The self-organised phases of manganites

N.D. Mathur  
Department of Materials Science, University of Cambridge, CB2 3QZ, UK  
and  
P.B. Littlewood  
Department of Physics, University of Cambridge, CB3 0HE, UK  
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Abstract

Self-organisation requires a multi-component system. In turn, a multi-component system requires that there exist conditions in which more than one component is robust enough to survive. This is the case in the manganites because the free energies of surprisingly dissimilar competing states can be similar — even in continuous systems that are chemically homogeneous. Here we describe the basic physics of the manganites and the nature of the competing phases. Using Landau theory we speculate on the exotic textures that may be created on a mesoscopic length scale of several unit cells.

1 Introduction

The doped perovskite manganites are fascinating because they can readily be tuned between radically different phase states. Broadly speaking one has either a ferromagnetic metal, a charge-ordered insulator, or a paramagnetic polaron liquid. The spatial extent of these three types of phase is potentially unlimited — but so, according to a growing body of evidence, are the number of alternative phases that occur over mesoscopic length scales.

What is the basis for such richness and complexity? The answer is that the magnetic, electronic and crystal structures of any given manganite are intimately related. Thus one may parameterise any given phase in the manganites by the nature of the spin, charge, orbital and structural degrees of freedom; the degree to which these degrees of freedom are static or dynamic; and, of particular interest here, the length scales over which these degrees of freedom are homogeneous. Note that we do not consider any texture that only extends over microscopic (i.e. unit cell) length scales to be a phase. For example, one stripe in a stripe phase is not in itself a phase — because at least one dimension is too small for the object to be considered a thermodynamic entity.

At a microscopic level one can understand the strong interaction between the magnetic, electronic and crystal structures as follows. The electronic sublattice of a perovskite manganite consists of a cubic network of corner-sharing $\text{MnO}_6$ octahedra in which potential charge carriers arise in certain orbitals if, for example, the interstitial A-site cations comprise a mixture of trivalent and...
divalent species such that they act as a charge reservoir. This electronic sub-lattice is also the home of the magnetic sub-lattice since the magnetic structure arises primarily from the magnetic nature of the manganese atoms. Therefore the electronic and magnetic sub-lattices are one and the same such that they must interact strongly. The intimate connection with the crystal lattice arises both because Mn is Jahn-Teller (JT) distorted by charge carriers, and also because the radius of the A-site cations is invariably less than ideal.

Several recent reviews provide colourful insights into the macroscopic and microscopic nature of the manganites [1, 2]. Here we concentrate on sub-micron mesoscopic length scales over which there is growing evidence for multi-phase coexistence. We argue that Landau theory will provide a natural explanation for these mesoscopic phenomena, and suggest a strategy that would enable self-organised structures to be generated in a controlled manner.

As a caveat we note that historically, evidence for phase separation in the manganites has come from several directions; an old reference known to us dates back to 1977 [3]. The evidence we describe in this article is by no means complete. For example, we concentrate on the cubic manganites and neglect the Ruddlesden-Popper layered manganites in which phase separation has been seen [4].

2 Basic physics of manganites

$La_{1-x}Sr_xMnO_3$ is a prototype for the broad class of cubic perovskite manganites, where with replacement of a trivalent rare earth by a divalent alkaline earth, the nominal valence of Mn can be continuously tuned between $3^+$ (corresponding to the Mn(III) configuration found at $x=0$) and $4^+$ (corresponding to the Mn(IV) configuration found at $x=1$). The important physical ingredients can be seen by reference to Fig. [1].
In a cubic environment, the Mn $d$ levels are crystal-field split into a low lying triplet of $t_{2g}$ symmetry and a doublet of $e_g$ symmetry. Mn is a strongly correlated ion whereby double occupancy of the tightly bound $d$ orbitals is suppressed by Coulomb repulsion, and the direct on-site exchange interaction aligns the spins in the different $d$ orbitals. The $t_{2g}$ levels are strongly localised, whereas an electron in the higher lying $e_g$ state is potentially itinerant. At $x = 0$, each $e_g$ level is singly occupied: double occupancy of these highest occupied $e_g$ levels is suppressed by Coulomb repulsion, and $LaMnO_3$ is an antiferromagnetic Mott insulator. At finite doping ($x > 0$), there are some empty $e_g$ levels, and hence hopping is possible. The exchange (Hund’s rule) coupling $J$ between the spin of an itinerant carrier and each core spin is rather larger than the hopping matrix element $t$ between neighbouring $e_g$-levels. Consequently, each conduction electron is forced to align with the core spin texture (this may be viewed as a strong-coupling version of the RKKY interaction). Thus the effective hopping matrix element between Mn sites is $t \cos(\theta/2)$, where $\theta$ is the relative angle between neighbouring core spins. Clearly, the kinetic energy of the conduction electrons is minimised (maximum bandwidth) if the core spins are parallel to one another, and this so-called double exchange is the fundamental mechanism of metallic ferromagnetism at low temperatures in the doped manganites. At a sufficiently high temperature the energy of this ferromagnetic configuration is overwhelmed by the entropy gain available from a randomisation of the manganese spin system. Thus the system lowers its free energy by entering the paramagnetic state.

Another important feature of the manganites arises from the doubly-degenerate $e_g$ level in Fig. 1. This degeneracy may be broken by a Jahn-Teller (JT) distortion of the oxygen cage away from cubic symmetry that lowers the energy of the occupied $e_g$ level on the $Mn^{3+}$ ion. In pure $LaMnO_3$, there is an antiferrodistortive arrangement of the distorted octahedra, leading to a “doubled” unit cell. This is to be distinguished from an equivalent and simultaneous source of doubling of the unit cell due to rigid rotations of the octahedra, which are promoted by the small size of the A-site cations. (These rotations mainly affect O-Mn-O bond angles whereas the Jahn-Teller distortions mainly affect O-Mn-O bond lengths.) Since the $e_g$ level is progressively depopulated with increasing $x$, the tendency toward JT distortion is suppressed; the long-range-ordered antiferrodistortive phase disappears near $x = 0.2$. It is important to note that the lattice displacements associated with the JT distortions are large and therefore the disappearance of the long-range order does not mean that (static or dynamic) JT fluctuations may not be pronounced. Such fluctuations have been discovered to be very prominent in the manganites.

On top of these JT fluctuations — be they static or dynamic — are the additional static distortions mentioned earlier that arise because the radii of the A-site cations are invariably less than the 1.30 $\text{Å}$ required for the ideal manganese perovskite structure. Looking through the Attfield chemical window one can see, for example, that at an electronic doping level that is particularly favourable for ferromagnetism ($x=0.3$), a high Curie temperature is achieved when the average A-site cation radius is large and the variance in this quantity is small — such that distortions and disorder are respectively minimised.

Both these JT fluctuations, and small A-site cations of varying radii, promote mixed-valent insulating phases of the manganites. The Mn (III) configuration will have a tendency to distort, whereas the Mn(IV) configuration will not.
Because every electron in a local $e_g$ level carries around its own JT lattice distortion, this would appear to provide a recipe for insulating phases at any composition.

2.1 Low temperature ferromagnetic metallic phases (FMM)

If one is close to the ideal perovskite structure in the $x=0.3$ Attfield chemical window then enough of the $O-Mn-O$ bonds are sufficiently linear to make $t$ so large that the ground state is ferromagnetic by the means described above — whence the charge carriers are delocalised such that JT fluctuations are suppressed. One of these delocalised charge carriers is like the quantum-mechanical “particle in a box”; its energy is lowered when the box is made bigger, provided that any internal structure within the box can be ignored.

2.2 Charge-ordered insulating phases (COI)

Even when the JT fluctuations do indeed make for an insulating ground state, there can be order because the oxygen octahedra share corners; distortions about one Mn site are anti-shared with a neighbour. Steric conflicts can be solved in ordered phases (such as undoped LaMnO$_3$), and in TEM it is common to observe “striped” phases consisting of diagonal arrays of Mn(III) and Mn(IV) [1]. These striped phases predominate in $x \geq 0.5$ where the larger and asymmetric Mn(III) species are in the minority such that packing is easier. In these localised phases, the spin couplings are via superexchange, mostly antiferromagnetic, and naturally somewhat smaller than the ferromagnetic double exchange interactions in the metal.

In fact the term COI is used here to refer to a multiplicity of phases, including the parent antiferrodistortive ($x=0$) phase, and the striped phases that have been reported with several different periods that are commensurate with the lattice, especially periods of 2 (near $x=1/2$) and 3 (near $x=2/3$) [1]. A naive counting of the ratio of Mn(III)/Mn(IV) would predict incommensurate phases with either one Mn(IV) stripe every $(1/x)$ in a Mn(III) environment ($0 < x \leq 0.5$), or one Mn(III) stripe every $1/(1-x)$ in a Mn(IV) environment ($0.5 \leq x < 1$). However, there are undoubtedly strong commensurability effects that will stabilise the commensurate phases away from their “correct” nominal composition. The nature of the repeating units in stripe phases — be they commensurate or not — is not universally agreed upon. In the prevailing “bi-stripes” picture the widths of the Mn(III) and Mn(IV) stripes are different. In the Wigner crystal model they are of equal width [10]. There are also phases that may be charge-ordered, but not orbitally ordered — i.e. the orientation of the JT distortions are random, or strongly fluctuating locally [11]. We shall suggest some other possibilities later.

2.3 The high temperature paramagnetic phase (PMI)

The recent burst of interest in the manganites was initially motivated by the discovery reported in 1994 of the bulk “colossal” magnetoresistive (CMR) effect in the paramagnetic phase at temperatures just around the Curie point [12]. In situations and compositions (e.g. $La_{0.7}Ca_{0.3}MnO_3$) where a large CMR is achieved in this way, the paramagnetic state is found to be quasi-insulating
(activated resistivity), and this has been tracked to the presence of large polaronic (JT) fluctuations in the paramagnetic insulator (PMI) which are strongly suppressed in the FMM \[\text{[13, 14, 15, 16, 17]}\]. In this case, the high temperature competition for the FMM is not with the ordered mixed-valent insulator, but with something resembling a melted version of it — let us call this a “polaronic liquid”.

Note that nearer to the ideal perovskite structure in the \((x=0.3)\) Attfield chemical window the dynamic polaronic fluctuations and hence CMR are suppressed in the paramagnetic phase. This is the case with \(La_{0.7}Sr_{0.3}MnO_3\) above \(T_C\) — which consequently has a metallic resistivity in that it rises with increasing temperature \[\text{[18]}\]. In fact, there is no symmetry distinction between this paramagnetic metal (PMM) and the PMI, and the crossover (with varying composition) between these phases is generally smooth.

### 3 Competing phases

The three basic phases described above (COI, FMM and PMI) compete to be the stable thermodynamic phase. What can happen near the FMM/COI boundary is of particular interest in this article because there is no reason of symmetry why charge ordering and ferromagnetism cannot coexist. Instead it depends on the driving physics. This suggests that the transition between the two types of ordered phases will be first order — which seems to be the case (at least at low temperatures).

Below we argue that the spatial extent of a “phase” cannot be too small, and go on to describe some of the evidence for texture in the manganites that arises over length scales that are at least microscopic. We then consider the strong evidence for texture over longer length scales, i.e. “phase separation”.

#### 3.1 Microscopic fluctuations

The PMM/FMM transition in \(La_{0.7}Sr_{0.3}MnO_3\) described in Section 2.3 is continuous (second order) and smooth at the microscopic level as evidenced by ferromagnetic resonance measurements \[\text{[19]}\]. The FMM/PMI transition (e.g. in \(La_{0.7}Ca_{0.3}MnO_3\) as also described in Section 2.3) is also usually continuous \[\text{[20]}\]. However more generally, a thermodynamically continuous (second order) transition is not necessarily smooth microscopically: it could be an order-disorder transition rather than a microscopically smooth “displacive” order-order transition. This order-disorder type of continuous (second order) transition can only be distinguished from a thermodynamically discontinuous (first order) transition if the length scale of the measuring probe is sufficiently long. Experimentally there is plenty of evidence to demonstrate the existence of at least short-range texture at the unit cell level, some of which we now describe below.

NMR studies in an applied magnetic field can probe both the ionisation state and the local magnetic environment of the \(^{55}\)Mn atoms. All around the phase diagram it is typical to find Mn(IV)/Mn(III) species coexisting with Mn species whose NMR signal is motionally narrowed \[\text{[21]}\]. Such motional narrowing is indicative of the presence of metallic regions. However, in principle, motional narrowing can also arise if the energy levels accessible to a somewhat localised electron become blurred (e.g. due to thermal or interaction effects). Therefore,
to be pedantic, we consider the existence of a motionally narrowed line to be
good evidence rather than concrete proof for the existence of metallic phases.
This technicality notwithstanding, NMR studies lead us to believe that there
are metallic clusters in surprising places: above $T_C$ on the $x < 0.5$ hole-doped
side [22] and at 3 K on the $x > 0.5$ electron-doped side where AF stripe phases
predominate [23]. A particularly interesting feature of NMR is that one can
see whether or not the frequency of a motionally narrowed resonance will fall
with the bulk magnetisation on increasing the temperature [21, 24]: if it does
fall then we have a second order displacive transition; if it does not then we
infer that the Mn atoms are not all sitting in the same environment. However,
since NMR is sensitive only to the local environment, this does not establish
the existence of two thermodynamic phases: the disorder might only arise at the
microscopic level.

Neutron data can reveal short-range order (as well as long-range order, dis-
cussed later). For example, in the $La_{1-x}Ca_xMnO_3$ system when $x = 0.3$, re-
cent zero-field neutron spin echo studies of the low temperature FM phase have
demonstrated inhomogeneity on a length scale of $\leq 30\,\AA$; and parallel muon
studies suggest that the spin dynamics in the different regions are very different
[25]. Moreover, inelastic neutron scattering experiments have revealed that this
low temperature FM phase contains soft zone boundary magnons and phonons
[26].

Short-range order in $x = 0.3$ systems has also been seen near $T_C$ using
neutrons: the spin wave stiffness is found to remain finite [23, 28] (c.f. the
NMR evidence described above); and a superlattice with correlation length $10\,\AA$
is found to develop [23]. This latter finding extends earlier studies near $T_C$
in which neutron pair distribution functions demonstrated the existence of JT
distortions with short-range correlations [14]. Similarly, early findings with
SANS revealed the existence of local magnetic clusters with a length scale of
$12\,\AA$ [13]. There is similar evidence for these short-range correlations near $T_C$
from a recent high energy x-ray powder analysis [16]; and EXAFS studies in
which the Mn K-edge resonance is affected by local correlations [17].

Regarding short-range order at other doping densities: in the $La_{1-x}Ca_xMnO_3$
system at $x = 0.55$, the FMM ground state found at higher $x$ is replaced with
a novel form of short-range orbital and charge order, according to bond valence
sum calculations based on neutron powder diffraction data [20]. It is around
doping density that canted spins [6] were originally postulated — effectively
as an interpolation between the antiferromagnetic end member at $x = 0$ and the
FMM region at higher $x$. The evidence for novel short-range order presented in
[29] and the presence of both “FM” and “AFM” peaks in NMR studies using an
applied magnetic field [30], tend to rule out canting in favour of the postulated
[6] microscopic texture. However the two scenarios are not mutually exclusive
and in $LaMnO_3_{0.02}$ the 250 MHz NMR line displays a field-dependent slope that
corresponds to half a gyromagnetic ratio; this indicates a canted state [21].

In $x \geq 0.5$ there is both neutron and TEM evidence for the so-called stripe
phases that constitute the COI phase. We discuss this region of the phase
diagram in the next section.

The experiments described above, and certain others, can be adduced as
evidence for the existence in the manganites of inhomogeneities that arise over
length scales that are comparable with unit cell dimensions. In some cases
such experiments point to, but do not prove, the existence of inhomogeneities
arising over somewhat longer length scales. These larger inhomogeneities form the subject of this review and in the next section we consider some of the strong and recent evidence for their existence. For now let us be clear: we reserve the term “phase separation” for the coexistence of mesoscopic and macroscopic thermodynamic phases.

3.2 Phase separation and coexistence

Whenever there is a first order phase boundary, there can be coexistence between phases. An unconstrained system in which there is a first order phase boundary should in principle be in one phase or the other at equilibrium. However in practice coexistence is liable to arise for several reasons.

Equilibrium coexistence of two thermodynamic phases generally occurs either because of disorder (where locally one phase is favoured over the other) or because of an imposed conservation law. The classic case of the latter is of the liquid/gas transition in a system of fixed volume, where the equilibrium fractions of the liquid and gas will adjust in order to fill the available space. When external parameters of the system are changed (e.g. temperature, volume), the two phases readjust in different proportions. If the readjustment is impeded, there will be hysteresis.

The phenomenon of hysteresis is often cited as evidence for phase coexistence. To be precise, it constitutes indicative but not conclusive evidence. For example, hysteresis loops of magnetisation versus applied magnetic field can arise in some rare-earth magnetic systems solely because the degree of saturation dictates the strength of the reverse field required to induce nucleation. In another example, hysteresis can be produced by supercooling, but this is a kinetic phenomenon.

Electronic phase separation is often discussed in the context of the manganites \[\text{MnO}_3\]. While it is no doubt a valid point of view to consider the mixed-valent charge-ordered phases as examples of microscopic electronic phase separation, the Coulomb energy associated with substantial charge density fluctuations on length scales longer than a few lattice constants is prohibitive. When we have coexistence between phases on long length scales, the electronic charge densities must be very nearly the same. We stress that in this and the subsequent sections of this article, we concern ourselves with phases that by definition (see section 3.1) extend over at least several unit cells.

A number of experiments have demonstrated that over wide ranges of compositions there can be coexistence between the FMM and COI phases (particularly period 2 or “1/2”-type). Perhaps the most visual and direct evidence for this type of coexistence comes from dark-field TEM images of \(La_{y/8-y}Pr_yCa_{3/8}MnO_3\) at 20 K \[\text{[23]}\]. Sub-micron domains appear bright because they contain the extra periodicity associated with a COI phase, whereas the interspersed dark regions of similar size are inferred to be FMM through percolative resistivity measurements \[\text{[22, 33]}\]. Neutron powder data taken for compounds of similar compositions reveal the presence of both FM and AFM peaks, each with a different temperature dependence \[\text{[34]}\]. This demonstrates directly the presence of two phase coexistence: each phase must extend over at least some hundreds of Angstroms in order to produce the neutron diffraction peaks. A more recent analysis estimates this distance to be not less than 500 Å and possibly even 1000 Å \[\text{[35]}\]. A slightly more complicated phase separation arises hys-
teretically in $Nd_{0.5}Sr_{0.5}MnO_3$ powder samples below 145-175 K: the majority of the orthorhombic crystal, part of which is a FMM, undergoes a transition to a monoclinic COI phase, as evidenced by neutron diffraction and strain gauge data [36]. Since a structural phase transition accompanies the appearance of the COI phase, one anticipates the eventuality of strain-driven phase separation in the manganites (see Section 4).

Further demonstrations of the FMM-COI interplay are found in sintered powder/thin film experiments. Sintered samples of the potentially COI material $La_{0.5}Ca_{0.5}MnO_3$ only develop a conducting path and a large magnetisation when the grain size is small, i.e. when there is a large amount of strained grain boundary material present [37]. Similarly, a strained epitaxial film of $La_{0.5}Ca_{0.5}MnO_3$ was found to possess a FMM ground state [38], but this strain must be of the correct type [39]. These experiments demonstrate the important role of strain, which is expanded upon below and in the next sections on Landau theory.

In the vicinity of the FMM/PMI phase boundary, Jaime et al. [40] argued some time ago that transport and thermodynamic data could be quantitatively described by a model of coexisting phases, rather than a homogeneous transition. There is also some very visual imaging evidence to support the strain-induced coexistence of the FMM and PMI phases in manganites. Scanning tunnelling microscopy scans suggest that a thin strained film of $La_{0.7}Ca_{0.3}MnO_3$ contains both metallic and insulating regions; and that the insulating sub-micron regions even persist at low temperatures and in high magnetic fields [41]. Alternatively, temperature dependent magnetic force microscopy studies near an artificial grain boundary in a thin strained film of $La_{0.7}Sr_{0.3}MnO_3$ reveal that the FMM state persists within a micron of the boundary at temperatures above which the ferromagnetism in the rest of the film survives [42]. Again, the most likely interpretation of these two experiments is that strain and strain relief respectively create the long-range inhomogeneity.

Mesoscale coexistence of the COI phase with an insulating spin glass phase over (500-2000) Å has been observed in a powdered sample of $Pr_{0.7}Ca_{0.3}MnO_3$ using neutrons [11]. This coexistence may be understood in terms of intragranular strain-driven segregation. The glassy phase melts into a metal under the influence of an applied magnetic field (c.f. melting the COI in $Nd_{0.5}Sr_{0.5}MnO_3$ [36]); and in a single crystal of similar composition ($Pr_{0.63}Ca_{0.37}MnO_3$) there is found to be a large latent heat associated with a similar transition (i.e. thermodynamic evidence from calorimetry for first order behaviour) and a time-dependent specific heat in the coexistence regime that relaxes on a scale of tens of seconds [43]. Relaxation phenomena have been observed elsewhere too, for example in ultra-thin strain films of $La_{0.7}Ca_{0.3}MnO_3$ [44] and in $Nd_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$ ($0 \leq y \leq 0.1$) crystals [45].

Various other measurements of hysteresis [46, 33], noise [47] and thermopower [48] also indicate two-phase coexistence; and various strategies for obtaining two-phase coexistence have been employed. For example, on the Mn(IV)-rich side of the $La_{1-x}Ca_xMnO_3$ phase diagram near $x = 0.9$ a cluster glass state develops and colossal magnetoresistance effects are seen [49]. Similarly replacing 15% of the Mn atoms with Cu to produce $La_{2/3}Ca_{1/3}Mn_{0.85}Cu_{0.15}O_3$ appears to generate both FMM and COI regions as evidenced by transport and magnetisation measurements as a function of field and temperature [50].

Regarding the interpretation of the above examples (and many more), it is
clear that the properties of a manganite are liable to be strongly dependent on
the nature of the sample: the strain states and defects will vary between single
crystals, powders, sintered powders and thin films. We note that from some
perspectives, the propensity for twinning in the manganites reduces the value
of single crystal studies in favour of free (non-sintered) powder samples since it
is possible for each micron-sized grain to act like an untwinned single crystal.
One is confident that the phase separation seen in neutron powder diffraction
studies is not due to surface effects since, as mentioned five paragraphs ago, each
phase must extend for hundreds of Angstroms to be seen at all with neutrons.
Twinning may also be avoided by recourse to thin films.

Remarkably, the proportions of two coexisting phases can be easily “tweaked”
by external parameters that include pressure [51], magnetic fields [52], tempera-
ture [33, 46], these three parameters together [53], strain [38], electrical currents
[54] and X-ray [55] or electron illumination [56].

We have argued elsewhere [57] that the

4 Landau theory

It would be desirable, if possible, to construct a complete theory for the man-
ganites from a fully microscopic basis. In fact, there is a good microscopic
understanding of the homogeneous phases [1, 2], and some evidence for texture
near first order transitions [58]. A full understanding of mesoscopic texture
from a microscopic basis is a complex exercise because of the vast phase space
to be explored. Moreover, such an exercise could turn out to be unnecessar-
ily reductionist. Instead then, it may be useful, at least initially, to simplify
the analysis by postulating a Landau theory for the various coupled order pa-
rameters (magnetism, charge-order, strain). Such an approach has turned out
to be very valuable in the case of ferroelectric/ferroelastic transitions [59], and
especially valuable for the case of incommensurate and commensurate phase
charge-density wave systems [61, 60]. A full Landau theory for the case at hand
is still very complicated and has not yet been fully explored [62]. We shall
restrict ourselves to a few simple scenarios. Of course, even with its simplifi-
cations, the Landau theory can only demonstrate possibilities, because the real
physics lies in the values of the parameters of the theory, which we can only
either guess at, or fit to experiment.

4.1 Strain effects in a commensurate striped phase

In a phase transition to a striped periodic phase, there is a development of an
order parameter with a wavevector $Q_i$, where the subscript denotes one of the
(several) directions of the possible stripes. Then we may write the full order
parameter as

$$\rho_i f(Q_i \cdot r)$$

(1)
so that $\rho_i$ is the amplitude, and the function $f$ is a periodic function of its argument. The simplest Landau theory for the transition would then be contained in the following expansion of the free energy

$$F_\rho = \sum_i \left( \frac{1}{2} a(T) \rho_i^2 + \frac{1}{4} b \rho_i^4 + \frac{1}{6} c \rho_i^6 + \ldots \right) + \sum_{i>j} b_{ij} \frac{1}{4} \rho_i^2 \rho_j^2 + \ldots \quad (2)$$

For diagonal stripes, the sum must run over the possible equivalent \{110\} directions (we index throughout with respect to the pseudo-cubic unit cell). For simplification we shall just consider the case when we may have one of the two (110) (labelled $i = 1$, say) and 1 $\bar{1}$0 ($i = 2$) directions in two dimensional symmetry.

It is conventional to assume that $a(T) = a_o \times (T - T_o)$, so that the quadratic coefficient changes sign below a temperature $T_o$. Depending on the sign of the coefficient $b$, the model will predict a first order ($b < 0$) or second order ($b > 0$) transition. We shall need to choose $b_{12} > 0$, so as to have a striped, rather than checkerboard phase as the lowest energy state.

Because the presence of the order parameters breaks the cubic symmetry, the order parameters must couple to shear strain $s$. This will lead to terms of the form

$$F_s = \frac{1}{2} K s^2 + ds(\rho_1^2 - \rho_2^2) \quad , \quad (3)$$

where $K$ is the elastic constant and $d$ is another constant that describes the strength of the lowest order coupling term allowed by symmetry. Note that the sign of this coupling is opposite for the two order parameters, because the stripes run in orthogonal directions (we have picked axes for the tetragonal distortion along the (110) and (110) directions).

Now imagine that we have a homogeneous situation, with $\rho_1 \neq 0$, and $\rho_2 = 0$, so that only one of the two kinds of stripes is present. We can determine the magnitude of the order parameter $\rho_1$, by looking for the minimum in the free energy. In the case where the strain is free to relax, we have from $\partial F_s / \partial s = 0$ that

$$s = -\frac{d \rho_1^2}{K} \quad . \quad (4)$$

As expected, a shear strain will accompany the stripe transition (c.f. the structural transition to a monoclinic COI phase described earlier [36]). Substituting this back into the free energy, which is now just a function of the single variable $\rho_1$, we have

$$F(\rho, s(\rho)) = F_\rho + \frac{d^2}{2K} \rho_1^4 \quad , \quad (5)$$

so that the strain relaxation makes the fourth-order coefficient more negative in the reduced free energy. This means that a transition that was already first order is made more strongly so such that $T_o$ is raised. It is also possible that initially $b > 0$, but that $b - 2d^2/K < 0$, so that a second-order transition — if the strain were clamped ($s = 0$) — can be driven first order if the strain relaxes. Even more dramatically, if $b$ is sufficiently large and positive, the transition might in fact only occur at all if the strain is allowed to relax. Such phenomena are quite common in ferro-electric and ferro-elastic oxides [59].

In principle, we should also have a term $F_m$, describing the magnetic free energy. In order not to complicate the discussion more than necessary, we...
Figure 2: (a) Frustrated and (b) non-frustrated “90°” twin boundaries between stripe domains. Arrangements like (a) guarantee a macroscopic amount of un-transformed material between the domains, whereas in (b) such material may only be present at the interface. In the manganites, any macroscopic amount of material that fails to transform into the COI phase will likely become a FMM.

shall not include it explicitly. Instead, we assume that the dominant terms are $F_\rho$, and $F_s$, and assert that (metallic) ferromagnetism will appear as the low temperature phase if the COI is suppressed — i.e. the ferromagnetism is slave to the absence of charge order.

In the manganites there is now a wide body of evidence to demonstrate that clamping the strain can produce pronounced effects. For example, as described earlier Section 3.2, compositions in which the equilibrium strain relaxed phase is the COI tend to adopt the FMM phase if the strain is clamped in the right way, either by imposed external stresses, or by internally generated stresses in multi-domain samples — such as micron-sized grains in free powders [11].

Strain-induced interactions are long-range, and can lead to pronounced kinetic effects, familiar in the martensites [63]. Since the shear strain induced by two orthogonal striped domains is of opposite sign, the strain cancels at long distances such that the arrangement shown in Fig. 2a is favoured by nucleation in a bulk or clamped environment. However the strain fields are incompatible unless the two domains meet in a macroscopically strain-free fashion as shown in Fig. 2b. Either way there is the possibility of untransformed material between the two domains, which if sufficiently large we may expect to become a ferromagnetic metal.

4.2 Twin boundary between striped domains

In a 90° twin boundary (Fig. 2b), the interface between the two different stripe domains bisects the 90° angle between the domain orientations. Such a configuration potentially allows macroscopic strain relaxation for both domains (Fig. 2b). If there are indeed domains in a sample, such twins have the lowest strain energy. However, the domain boundary cannot be atomically abrupt, especially because we do not expect the different order parameters for each domain to overlap ($b_{12} \gg 0$); neither, equally, do we expect these order parameters to jump abruptly to zero. More likely is the situation sketched in Fig. 3a, where the two order parameters decay over a length scale $\xi_0$ which is typically larger than a lattice constant (and even larger for smaller amplitude charge order modulations). If the coherence length $\xi_0$ is large enough, then it is clearly possible that the twin boundary itself is locally a ferromagnetic metal. Synchrotron x-
ray diffraction evidence consistent with this scenario is found in single crystal
La$_{5/8}$Pr$_y$Ca$_{3/8}$MnO$_3$ [64], but not, for example, in (Pr,Sr,Ca)MnO$_3$ [65], implying that the proposed scenario is not universal.

![Figure 3: Schematic picture of charge-order parameter (striped) and magnetisation (grey) at (a) a twin boundary and at (b) a magnetic domain wall, in situations where the COI and FMM phases are close in energy.](image)

4.3 Domain wall in the FMM

Competition between COI and FMM could also appear when the ferromagnetic phase is the stable ground state if we impose a magnetic domain wall, as in Fig. 3b. Usually magnetisation decays near a boundary over a long length scale determined by the (Heisenberg) exchange parameter and the magnetic anisotropy. One would therefore expect a negligibly small reduction in electronic bandwidth. If however, the suppression of the magnetisation at the FM domain wall were to lead to local charge order [66], this will produce a magnetic weak link akin to what is observed in fabricated magnetic tunnel junctions. Such effects may be responsible for the surprisingly large electrical resistance [67] of albeit apparently wide [68] magnetic domain walls in thin films.

4.4 Incommensurate striped and magnetic phases

In the case of the twin boundary and magnetic domain walls just described, we imagined that these configurations were imposed by external conditions. There is a further possibility, however, that such configurations may not be thus externally (or kinetically) imposed, but might also form long-period thermodynamic phases. To see how this might come about, we should understand how in the Landau theory we might incorporate the chemical tendency to match the period of the COI phases to the nominal Mn(III)/Mn(IV) ratio. Within the weak coupling approach of the Landau theory, one can allow for this by generalising the Landau theory to a complex order parameter

$$\psi_i = \rho_i(r)e^{i(Q_i \cdot r + \phi_i(r))},$$

where the physical charge density modulation is $|\psi_i(r)|$. If we choose the period $Q_i$ to be commensurate with the lattice $Q_i = G_i/n$, with $n$ an integer, and $G_i$ a reciprocal lattice vector of the parent phase, then we can incorporate the possibility of structures with incommensurate periodicities by the phase variable $\phi(r)$. New terms in the free energy dependent upon the phase can have the following form

$$F_\phi = \xi_0^2|\nabla - iq|\psi_i|^2 - gR(\psi^n e^{-iG_i \cdot r}) + ...$$

(7)
The first term represents the preference for an incommensurate phase (where $q$ changes with concentration), and the second term is a commensurability (Umklapp) term that lowers the energy when the density wave lines up appropriately with the underlying lattice ($g$ is a constant and the operator $\mathcal{R}$ returns the real part of its argument).

When the amplitude $\rho_i$ is stiff, these terms in the free energy can be simplified to give

$$F_\phi \approx \xi_0^2 \rho_i^2 |\nabla \phi - q|^2 - g \rho_i^n \cos(n\phi_i(r)).$$

(8)

Here, we assume that the amplitude $\rho_i(T)$ is already fixed by the minimisation of (2) and (3). The minimisation of (8) produces the well-known sine-Gordon equation, and solutions which are solitons. Without discussing the details, notice that if the first term in (8) were dominant, then the phase will tend to “wind” with gradient $q$, whereas the second term suppresses the phase slips and prefers the commensurate phases $\phi = 2\pi j/n$. Arrays of solitons (“discommensurations”) arise at the minimum of the free energy intermediate between these limits. Furthermore, note that for $n > 2$, the last term is of higher order in $\rho_i(T)$ than the first, so that there is generically the possibility of a transition from a commensurate to an incommensurate state with increasing $T$ (and reducing $\rho_i$), whereas no such transition is expected for $n = 2$. This may help to account for the great stability of “1/2” type ordering in the manganites, which exists for a wide range of dopings. Incommensurate states are seen near $x = 2/3$, however, and “frozen-in” discommensurations are sometimes visible in electron micrographs at low temperature in this region of doping [56].

That the phase and amplitude can be so cleanly separated is an approximation justified only in the weak coupling limit when $\rho_i \ll 1$, and $\xi_0|Q_i| \gg 1$. This is probably a poor approximation for the large amplitude distortions common to the manganites, in which case other potential long period phases may be favoured by the competition between the two principal order parameters, modulated by the imposed periodicity $q$ (note that $q$ acts like — and in fact couples to — a lattice strain). One speculation is the possibility of a novel incommensurate magnetic/CO phase, that can be made by a periodic arrangement of either of the configurations shown in Fig. 3. It is therefore possible that these types of configurations may not exist solely because they are externally imposed: they may be thermodynamically stable in their own right.

5 Manipulation of self-organised structures

We remarked near the end of Section 3.2 that it is not the coexistence of different phases in the manganites that is remarkable, but rather the fact that the proportions of these phases can readily adjust to small external forces. It seems therefore that the existing components are indeed in local equilibrium, and that their coexistence is not necessarily enforced because of strong hysteresis or pinning. The ideas framed in the Landau theory of the previous section allow for such a delicate balance, because of the pervasive effects of long-range strain fields.

Two (and perhaps more) broad possibilities allow for quasi-equilibrium coexistence. One is that the domain configurations are topologically frozen in. This is understandable because rearrangements that would remove large domains are kinetically disallowed. Nevertheless, local readjustments could easily be made.
— for example to the proportion of the FMM and COI phases in a frustrated configuration like the one sketched in Fig. 2a. Another class of possibilities is that one has not just the COI and FMM as stable thermodynamic phases, but in addition a host of incommensurate structures built out of periodic arrangements of these two basic subunits. This type of situation is certainly favoured by the natural tendency to incommensurability away from special doping values.

The potential range of self-organising structures in the manganites suggests that it should be possible to produce patterns in a controlled manner — in principle for the purpose of information storage. Strain templating is likely to be an effective means of achieving this because strain is so important in these materials — as discussed throughout this article. The possibility of x-ray lithography and the use of currents to pattern domains has already been suggested.

6 Conclusions

The mesoscale complexity that can arise in the manganites is reminiscent of the complexity that arises in the high temperature superconducting cuprates, or even organic systems. Because the crystal structure of a manganite interacts strongly with the corresponding magnetic and electronic structures, any imposed physical discontinuities in actual samples will likely create or destroy the delicate phase balances that we have described in this article. The challenge is therefore to better demonstrate the intrinsic nature of coexistence in the manganites, and to exploit this coexistence to produce self-organised structures over mesoscopic length scales.

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