Electronic phase separation and other novel phenomena and properties exhibited by mixed-valent rare-earth manganites and related materials

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Transition metal oxides, such as the mixed-valent rare-earth manganites Ln(1−x)A_xMnO_3 (Ln, rare-earth ion, and A, alkaline-earth ion), show a variety of electronic orders with spatially correlated charge, spin and orbital arrangements, which in turn give rise to many fascinating phenomena and properties. These materials are also electronically inhomogeneous, i.e. they contain disjoint spatial regions with different electronic orders. Not only do we observe signatures of such electronic phase separation in a variety of properties, but we can also observe the different ‘phases’ visually through different types of imaging. We discuss various experiments pertaining to electronic orders and electronic inhomogeneities in the manganites and present a discussion of theoretical approaches to their understanding.

It is noteworthy that the mixed-valent rare-earth cobaltates of the type Ln(1−x)A_xCoO_3 also exhibit electronic inhomogeneities just as the manganites.

Keywords: rare-earth cobaltates; rare-earth manganites; electronic phase separation; charge-ordering

1. Introduction

Transition metal oxides such as rare-earth manganites, cuprates and cobaltates exhibit a plethora of properties and phenomena (Imada et al. 1998; Rao 2000) that have stimulated sustained investigations by materials chemistry and physics communities. Many of the fascinating properties of these oxides arise from the fact that the transition metal ions can exhibit mixed valence with strongly correlated electrons giving rise to many ‘electronic orders’. By electronic orders, we mean spatially correlated arrangement of charge, spin, orbital and/or phase (as in a superconductor). In addition, there is overwhelming evidence that these oxides with high chemical homogeneity can show spatially inhomogeneous structures, i.e. regions showing different electronic orders (Mathur & Littlewood 2003; Rao 2000).

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While many issues pertaining to these oxides have been understood, their science has many puzzles and challenges in addition to the promise of applications. The development of new oxide materials via the methods of materials chemistry with controlled electronic orders, and their theoretical understanding, therefore, continue to be at the forefront of research in condensed matter science.

In this article, we discuss spin, charge and orbital orders in transition metal oxides, in particular, in the rare-earth manganites which have become famous since 1993 owing to the phenomenon of colossal magnetoresistance (CMR) exhibited by them (Rao & Raveau 1998). We also touch upon the issue of electronic inhomogeneities; we discuss the signatures of the presence of such inhomogeneities and theoretical approaches to understand the same.

2. Electronic orders in rare-earth manganites

Rare-earth manganites of the type Ln\(_{1-x}\)A\(_x\)MnO\(_3\) (Ln, rare-earth ion, and A, alkaline-earth ion) which crystallize in the perovskite structure were investigated several years ago by Wollan & Koehler (1955), but it was the discovery of CMR that stimulated their resurgence (Rao & Raveau 1998; Dagotto et al. 2001; Salamon & Jaime 2001; Tokura 2006). In the parent undoped compound LaMnO\(_3\), the manganese ions exist in a +3 state, while the doped system such as La\(_{1-x}\)Ca\(_x\)MnO\(_3\) contains (nominally) a fraction \((1-x)\) of Mn\(^{3+}\) and \(x\) of Mn\(^{4+}\) ions. This mixed-valent character of Mn underlies the rich phase diagrams (figure 1) exhibited by the manganites. A study of the phase diagram reveals a large number of electronic orders present in these systems. In what follows, we discuss some of these electronic orders.

LaMnO\(_3\) exhibits spin, orbital and lattice orders. The spin order is that of an A-type antiferromagnet (figure 2). This is accompanied by the orbital order, which couples strongly with the lattice distortion due to the Jahn–Teller (JT) effect, giving rise to the lattice distortion pattern shown in figure 2. Interestingly, the JT distortion pattern loses long-range order at approximately 750 K. This transition is also associated with a symmetry change of the crystal from an
orthorhombic structure at lower temperatures (due to the cooperative JT distortion) to a cubic structure at higher temperatures. At low temperatures, the combination of orbital ordering and JT distortion leads to an effective ferromagnetic (FM) exchange interaction between the spins on the plane, and a strong antiferromagnetic (AFM) exchange between spins between the planes, resulting in an A-type AFM arrangement of the spins. Other undoped manganites such as NdMnO₃ also show a similar electronic order.

Doping of manganites with alkaline-earth ions such as Ca²⁺ and Sr²⁺ results in a fraction of the manganese ions occurring in the +4 state, giving rise to a new electronic order, charge order, wherein the +3 and +4 charges of the Mn ions are arranged in a periodic fashion (figure 3). Charge order is known to occur in other metal oxides as well, Fe₃O₄ being a well-known example (Rao 2000). The charge-ordered state is found predominantly in manganites with small Ln and A ions. Further, charge order disappears at high temperatures. Thus, in Pr₀.₇Ca₀.₃MnO₃, charge order appears only below 230 K. Interestingly, Pr₀.₇Ca₀.₃MnO₃ also shows AFM order below 170 K, where both antiferromagnetism and charge order coexist. At low temperatures, this manganite is electrically insulating. In contrast, La₀.₇Ca₀.₃MnO₃ does not show charge order, although it enters a FM metallic phase below a Curie temperature of 230 K, showing a PM insulating behaviour above this temperature. In the Sr-based La₀.₇Sr₀.₃MnO₃, the high-temperature PM phase is metallic. Note that the average radius of the A-site cations, \( \langle r_A \rangle \), is larger in these two manganites than in Pr₀.₇Ca₀.₃MnO₃. CMR is observed at relatively moderate fields in La₀.₇Ca₀.₃MnO₃. Another important aspect of the doped manganites is that, when the size of the A-site cation (or the e₉ bandwidth) is large enough, electrons of the Mn³⁺ hop to Mn⁴⁺ by the double-exchange (DE) mechanism. The DE mechanism plays a crucial role in the occurrence of charge order.

Figure 2. (a) A-type antiferromagnetic spin order, (b) Jahn–Teller distortion pattern and (c) orbital ordering in LaMnO₃ (after Rao (2000)).
metallicity and ferromagnetism in these materials. The phenomenon of CMR is explained by invoking the DE mechanism along with certain competing interactions involving phonons. Charge ordering is exactly the opposite of DE, since it localizes electrons creating an AFM insulating state.

Half-doped manganites show many interesting electronic orders. For example, Nd$_{0.5}$Sr$_{0.5}$MnO$_3$, which is a FM metal at high temperatures, shows a transition to a charge-ordered AFM state at approximately 150 K. The charge-ordering temperature is usually somewhat higher than the magnetic-ordering temperature ($T_{\text{CO}} \gtrsim T_N$). Interestingly, the charge order can be ‘melted’ by a small magnetic field (Kuwahara et al. 1995). At low temperature, the charge-ordered state is associated with a CE-type AFM order (figure 3), orbital order and a regular pattern of JT distortions. The magnetic order consists of $ab$ planes stacked along the $c$-axis (figure 3) with an AFM coupling between spins on neighbouring planes. This may be contrasted with A-type order (figure 2). Note that there is no charge ordering in an A-type antiferromagnet unlike in a CE-type antiferromagnet. Usually, orbital and spin orders that are not accompanied by charge order show A-type antiferromagnetism.

The presence of charge and orbital orders can be observed experimentally by a study of the structures of the manganites. For example, Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ consists of distorted oxygen octahedra (figure 4) containing zigzag chains with alternate long and short Mn–O bonds. The bond lengths are 1.921 and 2.021 Å along $\langle 110 \rangle$ and 1.881 and 2.020 Å along $\langle -110 \rangle$ (figure 4). The emergence of a charge gap is also indicated by vacuum tunnelling measurements (Biswas et al. 1997). Intriguingly, the low-temperature gap (approx. 250 meV) is much larger than $T_{\text{CO}} \sim 12$ meV. Moreover, a magnetic field of 6 T (approx. 1.2 meV) can destroy the charge-ordered state. A consequence of this is the large magnetostrictive effect arising from the magnetic field-induced structural transition that accompanies the AFM charge-ordered insulator to FM-metal transition.

An interesting fundamental question that arises is, what controls the different electronic orders? At the level of the chemistry of the constituents, the mean A-site cation radius $\langle r_A \rangle$ is expected to play an important role. This arises from the

![Figure 3. Ordering of charge, spin and orbital in doped manganites. (a) CE-type order, the dashed line shows the unit cell and (b) A-type order. In both figures, circles correspond to Mn$^{4+}$ (after Rao (2000)).](http://rsta.royalsocietypublishing.org/)
fact that the bandwidth of the $e_g$ electrons of Mn ions is affected by the size of the A-site cation, i.e. increasing $h_{A}$ is equivalent to increasing the hydrostatic pressure, which increases the Mn–O–Mn bond angle and consequently the bandwidth. Detailed studies of the effect of $h_{A}$ on the electronic order have been reported by Woodward et al. (1998). Systems with very large $h_{A}$ tend to be FM and metallic, with a Curie temperature $T_{c}$ that increases with $h_{A}$. Charge ordering is also strongly affected by $h_{A}$, with a smaller $h_{A}$ stabilizing charge-ordered phase at low temperatures. It is evident that the tuning of $h_{A}$ via chemical means provides an important means of controlling the phase of the manganite.

3. Electronic inhomogeneities in rare-earth manganites

As noted in §1, there is strong experimental evidence to indicate that many correlated oxides are electronically inhomogeneous (figure 5). Nowhere is it manifested better than the rare-earth manganites. Thus, these materials of high chemical homogeneity consist of different spatial regions with different electronic order (Mathur & Littlewood 2003; Rao et al. 2004; Dagotto 2005; Shenoy et al. 2006), a phenomenon that has come to be known as ‘phase separation’. These regions can be static or dynamic and can be tuned by the application of external stimuli like a magnetic field. Moreover, the size scale of these inhomogeneities can vary from nanometres to as large as micrometres. The presence of electronic inhomogeneities raises many intriguing questions. What is the microscopic origin of these inhomogeneities? Why do they possess such a large range of length-scales? More importantly, are they responsible for the CMR and such responses exhibited by the manganites and related oxide materials? Indeed, there are suggestions in the literature that these features observed in correlated oxides indicate that they...
are ‘electronically soft’ providing the possibility of spatial tuning of electronic 
properties, not unlike the liquid crystalline materials (Mathur & Littlewood 2003; 
Dagotto 2005; Milward et al. 2005). In this section, we discuss the phase separation 
phenomena especially in the rare-earth manganites. Following a description of the 
experimental signatures of electronic inhomogeneities, we discuss the theoretical 
ideas put forth to understand this phenomenon in §3a.

(a) Signatures of electronic inhomogeneities

Investigations employing a variety of experimental probes indicate the presence 
of electronic inhomogeneities. When the length-scale of the inhomogeneities is large 
(a few hundred nanometres), structural and magnetic information from the X-ray 
and neutron diffraction patterns show clear signatures. Specialized local probes such 
as NMR and Mössbauer spectroscopies can be used to probe inhomogeneities at a 
smaller length-scale. Thermodynamic (e.g. magnetization) and transport measure-
ments also indicate the presence of inhomogeneities. Direct observational evidence 
provided by images employing transmission electron microscopy, scanning probe 
microscopy and photoemission micro-spectroscopy makes for a convincing case for 
the presence of the electronic inhomogeneities.

The pioneering work on manganites by Wollan & Koehler (1955) revealed the 
presence of electronic inhomogeneities. They observed both FM and AFM peaks 
in the magnetic structure of La$_{1-x}$Ca$_x$MnO$_3$ obtained from neutron scattering. 
They concluded that there is the simultaneous presence of ferromagnetism and 
antiferromagnetism in this material. A more recent neutron diffraction study is 
that of Woodward et al. (1999) on Nd$_{0.5}$Sr$_{0.5}$MnO$_3$. This material first becomes 
FM at 250 K, partially transforming to an A-type AFM phase at approximately 
220 K, followed by a transformation of a substantial fraction to a CE-type AFM 
phase at approximately 150 K. The CE-type AFM (abbreviated as CO-CEAF) 
phase has a simultaneous ordering of spins, orbitals and charge in a complex 
spatial arrangement as shown in figure 3. It is evident from the studies of 
Woodward et al. (1999) that the three phases coexist at low temperatures. 
The size scale of the inhomogeneities is at least in the mesoscopic range.

Figure 5. Schematic of electronic phase separation. Shaded portions indicate FM metallic regions; 
the unshaded portions correspond to AFM insulating regions. (a) FM metallic puddles in an 
insulating AFM background, (b) metallic regions with insulating droplets, (c) charged stripes and 
(d) phase separation on the mesoscopic scale.
(a few hundred nanometres or more), since they are large enough to produce well-defined reflections in neutron and X-ray diffraction patterns. The variation of the volume fraction of the three phases with temperature is shown in figure 6a. This phase diagram has an unusual feature with the three phases existing at the 150 K transition and below. The effect of the volume fractions of the electronic inhomogeneities due to an external magnetic field was studied by Ritter et al. (2000). The results shown in figure 6b demonstrate the evolution of the inhomogeneities where the FM fraction grows at the expense of the AFM regions in the presence of the applied magnetic field. Note the growth of one phase at the cost of another in figure 6. Clearly, the phase separation observed here is of a non-trivial type, in contrast to a situation where the sample is not phase-pure containing multiple phases that are both structurally and chemically distinct. Another interesting example (Radaelli et al. 2001) of phase separation is in Pr$_{0.7}$Ca$_{0.3}$MnO$_3$, which shows the presence of two distinct phases below the charge-ordering transition at 80 K. A charge-ordered AFM phase and a charge-delocalized phase have been observed by neutron diffraction.

Signatures of electronic inhomogeneities may be inferred from magnetic and electron transport measurements as well. Sudheendra & Rao (2003) studied these properties of (La$_{1-x}$Ln$_x$)$_{0.7}$Ca$_{0.3}$MnO$_3$, where Ln = Nd, Gd or Y. The lanthanide element was varied to control the average A-site cation radius $\langle r_A \rangle$. In the case of the La compound ($x=0.0$) with the largest value of $\langle r_A \rangle$, a clear FM transition with a saturation magnetization of 3$\mu_B$ is observed (figure 7a) up to a critical Nd doping of $x \leq x_c \approx 0.5$. At higher values of Nd doping ($x > x_c$), there is a monotonic increase of the magnetization with decrease in temperature, although the magnetization never attains the maximum value of 3$\mu_B$. Interestingly, reducing the value of $\langle r_A \rangle$ by Gd (intermediate value of $\langle r_A \rangle$) or Y (smallest value of $\langle r_A \rangle$) substitution decreases the $x_c$, i.e. the critical doping value $x$ above which the sharp FM transition vanishes,
Figure 7. (a) Temperature dependence of the effective magnetic moment per formula unit in (La$_{1-x}$Ln$_x$)$_{0.7}$Ca$_{0.3}$MnO$_3$. (b) Temperature dependence of the resistivity in (La$_{1-x}$Ln$_x$)$_{0.7}$Ca$_{0.3}$MnO$_3$. The insets show the ‘resistivity hysteresis’ upon warming of the sample. In graphs in (a) and (b), (i), (ii) and (iii) correspond to Ln=Nd, Gd and Y, respectively. (c) Variation of (i) magnetization and (ii) resistivity as with temperature. The data shown are in Ln$_{0.7-x}$La$_x$A$_{0.3-y}$A$_y$MnO$_3$ with mean radius of the A-site cation are fixed at 1.216 Å. The different curves show results for different $\sigma^2 ((a,b)$ after Sudheendra & Rao (2003) and (c) after Kundu et al. (2005b)).

reduces with the mean A-site cation radius $\langle r_A \rangle$. Moreover, the FM transition temperature $T_c$ for $x < x_c$ increases with $\langle r_A \rangle$ as expected. The precipitous reduction of the saturation magnetization at $x \geq x_c$ is a signature of electronic and magnetic inhomogeneities induced by the A-site cation disorder. Transport measurements also show the signature of electronic inhomogeneities. In figure 7b, we show the variation of resistivity with temperature to demonstrate that all the three substitutions of manganites with Ln=Nd, Gd and Y exhibit a metal–insulator transition for $x < x_c$. The insets in figure 7b show the resistivity hysteresis across the
transition. The insulator–metal transition temperature decreases linearly on doping and increases nearly linearly with \( h_A \). Electronic phase separation in such manganites generally occurs when \( \langle r_A \rangle \) is relatively small (<1.18 Å) and is favoured by size disorder arising from the size mismatch between the A-site cations. This disorder is quantified (Rodríguez-Martínez & Attfield 2001) by the parameter \( \sigma^2 = \sum_i x_i r_i^2 - \langle r_A \rangle^2 \), where \( x_i \) is the fractional A-site occupancy of species \( i \) with radius \( r_i \). A study of several series of manganites with fixed \( \langle r_A \rangle \) and varying \( \sigma^2 \) shows that, as \( \sigma^2 \) is lowered, the phase-separated system transforms to a FM metallic state. It has been demonstrated recently (Kundu et al. 2005b) that in a series of manganites of the type \( \text{Ln}_{0.7-x}\text{Lu}_x\text{A}_{0.3-y}\text{A}_y\text{MnO}_3 \), where \( \langle r_A \rangle \) always remains large (thereby avoiding effects due to bandwidth), a decrease in \( \sigma^2 \) transforms the insulating non-magnetic state to a FM metallic state (figure 7c).

The above examples, while being indicative of the existence of multiple electronic and magnetic phases within a single apparently structurally and chemically pure phase, do not provide direct evidence with regard to the length-scale of the

Figure 7. (Continued.)
inhomogeneities. While diffraction provides evidence of electronic phase separation on a mesoscale, NMR spectroscopy has revealed the possibility of phase separation at nanoscopic scales (Kuhns et al. 2003).

(b) Visual evidence for electronic phase separation

We now turn to the experimental work that shows direct visual evidence of electronic inhomogeneities, thereby allowing one to probe the length-scale of the inhomogeneity. One of the earliest reports of the direct evidence of electronic patterns in manganites was in the hole-doped side of (La, Ca)MnO₃. Mori et al. (1998) observed charged stripes in thin films of La₁₋ₓCaₓMnO₃ with 0.5 ≤ x ≤ 0.75 by high-resolution lattice images obtained by transmission electron microscopy. The spatial structure consisted of paired JT distorted oxygen octahedra surrounding the Mn⁴⁺ ions, separated by stripes of Mn⁴⁺O₆ octahedra. The spacing of the stripes, usually 5–10 lattice spacings, was found to be governed by the doping. The electronic inhomogeneity in this case was of a nanoscopic length-scale. Further evidence of nanoscopic electronic inhomogeneity in manganites was obtained by a scanning tunnelling microscopy study of Bi₁₋ₓCaₓMnO₃ (x ≈ 0.75) by Renner et al. (2002). They found nanoscopic charge-ordered and metallic domains which correlated with the structural distortions.

The first direct evidence of mesoscale inhomogeneities in manganites was provided by Uehara et al. (1999), who observed electronic inhomogeneities in La₀.₆₂₅₋ₓPrₓCa₀.₃₇₅MnO₃ by transmission electron microscopy. This work demonstrated the coexistence of charge-ordered (insulating) regions with
interspersed FM metallic domains with a typical size of approximately 0.2 \( \mu \text{m} \), bringing these features of inhomogeneity up to the mesoscopic scale. The authors suggested a possible mechanism for the colossal magnetoresistive response arising from such an electronic and magnetic inhomogeneity. The spin alignment of each of the FM metallic domains is random and the spin-polarized conduction electron of one domain cannot hop effectively via other domains due to the absence of available electronic states with the correct spin configuration on other randomly oriented magnetic domains. On application of a magnetic field, the spins of different magnetic domains align, enabling an unhindered hopping of electrons, thereby resulting in a drastic reduction of the resistance, known as the colossal negative magnetoresistance. This study suggested that such a mesoscopic phase separation is essential for colossal responses. Approximately at the same time, Fäth et al. (1999) used scanning tunnelling spectroscopy to study metal–insulator transitions in La\(_{0.7}\)Ca\(_{0.3}\)MnO\(_3\) and found evidence of electronic inhomogeneities with a mesoscopic scale of approximately 0.2 \( \mu \text{m} \), below the FM transition temperature, with FM metallic domains interspersed in insulating regions, just as in the work by Uehara et al. (1999). Most interestingly, the domains evolved as a function of the applied magnetic field, with the volume fraction of the magnetic (metallic) domains increasing at the cost of the non-magnetic (insulating) parts, closely accompanying the decrease in the resistivity with the magnetic field. This scenario contrasts with the spatially static phase separation scenario suggested by Uehara et al. (1999).

A magnetic force microscope study of La\(_{0.33}\)Pr\(_{0.34}\)Ca\(_{0.33}\)MnO\(_3\) by Zhang et al. (2002) has indicated that magnetic domains of mesoscopic scale evolved with temperature showing magnetic hysteresis coinciding with the resistivity hysteresis. This observation again suggested that mesoscale inhomogeneities are possibly crucial for colossal responses in magnetoresistance. Loudon et al. (2002) have studied La\(_{0.5}\)Ca\(_{0.5}\)MnO\(_3\) using transmission electron microscopy and electron holography and found mesoscopic domains of FM regions interspersed in insulating regions. They also found evidence that some of the FM regions were charge ordered. A possible interpretation of the result is that the mesoscopic FM region is itself inhomogeneous at the nanoscale with coexisting metallic and charge-ordered regions.

A final example of mesoscale electronic inhomogeneities is from the experiments of Sarma et al. (2004), who used photoemission spectromicroscopy which has the advantage of spatially resolving the local metallic/non-metallic nature and simultaneously determining the local chemical composition with a resolution of approximately 0.5 \( \mu \text{m} \). Using this technique, they studied La\(_{0.25}\)Pr\(_{0.375}\)Ca\(_{0.375}\)MnO\(_3\). The key finding was that the material showed very large (10\(\times\)5 \( \mu \text{m}^2 \)) domains of insulating regions interspersed in a metallic background. These regions evolved on increasing temperature, with the metallic regions undergoing a metal-to-insulator transition at higher temperatures. On cooling the sample back to low temperatures, the insulating regions appeared essentially at the same locations, indicating, for the first time, a memory effect associated with the electronic inhomogeneities.

4. Electronic phase separation in rare-earth cobaltates

Electronic phase separation in rare-earth cobaltates of the type Ln\(_{1-x}\)A\(_{x}\)CoO\(_3\) has come to the fore in the last 2 years. La\(_{0.5}\)Sr\(_{0.5}\)CoO\(_3\) and other members of this family were once considered to be itinerant electron ferromagnets
showing metallic behaviour, but it was recognized later that the FM ordering was not long range (Rao et al. 1977; Señaris Rodríguez & Goodenough 1995). It is now established that La$_{0.5}$Sr$_{0.5}$CoO$_3$ exhibits a glassy magnetic behaviour (Wu et al. 2005). Recent studies of the magnetic and electrical properties of several members of the Ln$_{1-x}$A$_x$CoO$_3$ family have revealed that they are electronically phase-separated (Burley et al. 2004; Kundu et al. 2005a; Wu et al. 2005). The phase separation is favoured by small $\langle r_A \rangle$ as well as size disorder (Kundu et al. 2006). Measurements of magnetic relaxation and memory effects have shown that glassy behaviour is common among the cobaltates (Kundu et al. 2005a, 2006). Studies employing local probes such as NMR and Mössbauer spectroscopy have provided direct evidence for different distinct species involving large magnetic/metallic clusters and small non-magnetic clusters (Bhide et al. 1975; Kuhns et al. 2003). Thus, the NMR and Mössbauer studies of La$_{(1-x)}$Sr$_x$CoO$_3$ show distinct signals corresponding to FM and PM species. Cobalt Mössbauer spectra show a signal due to the CM species, but are always accompanied by a signal due to the PM species even at low temperatures ($T<T_c$). In figure 8, we show the variation of the FM to PM ratio with composition in La$_{(1-x)}$Sr$_x$CoO$_3$. In the inset, the variation of the FM to PM ratio of La$_{0.5}$Sr$_{0.5}$CoO$_3$ with temperature is shown (Kundu et al. 2007). Cobalt NMR studies of a cobaltate with small $\langle r_A \rangle$ has shown the presence of two distinct signals varying in intensity with temperature (Kundu et al. 2007).

5. Theoretical approaches

We now turn to a discussion of theoretical ideas that have been proposed to explain the origin of the electronic inhomogeneities, with specific focus on manganites. The simplest possible description of manganites at a microscopic level
involves the Mn d-orbitals and the lattice distortion of the oxygen octahedron surrounding the Mn ion (Dagotto 2003). The octahedral crystal field splits the degeneracy of the five Mn d-orbitals into three degenerate t$_{2g}$ orbitals and two degenerate e$_g$ orbitals. In the doped manganites, both Mn$^{3+}$ and Mn$^{4+}$ configurations are present; both have three electrons in the t$_{2g}$ orbitals, and Mn$^{3+}$ has, in addition, a lone electron in one of the e$_g$ orbitals. The spins of the t$_{2g}$ electrons are aligned parallel due to strong Hund coupling, and it is only the resulting ‘core spins’ ($S=3/2$) of the t$_{2g}$ electrons that affect the low-energy physics of manganites. Thus, the relevant degrees of freedom at each manganese site are: an average of $(1-x)$ electrons per site populating the two e$_g$ orbitals, the t$_{2g}$ core spins and lattice (phonon) degrees of freedom corresponding to the distortion of the oxygen octahedra surrounding the manganese ion. The e$_g$ electrons hop from a Mn site to neighbouring Mn sites with an amplitude $t$ (approx. 0.2 eV). The spin of the e$_g$ electron has a strong FM Hund coupling $J_H$ (approx. 2.0 eV) with the local t$_{2g}$ core spin. Another important energy scale is the on-site Mott–Hubbard repulsion $U$ (approx. 5.0 eV) which forbids double occupancy of the local e$_g$ sector. Neighbouring t$_{2g}$ spins interact with each other via an AFM superexchange coupling $J_{SE}$ (approx. 0.02 eV). Finally, the energy gained by the JT distortion of the oxygen octahedron is given by $E_{JT}$ (approx. 0.5 eV). Competition between these different interactions, leading to a variety of states very close in energy, is responsible for the complex phase diagram of manganites with many electronic orders, and their extreme sensitivity to external perturbations such as temperature, magnetic field and strain (Sarma et al. 1995; Satpathy et al. 1996; Millis 1998; Ramakrishnan et al. 2003; Cepas et al. 2006).

Owing to the difficulties of dealing with all the degrees of freedom and competing interactions mentioned above, much of the early work aimed at understanding colossal responses and electronic inhomogeneities in manganites has been based on simplified models which neglect one or more of them. A prominent example is the work of Dagotto and coworkers (Dagotto 2003), who studied simple magnertic Hamiltonians with competing phases that are separated by a first-order transition. Based on these studies, they suggested that the system is prone to macroscopic phase separation, which is frustrated by disorder leading to the electronic inhomogeneities at various scales, the magnitude of the disorder determining the scale. From the real-space structure obtained from simulations, they constructed a random resistor network to explain the colossal responses by a mechanism similar to the one proposed by Fäth et al. (1999), again suggesting that the phase separation is key to colossal responses. Other simplified models have been studied, and alternate scenarios have been proposed. There are also suggestions that manganites close to half doping are near a multicritical point with competing phases affected by disorder (Motome et al. 2003; Tokura 2006). Ahn et al. (2004) consider a model Hamiltonian including electron–phonon interaction, and long-range elastic coupling between local lattice distortions. They present a scenario for mesoscopic/microscopic inhomogeneities and suggest that these are responsible for the colossal responses.

We now turn to a recent study of electronic inhomogeneities in manganites (Shenoy et al. 2007), which attempts to take into account all the degrees of freedom and their interactions based on the $\ell\delta$ model (Ramakrishnan et al. 2003, 2004; Krishnamurthy 2005).
(a) The \(lb\) model for manganites

The \(lb\) model (Pai et al. 2003; Ramakrishnan et al. 2004) uses the idea that, under the conditions prevailing in doped manganites, the electrons populating the doubly degenerate e\(_g\) states centred at the Mn sites spontaneously reorganize themselves into two types of coexisting electron fluids. One is obtained by populating essentially site-localized states labelled \(\ell\) which are polaronic, with strong local JT distortions of the oxygen octahedra, an energy gain \(E_{\text{JT}}\) and exponentially reduced intersite hopping. The other, labelled \(b\), is a fluid of broadband, non-polaronic electrons, with no associated lattice distortions and undiminished hopping amplitudes. There is a strong local repulsion between the two fluids, as double occupancy on a site costs an extra Coulomb of energy \(U\). The spins of the \(\ell\) electrons can be regarded as spinless, leading to the Falicov–Kimball (Freericks & Zlatić 2003) like \(lb\) Hamiltonian

\[
H_{lb} = -E_{\text{JT}} \sum_i n_{\ell_i} - \sum_{\langle ij \rangle} (b_i^\dagger b_j + \text{h.c.}) + U \sum_i n_{\ell_i} n_{bi}. \tag{5.1}
\]

Here, \(\ell_i^\dagger\) and \(b_i^\dagger\) create \(\ell\) polarons and \(b\) electrons, respectively, at the sites \(i\) of a cubic Mn lattice, and \(n_{\ell_i} \equiv \ell_i^\dagger \ell_i\), and \(n_{bi} \equiv b_i^\dagger b_i\) are the corresponding number operators.

(b) The extended \(lb\) model and the effects of long-range Coulomb interactions

This model assumes that the Mn ions occupy the sites of a cubic lattice (taken to be of unit lattice parameters), while the dopant A ions occupy an \(x\) fraction of the ‘body centre’ sites of each unit cube formed by the Mn ions. Since the aim is to study the effect of long-range Coulomb interactions on phase separation, we make further simplifying assumptions. It is assumed that the t\(_{2g}\) core spins are aligned ferromagnetically and that \(J_H \rightarrow \infty\); this effectively projects out \(\ell\) or \(b\) electron spin opposite to that of the t\(_{2g}\) core spins—we obtain an effectively spinless model. The above considerations lead us to the following extended \(lb\) Hamiltonian

\[
H = H_{lb} + H_C \quad \text{and} \quad H_C = \sum_i \Phi_i q_i + \frac{V_0}{2} \sum_{ij} \frac{q_i q_j}{r_{ij}}. \tag{5.2}
\]

Here \(\ell_i^\dagger\) and \(b_i^\dagger\) create \(\ell\) and \(b\) electrons, respectively, at site \(i\), and \(n_{\ell_i} \equiv \ell_i^\dagger \ell_i\) and \(n_{bi} \equiv b_i^\dagger b_i\) are the corresponding number operators. In terms of the hole operator \((h_i^\dagger \equiv \ell_i^\dagger\), which removes an \(\ell\) polaron at site \(i\)), the electron charge operator \(q_i \equiv h_i^\dagger h_i - b_i^\dagger b_i\) and has the average value \(x\) per site owing to overall charge neutrality. The Coulomb term \(H_C\) has two parts; the charge at site \(i\) has energy \(q_i \Phi_i\), where \(\Phi_i\) is the electrostatic potential there due to \(\text{A}^{2+}\) ions, and the interaction between the charges at sites \(i\) and \(j\) leads to an energy \(V_0((q_i q_j)/r_{ij})\). In what follows, we take the short-range Coulomb correlation \(U\) to be large (\(\infty\)).

We now discuss the results of full-scale numerical simulations of the Hamiltonian (5.2) on finite three-dimensional periodic lattices, allowing for a random distribution of the A ions following Shenoy et al. (2007). Here, all the energy scales are normalized by the bare intersite hopping amplitude \(t\). Systems as large as \(20 \times 20 \times 20\) have been considered. The numerical determination of the groundstate of (5.2) requires further simplifying approximations. The most important approximation is the Hartree approximation, i.e. the charge operator \(q_i\).
is replaced by its expectation value in the groundstate $\langle q_i \rangle = h_i^\dagger h_i - \langle b_i^\dagger b_i \rangle$. Since we have assumed that $U \to \infty$, the $b$ electrons do not hop to sites where an $\ell$ polaron is present. This leads to the segregation of the two types of electron into disjoint clusters. In a cluster of hole sites (which has at least two nearest neighbour hole sites), which we call a ‘clump’, the $b$ electron states are determined by solving the quantum kinetic energy Hamiltonian exactly. This is a new generalization of the common Coulomb glass simulation (Baranovskii et al. 1979; Davies et al. 1984; Vojta & Schreiber 2001), which includes the quantum mechanically obtained $b$ states within their clump or puddle. The electrostatic energy is calculated accurately using the Ewald technique and fast Fourier transform routines.

In the absence of the long-range Coulomb interaction ($V_0 = 0$), this procedure leads to the macroscopically phase-separated state (see inset of figure 9). The holes aggregate to one side of the simulation box and a fraction of the electrons occupying the $\ell$ states is promoted to the $b$ states in the one large hole clump—with their concentrations determined by the equality of the chemical potential in the two regions (i.e. the highest occupied $b$ level equals $-E_{JT}$). This phase separation is due to the strong Coulomb repulsion between the two types of electron fluids and is in agreement with known results on the Falicov–Kimball model (Freericks et al. 2002; Freericks & Zlatić 2003).

Long-range Coulomb interaction ‘frustrates’ phase separation, i.e. macroscopic phase separation costs prohibitive energy in the presence of long-range Coulomb interactions. The precise nature of the resulting groundstate electronic configuration depends on the JT energy $E_{JT}$ and the doping level $x$. There are two critical doping levels $x_{c1}$ and $x_{c2}$ for any given JT energy $E_{JT}$. When the doping level is less than $x_{c1}$, i.e. $x < x_{c1}$, no $b$ states are occupied—the holes (and hence also the $\ell$ polarons) form a Coulomb glass (Efros & Shklovskii 1975). When the doping exceeds $x_{c1}$, some of

Figure 9. Real-space electronic distribution obtained from simulations on a $10^3$ cube. Magenta (darkest) denotes hole clumps with occupied $b$ electrons, white (lightest) denotes hole clumps with no $b$ electrons, cyan (2nd lightest) denote singleton holes, and light blue (2nd darkest) represents regions with $\ell$ polarons. (a) Isolated clumps with occupied $b$-electrons ($b$-electron puddles). (b) Larger doping; percolating clumps. Inset: ‘macroscopic phase separation’ absence of long-range Coulomb interaction ($V_0 = 0.0$) (after Shenoy et al. (2007)).

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the hole clumps are occupied and the groundstate consists of isolated $b$-electron puddles dispersed in a polaronic background (figure 9). There is a second critical doping level $x_{c2}$ (see Shenoy et al. 2007); when $x \geq x_{c2}$ the occupied $b$-electron puddles percolate and the system attains metallicity (figure 9).

The size scale of the electronic inhomogeneity is nanometric. However, its dependence on $V_0$ differs fundamentally from the analytical results of the same model, which assumed a homogeneous distribution (jellium) of the dopant A ions. For the more realistic, random distribution of the A ions, the size of the electronic inhomogeneity is almost independent of the long-range Coulomb parameter $V_0$, in that even an extremely small $V_0$ produces clump sizes that are of the size scale of a few lattice spacings. The dependence of the average size of the electronic inhomogeneity is thus due to the long-range Coulomb interaction which along with the random distribution of A ions acts as a ‘singular perturbation’ that frustrates macroscopic phase separation. However, the sizes and the distribution of the clumps are determined by the random distribution of the A ions, and thus we conclude that doped manganites (and similarly, possibly many other correlated oxides) are necessarily and intrinsically electronically inhomogeneous, on a nanometric scale.

The results of the extended \[lb\] model with realistic energy parameters presented here provide several new insights into the complex electronic inhomogeneities seen in correlated oxides, and in particular the low-bandwidth manganites with a large FM region in their phase diagram. These arguments may be sharply contrasted with earlier work. In particular, this work suggests that the nanoscale inhomogeneities in manganites arise not out of ‘phase competition’-induced phase separation frustrated by disorder as argued from the studies of model spin Hamiltonians (Dagotto 2003), but from short-range Coulomb correlation-induced phase separation frustrated by long-range Coulomb interaction, similar to what has been suggested in cuprates (Emery et al. 1990; Emery & Kivelson 1993). Most importantly, nanoscale electronic inhomogeneities are present in both the insulating and metallic phases of doped manganites. As is evident from figure 9, each of these constitute a single thermodynamic phase that is homogeneous at mesoscales. One has a metal–insulator transition between two such nanoscopically inhomogeneous phases at $x_{c2}$ as a function of doping. These observations are in agreement with experiments. Indeed, the electron holography results of Loudon et al. (2002) show that even the ferrometallic regions have interspersed in them charge-ordered insulating regions which can be interpreted as the cluster of $\ell$ states.

6. Concluding remarks

A number of competing energy scales are operative in mixed-valent correlated oxides giving rise to a large number of electronic orders. In the Ln(1-$x$)A$_x$MnO$_3$ manganites, a variety of spin, charge and orbital (and associated lattice order) is found. The emergence of these orders can be understood based on a simple parametrization, i.e. the mean A-site cation radius which controls the bandwidth of the $e_g$ electrons. An intriguing aspect of these materials is that small perturbations can drive a transition from one type of electronic order to another, as is evident from the effect of a small magnetic field on the charge-ordered state.

In addition to the large number of electronic orders, it is found experimentally that there is coexistence of different electronic orders in disjoint spatial regions,
i.e. these materials are electronically inhomogeneous showing signatures in thermodynamic and transport properties and can be seen directly in several experimental probes. These inhomogeneities can be of varied scales (nm to μm) and can be static or dynamic. Although the phenomenon has been called phase separation, it is clear that the regions of distinct electronic order may not necessarily be ‘thermodynamic phases’, particularly in the case where they are of nanometric scale. Indeed, the theoretical model discussed in the paper shows that a single ‘phase’ of the manganite itself is inhomogeneous on a nanometric scale.

Although, we have focused on manganites and cobaltates, electronic inhomogeneities are important in many other oxides. In the high $T_c$ cuprate $La_2CuO_4$, the electronic phase separation is caused by compositional variations with superconducting clusters of $La_2CuO_{3.06}$ and AFM clusters of $La_2CuO_{3.01}$ (Sigmund & Müller 1994). Even in the cuprates that possess chemical homogeneity on a mesoscale, it has been suggested that the unusual variation of zero-temperature superfluid density with the superconducting transition temperature is due to the possible coexistence of AFM and superconducting domains (Broun et al. 2005). Neutron-scattering measurements suggest the presence of charge stripes (Tranquada et al. 2004), while scanning probe microscopy indicates a spatially inhomogeneous superconducting gap (McElroy et al. 2005).

Theoretical understanding of the phenomenon of electronic inhomogeneities is still incomplete. Although a large body of previous work based on model Hamiltonians and phenomenological models exists, the microscopic mechanisms and the length-scales that arise in these systems remain poorly understood. The microscopically motivated theoretical model that we have discussed here clearly indicates that these materials are electronically inhomogeneous at nanoscales due to strong correlation physics. Naturally, the question of the origin of mesoscale inhomogeneities remains. There are several scenarios that could explain the origin of the mesoscale patterns. There is a possibility that, since many of the transitions are of first order, many of the inhomogeneities are due to an ‘incomplete transition’, i.e. they are metastable states. The second possibility is the presence of long-range elastic strain fields which are unscreened. Indeed, it is well known that pressure (strain) can drive transitions in the manganites (Soh et al. 2002; Postorino et al. 2003). The key question is whether strain effects are extrinsic (caused by defects, etc.) or intrinsic, i.e. the system reorganizes spontaneously into domains (much like a martensite).

The need for further exploration of electronic orders and inhomogeneities in oxides is evident. Experiments need to be designed so as to isolate long-range strain effects, with theoretical efforts towards building coarse-grained models to understand the mesoscale physics. This issue is particularly important for exploiting the electronic softness of these materials for applications.

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