phases must then be present, as previously surmised on less direct grounds [6]. These mesoscopic results thus provide direct evidence that the broad mixed-phase regime is stabilized, at least in the film, by long-range interaction terms, not just by inhomogeneity of the material.

The plausible explanation for the switchers with reversed T dependence in the film would then be that when a domain goes conductive, it can be accompanied by a smaller domain switching out of the conducting state. The net sign of the effect on R would not consistently follow the majority microphase change (which determines the sign of the thermodynamic dependences) because, as we have seen, the sensitivity of R to the local conductivity is very inhomogeneous.

In the film, the long-range interaction terms may arise from strain clamping by the substrate. Clamping sample dimensions should, as with any first-order phase transition accompanied by a strain change, give a coexistence regime. The largest characteristic scale of the inhomogeneity would then be a fraction of the film thickness, consistent with our measured mesoscopic scale. Such effects would not be expected in the bulk, and we at present cannot say whether the larger mesoscopic scale found there results from some other intrinsic long-range effects favoring the mixed phase or from some less fundamental effects. The existence of macroscopic Barkhausen-like jumps and even large overall hysteresis in bulk samples of related materials [11] suggests that the largest size scale of the inhomogeneity is strongly dependent on detailed material properties at least in the bulk.

Although for T well below the resistance peak there are localized carriers [5] and images show insulating islands [7], there is no obvious reason for the reentrance of non-Gaussian effects near the crossover to fully metallic conductivity in the film. We leave further investigation of this effect to future work.

In conclusion, noise measurements on several CMR materials near the transition clearly show domains of 10^4 to 10^6 unit cells undergoing concerted equilibrium fluctuations between the less conducting and the more conducting, more magnetic, less entropic state. The effects of these switchers on R are disproportionately large, showing that the current is highly inhomogeneous. A few fluctuators in the film have the unexpected sign for the dependences of their Boltzmann factors on T, strongly indicating that the stability of the mixed phase comes from a term in the free energy favoring mixture of the two microphases, not just from material inhomogeneities. Substrate-clamping strain effects could provide such a term.

The mesoscopic switchers found in the bulk crystal are very strongly sensitive to fields of a few Gauss, suggesting possible applications. The film results suggest that substrate strain effects will need to be controlled if such very low-field applications are to employ films.

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