Sliding charge-density wave in manganites

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Stripe and chequerboard phases appear in many metal oxide compounds, and are thought to be linked to exotic behaviour such as high-temperature superconductivity and colossal magnetoresistance. It is therefore extremely important to understand the fundamental nature of such phases. The so-called stripe phase of the manganites has long been interpreted as the localization of charge at atomic sites. Here, we present resistivity measurements on La_{1-\delta}Ca_xMnO_3 that strongly suggest that this state is in fact a prototypical charge-density wave (CDW) that undergoes collective transport. Dramatic resistance hysteresis effects and broadband noise properties are observed, both of which are typical of sliding CDW systems. Moreover, the high levels of disorder typical of manganites result in behaviour similar to that of well-known disordered CDW materials. The CDW-type behaviour of the manganite superstructure suggests that unusual transport and structural properties do not require exotic physics, but could emerge when a well-understood phase (the CDW) coexists with disorder.

The stripe phase in manganites of the form La_{1-x}Ca_xMnO_3 appears as the temperature is lowered through \( T \simeq 240 \text{ K} \), and the superstructure wavevector settles on a final value of \( q \simeq (1-x)a^* \) (ref. 3) (where \( a^* \) is the reciprocal lattice vector) for \( 0.5 \leq x < 0.85 \), at \( T \simeq 120 \text{ K} \) (ref. 4). On the basis of the insulating nature of the manganites up to room temperature, and the observation of stripes of charge order in transmission electron microscopy (TEM) images, early studies concluded that the superstructure arose from localization of charge at atomic sites. However, neutron and X-ray studies found the degree of charge localization at Mn sites to be small, and subsequent theoretical work suggested that a charge-density-wave (CDW) model may be more applicable. This suggestion is supported by the observation that \( q/a^* \) is strongly temperature dependent, indicating that a model in which the superstructure periodicity is derived from the sample stoichiometry cannot be valid. In addition, heat capacity peaks at the transition to the stripe phase can be modelled as ‘dirty Peierls transitions’, as expected in a disordered CDW system. However, the possibility of the stripe phase exhibiting sliding behaviour, as seen in many other CDW systems, could not be probed without the ability to make orientation-dependent resistivity measurements. Here, we describe the first such measurements on the manganite stripe phase, which reveal dramatic orientation-dependent resistivity and broadband noise effects that are characteristic of CDW sliding.

Orientation-dependent resistivity measurements require thin films, because untwinned single crystals of the insulating manganites cannot be grown. The 80-nm-thick La_{0.5}Ca_{0.5}MnO_3 thin film was grown on a NdGaO_3 substrate as described in ref. 12. It should be noted that the La_{0.5}Ca_{0.5}MnO_3 thin-film phase diagram differs from the bulk polycrystalline phase diagram in that there is no intersection of the ferromagnetic and stripe phases at \( x = 0.5 \); instead, the ferromagnetic phase is present for \( x < 0.42 \); for \( x > 0.42 \), a paramagnetic insulating phase appears (Fig. 1a, inset). The film was prepared for TEM by conventional grinding of the substrate to 50 \( \mu \text{m} \) and then milling a small window using a focused...
Figure 2 Variation of the differential resistance with current at different temperatures and with the current passed parallel and perpendicular to the superstructure. a, Linescan of TEM image in the \( a \) (red line) and \( c \) (blue line) directions showing the superstructure reflections present in only the \( a \) direction. b–f, Differential resistivity of \( \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) versus d.c. bias with bias applied in the \( a \) (red lines) and \( c \) (blue lines) directions at various temperatures. In each case, the upper curve is the differential resistivity obtained after cycling the temperature to 300 K, and the lower curve is the path followed by subsequent bias sweeps.

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Other mechanisms such as avalanche breakdown or sample heating cannot account for the data in Fig. 2. Although these effects might produce a falling differential resistivity as the field increases, they would not produce a history-dependent result; on removing the field, the sample would return to its initial state. Moreover, whereas the d.c. resistivity for currents in the c direction is two times higher than that for currents parallel to a, the drop in resistivity as the field increases is five times larger in the latter direction (Fig. 2); this anisotropy both fits naturally into the CDW picture and excludes heating and breakdown as possible mechanisms. The final model to consider is that of percolating ferromagnetic domains, which has been used successfully to describe the resistivity behaviour in the ferromagnetic manganites, particularly at the metal–insulator transition11. In the simple case of non-orientated domains, the anisotropy in the effects observed here rules out this mechanism. A more complex model with orientated domains is also ruled out as there is no evidence from the TEM data that a ferromagnetic phase is present (and indeed, it would be unexpected from the phase diagram, see Fig. 1a, inset). Finally, the model of percolating ferromagnetic domains can be ruled out.

Figure 3 Frequency and current dependence of the broadband noise. a,b, 97 K data with the current parallel (a) and perpendicular (b) to q. c,d, 123 K data with the current parallel (c) and perpendicular (d) to q. e,f, 156 K data with the current parallel (e) and perpendicular (f) to q. The colour scale shows the magnitude of the power spectral density of the noise, in units of V^2 Hz^{-1}.
because the nonlinear resistivity shows activated behaviour for both low and high electric field biases, indicating that in both states the system is insulating, rather than one of the states having a strong metallic component.

Having explained the hysteresis when the bias is along $a$, we attribute the small amount of hysteresis seen when the bias is along $c$ (Fig. 2) to imperfect contact geometry; that is, misalignment results in a small amount of bias being applied in the perpendicular direction.

It is initially surprising that it is possible to depin the CDW using moderate electric fields, as the expected wavevector of $q/a^* = 0.5$ (that is, commensurate with the lattice)\textsuperscript{22} would
generally lead one to expect the CDW to be strongly locked to the lattice. However, in the manganites it is well documented that the wavevector varies with increasing temperature and from grain to grain within a polycrystalline sample. These observations suggest that the energy gain from locking into the lattice must be relatively small, in accordance with the relatively low depinning fields observed.

Another distinguishing feature of CDWs is that they exhibit a broadband noise spectrum with an amplitude proportional to $f^{-\alpha}$, where $f$ is the frequency. Noise measurements were carried out in the range 10 Hz to 2.5 kHz using a low-noise current source. The noise signal was amplified with a high-input-impedance, low-noise preamplifier and was recorded via a digitizing oscilloscope. Lead capacitance, and the typical 10$^8$ S sample resistance, limited noise measurements to below 10 kHz. Other techniques commonly used on CDW systems such as NbSe$_3$, were considered or attempted but typical properties of manganite films rendered them impossible; manganite film resistivities and geometries lead to RC time constants that are too high to carry out experiments that measure effective pulse line or duration memory effects.

Figure 3 shows that significant broadband noise is observed in La$_{0.5}$Ca$_{0.5}$MnO$_3$ when the d.c. bias is applied in the superstructure direction. In contrast, the noise amplitude is much smaller when the bias is in the non-superstructure direction. The exponent $\alpha$ in La$_{0.5}$Ca$_{0.5}$MnO$_3$ runs from 0.8 (156 K) to 2.0 (100 K), a similar range to values seen in the prototypical CDW system NbSe$_3$ (0.8–1.8) (ref. 10). However, the magnitude of the broadband noise in La$_{0.5}$Ca$_{0.5}$MnO$_3$ is much larger than that observed in clean CDW systems; for La$_{0.5}$Ca$_{0.5}$MnO$_3$ the effective noise temperature at 300 Hz is $\sim$10$^5$ K for a sample temperature of 100 K, whereas in pure NbSe$_3$, the effective noise temperature is $\sim$10$^6$ K. This is attributable to the large amount of disorder present in La$_{0.5}$Ca$_{0.5}$MnO$_3$ (ref. 9; see above), so that there are many more pinning–depinning events compared with, for example, pure NbSe$_3$. Although broadband noise has previously been observed in impurity-pinned CDWs, narrowband noise has not been observed in an impurity-doped or radiation-damaged sample, probably because the width of the narrowband noise peak is proportional to the magnitude of the broadband noise. Therefore, a high level of disorder or impurity pinning will lead to a large amount of broadband noise and observably small narrowband noise, as seen here in La$_{0.5}$Ca$_{0.5}$MnO$_3$.

In the well-tested Lee–Rice model for a pinned CDW, the threshold field $E_1$ can be used to estimate the characteristic pinning length $L$ over which impurities or disorder deform the CDW sufficiently to pin it, that deformation being resisted by the elastic modulus $\kappa$ of the CDW. We obtain $L = \sqrt{E_1/e\kappa}$, and estimating a Fermi energy $E_F \sim 1$ eV (ref. 30), the threshold depinning field $E_1 \sim 10^5$ V m$^{-1}$ (this work) and superstructure wavevector $Q \sim 10^{10}$ m$^{-1}$ (ref. 10), we find that $L \approx 300$ nm, much larger than the estimated impurity spacing, and justifying the weak pinning approximation. As a corollary, oscillation of the CDW in the pinned potential would be predicted to occur at a characteristic pinning frequency $\omega_p \sim (m/m_0)^{1/2}$, which we estimate to be around 1 THz. This is in the same frequency range as an earlier reported feature in a striped manganite of a different composition, which was tentatively assigned to a pinned CDW model.

As seen in other sliding CDW systems, the amount of broadband noise decreases with increasing temperature (Fig. 3a,c,e). For a bias above $E_1 (\sim 10^5$ V m$^{-1}$) in the superstructure direction, this decrease is approximately linear with temperature (Fig. 4c), as observed in the CDW system TaS$_2$ (ref. 27). With the bias in the non-superstructure direction, the noise increases much more slowly; at 100 K, it is more than an order of magnitude smaller than that with the bias along a (Fig. 4c). The small noise observed at high electric fields when the bias is along c is due to imperfect contact geometry, as discussed with regard to the differential resistance measurements above.

Figure 4a,b shows the variation of the broadband noise amplitude with applied field between the first bias sweep after cooling from 300 K and on a subsequent sweep. On first biasing, the amplitude noise shows a large peak at the same point as the large fall in differential resistance (Fig. 4a). On subsequent bias sweeps, the noise increases more slowly with bias (Fig. 4b). The large peak during the first bias sweep is caused by a high level of random telegraph signal noise, which occurs in CDW systems as they switch from pinned to depinned states and back again close to the threshold field. The distinctive shape of the random telegraph signal noise is shown in Fig. 4d, another factor adding weight to our identification of a CDW in La$_{0.5}$Ca$_{0.5}$MnO$_3$.

In summary, our resistivity and noise measurements strongly suggest that the superstructure in the stripe phase of manganites is a CDW that slides in the presence of an electric field. Such a manganite CDW would be a fully gapped system with no screening electrons, previously only observed in extremely clean organic materials. However, our data suggest that the manganite CDW exists with a high level of impurities, leading to dramatic hysteresis effects in the resistance. Our findings call for a reanalysis of the large region of the manganite phase diagram, 0.5 $\leq x < 0.85$, that is occupied by the stripe phase. In a wider context, this result is important because of the prevalence of stripe and chequerboard phases in oxide materials, including chelates, cobaltites, nickelates and cuprates; in particular, evidence is mounting that a glass of the stripe phase in cuprates may be linked to high-temperature superconductivity, making an understanding of the stripe phase a matter of urgency.
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