Open questions in CMR manganites, relevance of clustered states and analogies with other compounds including the cuprates

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Open questions in CMR manganites, relevance of clustered states and analogies with other compounds including the cuprates

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Abstract. This is an informal paper that contains a list of 'things we know' and 'things we do not know' in manganites and other compounds. It is adapted from the Conclusions chapter of a recent book by the author, *Nanoscale Phase Separation and Colossal Magnetoresistance. The Physics of Manganites and Related Compounds* (Berlin: Springer-Verlag; 2002), but it also contains a summary of some of the most important recent results in the field. It is argued that the current main theoretical and experimental frameworks to rationalize the results of recent manganite investigations are based on the discovery of tendencies towards nanoscale inhomogeneous states, both in experiments and in simulations of models. The colossal magnetoresistance effect appears to be closely linked to these mixed-phase tendencies, although considerably more work is needed to fully confirm these ideas. The paper also includes information on cuprates, diluted magnetic semiconductors, relaxor ferroelectrics, cobaltites and organic and heavy fermion superconductors. These materials potentially share some common phenomenology with the manganites, such as a temperature scale T^* above the ordering temperature where anomalous behaviour starts. Many of these materials also present low-temperature phase competition. The possibility of colossal-like effects in compounds that do not involve ferromagnets is briefly discussed. In particular, colossal effects in cuprates are explained. Overall, it is

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concluded that inhomogeneous 'clustered' states should be considered as a new paradigm in condensed matter physics, since their presence appears to be far more common than previously anticipated.

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1. Introduction

In this paper, a list of 'things we know' and 'things we do not know' about manganites and related compounds is presented. This text is adapted from the last chapter of a book the author recently presented on manganites [1], after receiving the suggestion by some colleagues of making the

'open questions' discussion available to a wider readership. The presentation is very informal to keep the discussion fluid, and it is intended for researchers with some background in manganites (other materials, such as cuprates, are also addressed). Only a handful of references are included here for simplicity. However, close to 1000 citations can be found in the original source [1] in addition to a detailed justification of many of the matter-of-fact statements expressed here, particularly in the 'things we know' section. Many reviews are also available [2] with plenty of references: this paper is not a review article but an informal discussion, with many comments and sketchy ideas. Also, some items reflect the personal opinion of the author and may be debatable. In addition, this paper discusses the results for the other families of compounds which exhibit similarities to manganites. It is conceivable that the knowledge accumulated on Mn oxides may be applicable to the famous high-T_c cuprates, as well as other materials discussed here and in other chapters of [1]. The stability of 'clustered' states—often called phase-separated or mixed-phase states—appears to be an intriguing property of a variety of compounds, and 'colossal effects' should be a phenomenon far more common than previously believed. There is plenty of work ahead, and surprises waiting to be unveiled.

2. Facts about manganites believed to be understood ('things we know')

After the huge effort made in recent years in the study of manganites, involving both experimental and theoretical investigations, much progress has been achieved, described in the bulk of [1] and also in [2]. Here, a brief list of established results is presented. In section 3, the discussion will be more detailed when issues that remain to be understood are addressed.

1. At hole density $x = 0$, as in $LaMnO_3$, the ground state has staggered OO (orbital order) (a concept first discussed by Khomskii and Kugel). The spins form an A-type antiferromagnet (antiparallel spins along one direction, parallel along the other two), although very recently more exotic spin arrangements at $x = 0$ have been proposed for some manganites [1].[1] Several other doped Mn oxides have OO as well. This orbital ordering appears to be triggered by a large electron–JT (Jahn–Teller) phonon coupling, as discussed by Kanamori and more recently in Mn oxides by Millis and collaborators. The orbital degree of freedom plays a role as important as the spin, charge and lattice degrees of freedom. This leads to a complex phase diagram, with many competing phases, a characteristic of most of the correlated electron systems. The author believes it is time to fully bring manganites within the umbrella of 'correlated electrons', since the subject's complexity goes well beyond standard issues of plain 'magnetism'.
2. At $x = 1$, fully hole-doped, the spin arrangement is of G-type (antiparallel spins in the three directions).
3. There are many manganites with a ferromagnetic (FM) metallic ground state at intermediate densities. The Zener mechanism—for historical reasons widely known as 'double exchange'—appears to capture the essence of the tendency to ferromagnetism. This FM metallic state is a poor metal, and it is only one of the several possible states of manganites. Some authors believe that orbital correlations may play a role in this ferromagnet. It is also unclear to what extent oxygens should be explicitly included in the electronic sectors of

[1] Recently, a new FM charge-ordered phase was observed experimentally in [55]. This phase has been predicted in [18].

manganite models and whether they can be 'integrated out' as is usually assumed in theoretical studies of Mn oxides. This also occurs in t-J models for cuprates that invoke Zhang–Rice singlets and only focus on the Cu sites. Thus, there is still some discussion about the fine details of this state, but the essential features of the FM phase appear to be qualitatively understood.

4. At other hole densities, such as $x = 0.5$, charge/orbital/spin-ordered states can be stabilized, leading to a phase diagram interestingly asymmetric with respect to half-doping. The existence of these half-doped charge-ordered (CO) states has been established in Monte Carlo simulations, as well as in mean-field studies, in spite of their complicated structure. This gives hope that the theoretical studies are on the right track. The CO states strongly compete with the FM metallic state, both in real experiments and theoretical studies. This is a key observation leading to potential explanations of the CMR, since this phenomenon appears to occur when two phases—metal and insulator—are in competition. It happens at the boundaries between FM metal and paramagnetic insulator states or between FM metal and CO/OO/antiferromagnetic (AF) states. This line of thinking—CMR as caused by phase competition—is relatively new but currently dominates the literature. We simply cannot understand the CMR effect from the FM metallic state alone.
5. The existence of intrinsic inhomogeneities in single crystals has been established experimentally (the list of experimental groups involved is too long to be provided here, please see [1, 2]). This can occur within the ordered phases, or above the ordering temperatures, and even in the high hole-doping region (see the work by Neumeier and collaborators). CO *nanoclusters* above the Curie temperatures have been found in many low- and intermediate-bandwidth manganites. In the interesting CMR regime, this behaviour is correlated with the resistivity, according to neutron scattering experiments carried out by groups in Japan, Oak Ridge, Maryland, Brookhaven, Rutgers and other locations that have studied hidden structures near Bragg peaks (diffuse scattering). These nanoclusters are believed to be crucial for the occurrence of CMR. A very recent work [8] confirms the importance of nanoscale inhomogeneities to understand CMR physics.
6. Related to the previous item, percolative tendencies in manganites have been unveiled experimentally and in theoretical studies. But a sharp first-order metal–insulator transitions have also been reported, again both in theory and experiments. In some compounds, a mixture of these behaviours—percolation and first-order features—has been found (for more information, see section 6 below). These different behaviours may depend on the strength of the inevitable disorder in the samples.

   Some experiments—notably those by Cheong's and Mydosh's groups—have revealed the presence of sub-μm-size regions, to be contrasted with the more common occurrence of nanometre-size clusters (see above). This is a remarkable effect that deserves to be analysed in detail. It is unclear to what extent the sub-μm clusters are truly needed to understand the CMR and whether they are present in single crystals.
7. The presence of phase separation tendencies in theoretical models has been unveiled and confirmed after a study by Yunoki, Moreo and collaborators in 1998 using Monte Carlo simulations of realistic models, followed by a large number of other studies that reached similar conclusions (see work by Arovas, Guinea, Khomskii, Kagan and others cited in [1, 2]). Phase separation can be caused by at least two tendencies: (1) Electronic phase separation, where competing states have different hole densities and $1/r$ Coulomb effects lead

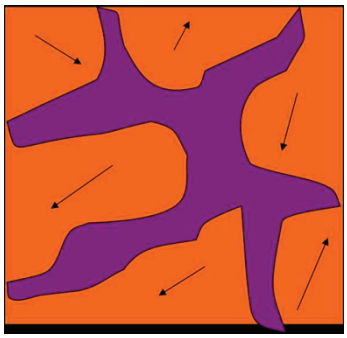

Figure 1. Cartoon representation of the CMR state discussed in [1, 10], with FM islands (orange) with randomly oriented magnetizations, separated by the walls of the competing insulating state (purple). Upon the application of small magnetic fields, the magnetic moments rotate, the walls melt and a FM metallic state is obtained.

to nanocluster coexistence. This is similar in spirit to the phase separation much discussed in cuprates (see Kivelson, Tranquada, Zaanen, Di Castro and others). (2) Disorder-driven phase separation near first-order transitions (see [9]), with competing states of equal density that leads to large coexisting clusters.

8. Theories based on states composed of small FM islands with randomly oriented magnetizations appear to capture the essence of the CMR phenomenon [1, 2, 10] (see figure 1). Electrons with spin, say, up are mobile within ferroclusters with magnetization up. However, they cannot travel through magnetization-down clusters, which effectively act as insulators to the spin-up electron carriers. However, the large effective spin of these clusters can be easily rotated upon the application of very modest fields, much smaller than the natural scales in the problem, leading to a metallic state [10, 11]. Note that, in these simulations, there was no need to carry out studies using sub-μm-size clusters, since nanoclusters were sufficient.
9. Theoretical studies have predicted that the metal and insulator phases of manganites are separated by first-order transitions leading to bi- or tricritical behaviour in the clean limit (see [1, 2, 10]). Experiments by Tomioka and Tokura have recently reported an example with such a behaviour. When quenched disorder is sufficiently strong, a 'window' with disorder characteristics opens in between the two phases as shown in the figure below. The group of Ibarra has reported results for a material that indeed has a glassy state between the FM metal and the AF insulator. The particular case of a quantum critical point is only obtained in this context by fine tuning of parameters (although multicritical phenomena may still be of relevance in this context as proposed by Nagaosa and collaborators).
10. Related to the previous item, theoretical and experimental studies have unveiled the existence of a new temperature scale T^* where clusters start forming well above the Curie temperature (see figure 2). Independent studies by Burgy *et al* and Salamon *et al* have characterized this critical temperature as a Griffiths temperature. Griffiths effects appear to be larger than usual due to phase competition.

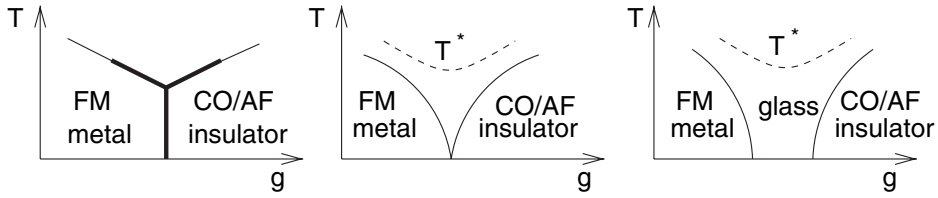

Figure 2. (Left panel) Generic phase diagram of two competing phases in the absence of quenched disorder (or when this disorder is very weak). Thick (thin) lines denote first (second)-order transitions. Shown is a tricritical case, but it could be bi- or tetracritical as well. g is some parameter needed to change from one phase to the other. (Middle panel) With increase in disorder, the temperature range of first-order transitions separating the ordered states is decreased, and eventually for a fine-tuned value of the disorder, the resulting phase diagram contains a quantum critical point. In this context, this should be a rare occurrence. (Right panel) In the limit of substantial disorder, a window opens between the ordered phases. The state in between has glassy characteristics and it is composed of coexisting clusters of both phases. The size of the coexisting islands can be regulated by disorder and by the proximity to the original first-order transition. For more details, see [1, 2, 10]. The T^* discussed in the text—a remnant of the clean-limit transition—is also shown.

3. Are theories that do not include phase separation suitable for understanding the CMR effect?

The enormous experimental effort on Mn oxides has already provided sufficient results to decide whether or not some of the theories proposed in recent years realistically explain the unusual magnetotransport properties of these compounds. Indeed, some of the early proposals for theories of CMR manganites have already been shown to be incomplete and the current leading effort centres around inhomogeneities and first-order metal–insulator transitions. The details are given below:

1. In theories sometimes referred to as 'double exchange', electron hopping above the Curie temperature T_C is simply described by a renormalized hopping '$t\langle\cos\theta/2\rangle$'. These theories are based on the movement of electrons in a disordered spin-localized background (see figure 3(a), for a crude sketch), without invoking other phases. However, quantitative investigations have shown that this approach does not appear to be sufficient to produce neither an insulating state nor a CMR phenomenon, although this simple idea may be suitable for large bandwidth manganites, such as $x = 0.4$ LaSrMnO.
2. Some theories rely on Anderson localization to explain the insulating state above T_C. However, the amount of disorder needed to achieve localization at the densities of relevance is very large (at least in a simple 3D (three-dimensional) Anderson model). Computational studies [12] locate the critical value at $W_c \sim 16$ (in units of the hopping), assuming a uniform box distribution of random on-site energies $[-W/2,\ +W/2]$, and with the Fermi energy at the band centre. Perhaps this large-disorder strength effectively mimics the influence of large electron–phonon couplings, strong Coulomb correlations, nanoclusters, strain and quenched disorder present in the real materials. But, even in this case, it is difficult to explain the

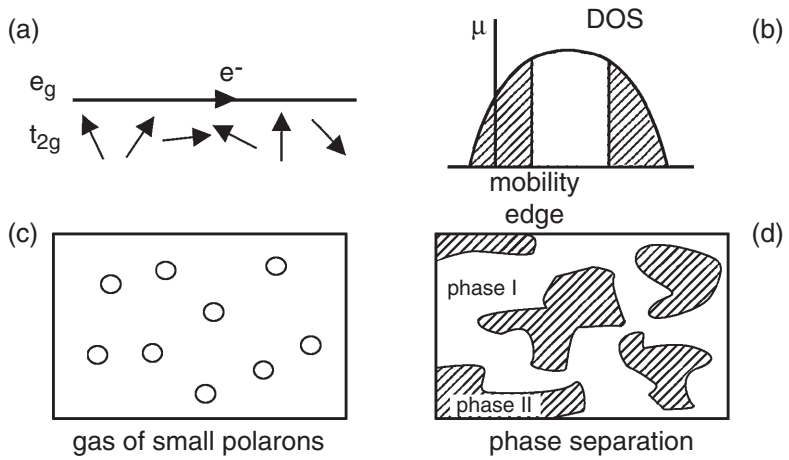

Figure 3. Schematic representation of theories for manganites. (a) A simple 'double exchange' scenario, without phase competition. (b) Relies on Anderson localization as the origin of the insulating state that competes with FM. (c) Based on a gas of polarons above the Curie temperature T_C, also without phase competition. (d) A phase-separated state above the ordering temperatures is sketched. Details can be found in the text.

density-of-states pseudo-gap (PG) found in photoemission experiments by Dessau's group. Anderson localization does not produce such a PG (figure 3(b)). In addition, experimentally, it is clear that the CMR originates in the competition between phases, typically FM-metallic and AF/CO-insulating, but this fundamental effect is not included in simple Anderson localization scenarios, where ordering and phase competition are absent. For these reasons, the author believes that Anderson localization does not seem to be the best approach to explain manganite physics.

3. Some theories are based on a picture in which the paramagnetic insulating state is made out of a gas of small and heavy polarons (figure 3(c)). These theories do not address neutron experiments reporting CE CO clusters above T_C, correlated with the resistivity, nor the many indications of inhomogeneities. A polaron gas may be a good description at much higher temperatures, well above room temperature, but such a state does not appear to be sufficient in the region for CMR, close to the Curie temperature. The CO small clusters found experimentally above T_C have properties corresponding to phases that are stable at low temperatures, such as the CE phase. These complex clusters certainly cannot be considered as mere polarons. They are more like 'correlated polarons', as some researchers in this field prefer to call the CO islands.

Theories based on microscopic phase separation (figure 3(d)) appear to provide a more realistic starting point to manganites since they are compatible with dozens of experiments.

4. Some of the open issues in Mn oxides ('things we do not know')

4.1. Potentially important experiments (in random order)

- The evidence for CO nanoclusters above T_C should be further confirmed. It is important that a variety of techniques reach the same conclusions regarding the presence of nanoclusters above

T_C, definitely ruling out a homogeneous state as the cause of the CMR effect. For instance, it would be important to find out the role played by nanoclusters in optical conductivity results, which have been described mainly as consisting of 'small polarons' (Noh and collaborators). How do the nanoclusters manifest themselves in the optical spectra? Recent results at $x > 0.5$ by Noh's group contribute much to this issue, since a PG was observed compatible with photoemission results. Even more recent results by D D Sarma *et al* [13], Argyriou *et al* [14], Mathieu *et al* [15], Kiryukhin *et al* [16] and several others (list just too long, please wait for the second edition of [1] for a complete citation!) have provided overwhelming evidence that the original scenario of nanoscale phase separation is correct. But many more investigations (see below) are needed for a full confirmation of these ideas.

- The existence of the predicted new temperature scale T^* above the Curie temperature should be further investigated. (i) Thermal expansion, magnetic susceptibility, x-rays, neutron scattering and other techniques have already provided results supporting the existence of a new scale T^*, where clusters start forming upon cooling. In fact, very early in manganite investigations, the group of Ibarra at Zaragoza reported the existence of such a scale, in agreement with more recent theoretical and experimental developments. Recent results by Deisenhofer *et al* [17] also report the existence of T^*, using electron spin resonance and magnetic susceptibility measurements. This scale should manifest itself even in the dc resistivity, as it does in the high-temperature superconductors at the analogue T^* 'PG temperature'. Are there anomalies in ρ_{dc} versus temperature in Mn oxides as well? Are the T^* scales in cuprates and manganites indicative of a similar physics? (ii) In addition, the specific heat should systematically show the existence of structure at T^* due to the development of short-range order (at T^*, even a glassy phase transition may occur, as recently proposed by Argyriou *et al*). (iii) The dependence of T^* with doping and tolerance factors should be analysed systematically. Theoretical studies [10] suggest that the tolerance factor may not change T^* substantially, although it affects the ordering temperatures significantly. Is there experimental support for this prediction? (iv) Is the crude picture of the state between T_C and T^* shown in figure 4 qualitatively correct?
- X-rays and neutron-scattering studies of $(La_{1-y}Pr_y)_{1-x}Ca_xMnO_3$ (LPCMO) are needed to analyse the evolution of CO nanoclusters. There is considerable evidence that LCMO $x = 0.3$ at temperatures above T_C presents CO nanoclusters, correlated with the behaviour of the resistivity, as already discussed. It is important to track the intensity and location in momentum space of the peaks associated with charge ordering as La is replaced by Pr. This replacement enhances charge-ordering tendencies, as discussed by Cheong and collaborators. It is also important to notice that the substitution of Ca by Sr decreases that tendency. Is there a smooth evolution from LCMO to the regime found by Cheong's group in LPCMO with phase separation at low temperatures, as well as from LCMO to the more 'double exchange' homogeneous regime of LSMO?
- Are the mesoscopic clusters found in LPCMO using electron diffraction representative of the bulk? Are there other compounds with the same behaviour? The evidence for nanocluster formation appears robust in manganites. However, the evidence for larger structures of the mesoscopic kind is based on a smaller number of experiments: electron diffraction and STM techniques (see section 2). Are these results representative of single-crystal behaviour? To what extent should one consider two kinds of phase separation, i.e. nanoscale and microscale? Can one evolve smoothly from one to the other as the Curie temperature decreases?

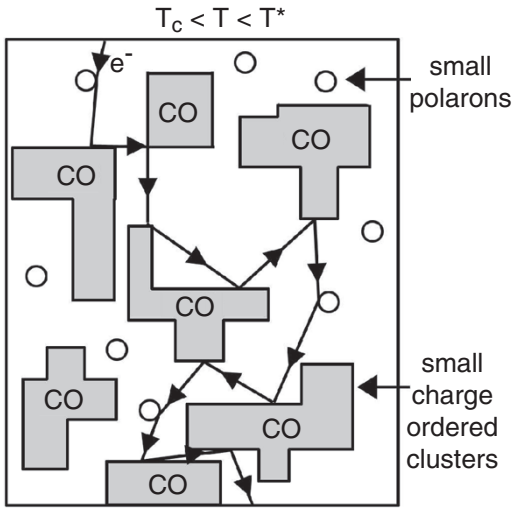

Figure 4. Crude cartoon representation of the proposed state in the regime between T_C and T^*. Small polarons are represented by circles, and electrons travelling across the sample (thick line) may not scatter much from them. The grey areas are the CO clusters where scattering is more severe. The FM regions, expected to be present in this state according to some experiments, are not shown. They may also contribute substantially to scattering, since their orientations are random.

- What is the nature of the FM insulating phases that appear in some phase diagrams? Is this phase truly qualitatively different from the FM metallic phase, or are they very similar microscopically? In other words, is there a spontaneously broken symmetry in the ferro-insulator state? Does charge ordering and/or orbital ordering exist there? Theoretical studies by Yunoki, Hotta and others have shown the presence of many novel spin FM phases, with or without charge and orbital order [18]. There is no reason why these phases could not be stabilized in experiments. In fact, a new 'E-phase' of manganites at $x = 0$ has recently been discussed [3]. This is an exciting new area of investigations and plenty of phases found in simulations could be observed experimentally, as recently exemplified by the FM-CO phase discussed by Loudon and collaborators (see [3]), which had been predicted by Yunoki *et al* [18].
- Atomic resolution STM experiments should be performed, at many hole densities. The recent atomic-resolution STM results for BiCaMnO by Renner *et al* are very important for clarifying of the nature of manganites and for the explicit visual confirmation of phase separation ideas. Extending experiments of this variety to other hole densities, particularly those where the system becomes FM metallic at low temperatures, is of much importance. In the area of cuprates, high-resolution STM results in recent years by Davis, Pan and collaborators have made a tremendous impact and, hopefully, similar experiments can be carried out in manganites.
- The regime of temperatures well above room temperature must be carefully explored, even beyond T^*. At $T > T^*$, the CO clusters are no longer formed but a gas of polarons may still be present. Does this perhaps lead to another temperature scale, denoted by $T^{\rm pol}$ in

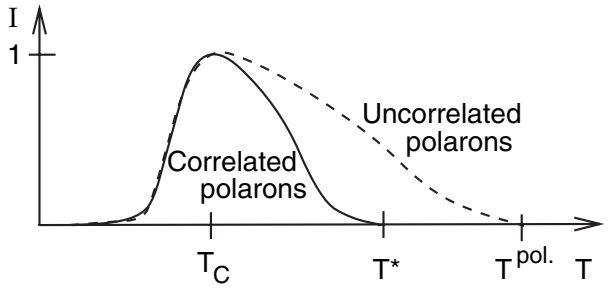

Figure 5. Schematic representation of an idealized diffuse neutron-scattering experiment. Intensities I in the vertical axis correspond to momenta associated with (1) correlated polarons (also known as CO clusters) and (2) uncorrelated polarons. Two proposed temperature scales, T^* and $T^{\rm pol}$, are shown. The results are normalized to the same intensity at the Curie temperature $T_{\rm C}$. For a discussion, see text and [1]. These are theoretical proposals that need further experimental confirmation.

figure 5, where individual polarons start forming? Is the system metallic upon further increasing the temperature? We may have interesting physics even at temperatures close to 1000 K in this context.

- Is the glassy state in some manganites of the same variety as a standard spin glass or does it belong to a new class of 'phase-separated glasses'? The issue is subtle since, as of today, proper definitions of glasses and associated transitions are still under much discussion. Can glasses be classified into different groups? Are glassy manganites a new class? What is the actual nature of the 'cluster glasses' frequently mentioned in manganites? Important work by Schiffer's group, by Levy, Parisi and collaborators in Buenos Aires [4] and by many other researchers has added key information to this subarea of manganite investigations. Studies of time-dependent phenomena in the $x = 0.5$ regime have provided fascinating results that deserve further research.

  Related to the previous item, should nanocluster phase-separated states be considered as a 'new state of matter' in any respect? This issue is obviously very important. In order to arrive at an answer, the origin of the nanocluster formation must be fully clarified. Is it purely electronic-driven, or a first-order transition rendered continuous by quenched disorder, or strain-driven? If the inevitable disorder related to tolerance factors could be tuned, what happens to the nanoclusters and critical temperatures?

- What is the nature of the CO states at $x < 0.5$, such as those in PCMO? It is accepted that these states 'resemble' the CE state in their charge distribution, but what is the actual arrangement of spins and orbitals? Is the excess of electronic charge distributed randomly in the $x = 0.5$ CE structure or is it uniformly distributed, for instance by increasing uniformly the amount of charge in the Mn^{4+} sites? Theoretical studies are difficult at these hole concentrations. It is important to know whether entropy is large in the CO states at these densities, to justify thermodynamically their existence (as discussed by Khomskii). Otherwise, how can a putative low-entropy CO state be stabilized at high temperature? The opposite, an FM state stable above the CO state, is more reasonable and has been already shown to be the case in simulations studies by Aliaga and collaborators [6].

- Is there any compound with a truly spin-canted homogeneous ground state? As far as I know, theoretical studies using robust techniques have not been able to find spin-canted homogeneous states in reasonable models for manganites (of course, if no magnetic field is added). Are there experiments suggesting otherwise? So far, experimental evidence for canting can be always alternatively explained through inhomogeneities in the ground state. A counterexample is perhaps bilayers in the direction perpendicular to the planes (see the many results obtained by the Argonne group), but this may be a different kind of state, unrelated to the original proposal by DeGennes that postulated a homogeneous spin-canted state interpolating between FM and AF limits.
- Temperature dependence of the dc resistivity of manganites has not been sufficiently analysed. Can non-Fermi-liquid (NFL) behaviour be shown to be present in metallic manganites, as it occurs in many other exotic metals?
- Are the nanoclusters found in manganites and cuprates (see below) characteristic of other oxides as well? The answer seems to be yes. In chapter 21 of [1], many materials that behave similar to Mn oxides and Cu oxides are listed. Nickelates are another family of compounds that have stripes and charge-ordering competing with AF. Below, other materials with similar characteristics are briefly discussed. These analogies are more than accidents. They suggest that many compounds are intrinsically inhomogeneous. Theories based on homogeneous states appear unrealistic.
- Are Eu-based semiconductors truly described by FM polarons as believed until recently or is a nanocluster picture more appropriate? Studies by Lance Cooper's group using Raman scattering suggest the existence of close analogies between Eu semiconductors and manganites. Perhaps phase separation dominates in Eu compounds as well, and the long-held view of Eu-semiconductors as containing simple 'FM polarons' (one carrier, with a spin polarized cloud around) should be revised. Very recent work by Ott and collaborators finds CMR and percolation in Eu-based hexaborides [5].

5. Some of the unsolved theoretical issues

- The study of the phase diagrams of models for manganites is far from over! Although much progress has been made [1, 2], many important issues are still unexplored or under discussion. For example, the phase diagram in 3D of the two-orbital model may contain many surprises. It is already known that the 1D and 2D models have a rich phase diagram, with a variety of competing phases. In addition, studies by Hotta *et al* in 2D including cooperative effects have also revealed the presence of stripes at densities $x = 1/3$ and 1/4 and probably others. Then, one can easily imagine a surprisingly rich phase diagram for bilayers or 3D systems. Perhaps the dominant phases will still be the A-type AF at $x = 0$, ferro-metal at $x \sim 0.3$, CE-type at $x = 0.5$, C-type at $x \sim 0.75$ and G-type at $x = 1.0$. However, the details remain unclear.
- The theory of phase separation should be made more quantitative. Can a rough temperature dependence of the dc resistivity be calculated within the percolative scenario? We do have resistor-network calculations that match the experiments, but not a simple anybody-can-use formula. This is a complicated task due to the difficulty in handling inhomogeneities.

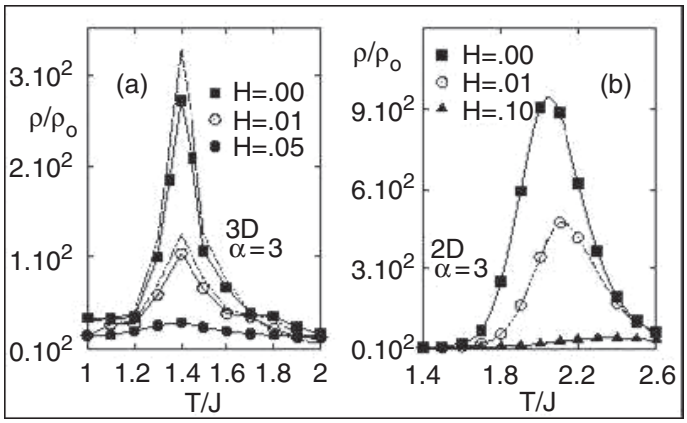

Figure 6. Resistivity versus temperature, parametric with magnetic fields, reproduced from [11], showing the similarity in results between 2D and 3D lattices once correlated disorder is used in the simulation. Details can be found in the original reference.

- Is the 'small' J_{AF} coupling between localized t_{2g} spins truly an important coupling for manganites? The Heisenberg coupling between localized spins appears to play a key role in the stabilization of the A-type AF state at $x = 0$. This small coupling selects whether the system is in a FM, A-, C- or G-type state, namely its influence is amplified in the presence of nearly degenerate states. This coupling is also important in the stabilization of the correct spin arrangement for the CE phase (if J_{AF} is too small, FM wins, and if too large, G-type AF wins) and in the charge stacking of the CE-phase, according to studies by Yunoki, Hotta, Terakura, Khomskii and others. This key role appears not only in JT-based theories but also in Coulomb-based theories as well, as shown by Ishihara, Maekawa and collaborators. Are there alternative mechanisms for stabilization of A-type, CE-type and charge-stacking states? The importance of J_{AF} may be magnified by the competition between many phases in manganites, with several nearly degenerate states.
- Is there a fundamental problem with current phase-separation theories regarding the dimensionality dependence of the results? Early studies, such as those in [10], heavily rely on the Imry–Ma argumentation that is well known to have a critical dimension $D = 2$. Then, the question was raised whether the phase separation scenario would work only in $D = 2$ but not in $D = 3$. However, recent results [11] have demonstrated that, at least in toy models, this problem can be avoided by using correlated disorder to mimic the cooperative oxygen effects in oxides. Physically, if a oxygen octahedron is distorted, the neighbours must be distorted as well since they share the same oxygens. This effect alters the critical dimension of the problem [11], and now $D = 2$ and 3 present very similar results (see figure 6). Of course, further work is needed using more realistic Hamiltonians to confirm these ideas.
- Why is the CE state so sensitive to Cr doping? Experimentally, it is not expected that a robust CO state could be destabilized by a relatively very small percentage of impurities. Can this be reproduced in MC simulations? Indeed this is the case, according to recent studies by Aliaga *et al* [6] and Motome *et al* [7]. Note that high-T_c cuprates are also very sensitive to impurities. It is natural to expect that materials near percolative transitions are sensitive to disorder. These effects may provide further evidence for the relevance of inhomogeneous states in oxides.

- For the explanation of CMR, is there a fundamental difference between JT- and Coulomb–based theories? Technically, it is quite hard to handle models where simultaneously the Coulomb–Hubbard interactions as well as the electron–phonon couplings are large. However, so far, for CMR phenomena, the origin (JT versus Coulomb) of the competing phases does not appear to be crucial, but only the competition itself is. Is this correct?
- In the calculations by Burgy *et al* [10], phenomenological models were used for CMR. Can a large MR effect be obtained with more realistic models? Of course, the calculations are very complicated in this context, if unbiased robust many-body techniques are used, due to cluster-size limitations.
- Are there models with spin-canted homogeneous ground states? So far, when models for manganites have been seriously studied with unbiased techniques, no homogeneous spin-canted states have been identified (at zero magnetic field). Perhaps other models?
- Can a model develop a CO AF phase at intermediate temperatures while having a FM metallic phase at low temperatures? This is quite hard and perhaps can only occur if the CO phase has an associated high entropy, as has been discussed by Khomskii (see a related discussion in the previous section).

6. Some issues that are not as well-known to the community as they should be

6.1. Quenched disorder is crucial to have the CMR effect

Some of the most important recent experiments in the manganite context are those recently presented by Akahoshi *et al* [19]. These investigators studied half-doped manganites $RE_{1/2}Ba_{1/2}MnO_3$ (RE = rare earth) that have two possible forms of the crystal structure, depending on the synthetic preparation conditions. One is the A-site disordered or solid-solution structure, and the other is A-site ordered with alternating stacks of REO and BaO sheets in between MnO_2 sheets. The ordered compound has a bicritical behaviour (figure 7 (left panel)), with a first-order transition separating the FM and AF phases, as clearly predicted by theory in the clean limit [1]. The disordered structure, in the same figure, presents a drastic reduction of the Curie temperature with decrease in bandwidth, leading to a glass state and, presumably, to a CO state upon further bandwidth reduction if that could be done. This is also in excellent agreement with theory [1, 10]. Although just these results by themselves show great progress in the field, the real punchline comes when the transport properties are investigated. It is only the disordered sample that shows the CMR effect, in excellent agreement with the theoretical scenario [10]. These results are reproduced in figure 7 (right panel). Thus, evidence is accumulating that quenched disorder ('dirt') is needed for the CMR effect to exist, a remarkable result. If the crystal is too clean, the transition FM–AF is sharp, and a T^* does not exist. Nanoscale phase separation is needed for the manganite to reveal its CMR behaviour. Issues of this nature are crucial for future applications of these materials (see below).

6.2. There are two types of CMR

The manganite $(Nd_{1-y}Sm_y)_{1/2}Sr_{1/2}MnO_3$ investigated by Tokura and collaborators has an interesting behaviour, as shown in figure 8. This compound presents two types of CMR phenomena: (i) at temperatures in the vicinity of 250 K ($y = 0$) and 150 K ($y = 0.75$), a somewhat

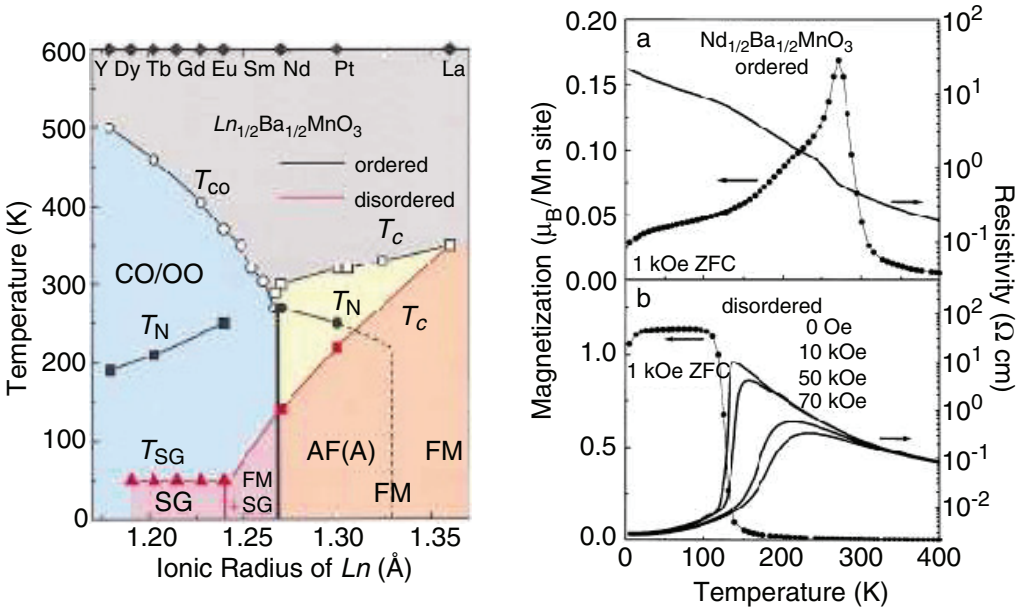

Figure 7. (Left panel) The phase diagram of $RE_{1/2}Ba_{1/2}MnO_3$ as reported in [19], for both the ordered and disordered structures. (Right panel) The transport properties of both structures. Only the disordered case shows the CMR effect. Note that this effect occurs in a range of temperatures starting from cooling at a T^* close to 300 K that happens to be the clean-limit (ordered structure) critical temperature, as predicted by theory [1, 10, 11].

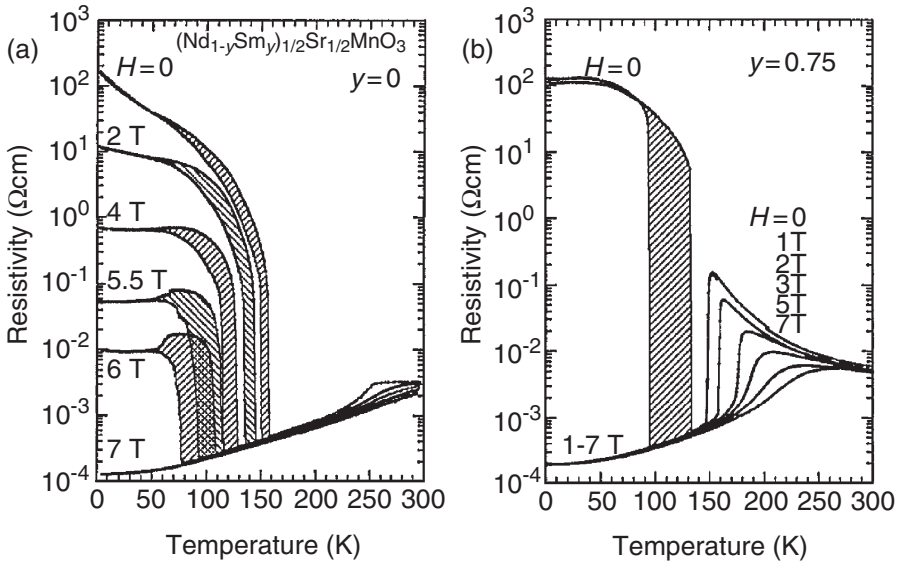

Figure 8. Temperature dependence of resistivity under various magnetic fields for $(Nd_{1-y}Sm_y)_{1/2}Sr_{1/2}MnO_3$ with $y = 0$ (a) and $y = 0.75$ (b). The hatched area represents thermal hysteresis. Results from Tokura *et al* [20].

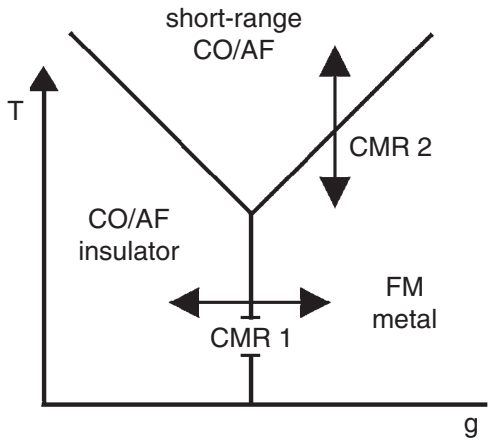

Figure 9. Schematic representation of the generic phase diagram in the presence of competing metal and insulator, and for quenched disorder not sufficiently strong to destroy entirely the first-order transition at low temperatures. g is a generic variable needed to transfer the system from one phase to the other. CMR1 and CMR2 are the regions with two types of large MR transitions, as described in the text and in [1].

'standard' CMR is observed. Here, by standard, it is understood as the CMR behaviour described in reviews and [1], with the canonical shape of the resistivity versus temperature. However, (ii) at lower temperatures where the system is insulating, a *huge* MR effect is observed as well. Results for two values of 'y' are shown in the figure. Is this indicative of two independent mechanisms for CMR?

Related to this issue is the work of Fernandez-Baca and collaborators studying $Pr_{0.70}Ca_{0.30}MnO_3$, where they reported the discontinuous character of the insulator–metal transition induced by an external field. Those authors argued correctly that the CMR phenomenon can be more complex than the percolation of FM clusters proposed for the standard CMR. Their results are in qualitative agreement with those of figure 8 where, at low temperatures, a fairly abrupt transition is observed. In fact, it is known that, even in percolative processes such as those in LPCMO (see the work by Cheong and collaborators), hysteresis has been found in the resistivity. This suggests that a mixture of percolation with first-order features could be at work in manganites, as theoretically discussed by Burgy *et al* [1, 10].

Can theory explain the presence of two types of CMR transitions? The answer is tentatively yes, although more work is needed to confirm the picture. The main reason for expecting two types of CMR is already contained in the phase diagram of the models studied by Burgy *et al* [10] to address the competition of two phases, as schematically reproduced in figure 9. Two possible regions with CMR effects are shown in the figure. One corresponds to the 'standard' region, at the transition from a 'clustered' short-range ordered phase to the FM metallic phase with decreasing temperature (CMR2). However, at low temperatures, and if the quenched disorder is not too strong, the transition between the competing phases can remain of first order in a finite range of temperatures (see figure 1 and the discussion in section 2). As a consequence, if the system is very close to the metal–insulator transition and on the insulating side, a small magnetic field can cause a first-order transition between the two phases (in the CMR1 region in the figure), which will imply a significant and discontinuous change in the resistivity. This effect has been recently

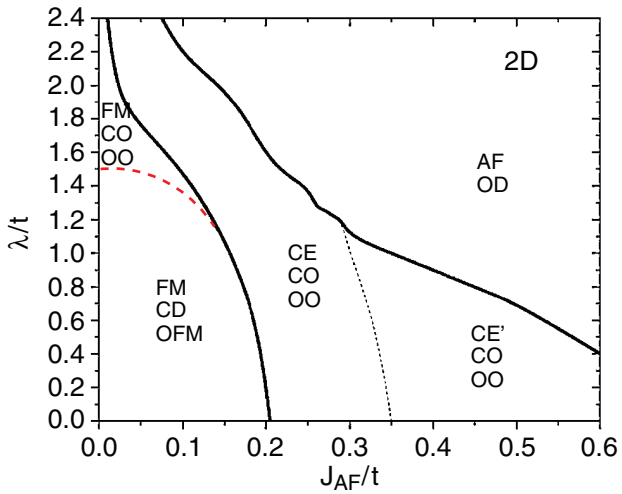

Figure 10. Phase diagram of a model for manganites, obtained with Monte Carlo simulations at half-doping, reproduced from [6]. For details and the meaning of the various phases, the reader is referred to the original reference. The main issue to note is the transition from an FM metallic to a CE insulating phase at $\lambda = 0$, namely without JT distortions, as the J_{AF} coupling varies. The stability of the CE phase even at $\lambda = 0$ was first explained by Hotta and collaborators.

confirmed in simulations of the two-orbital model with JT phonons by Aliaga and collaborators [6]. Clearly, the theory predicts two types of CMR transitions and this is already in agreement with experiments. Note that if there was an external means to favour the CO/AF phase over the FM phase (for instance, by an 'external staggered field'), then the process could be reversed and a metal–insulator exotic transition would be induced. Read more about this issue when potential 'colossal' effects are discussed for cuprates.

6.3. The famous CE phase can exist even in the absence of JT distortions and large Coulomb repulsion

Until recently, it was widely accepted that the insulating phase of half-doped manganites was a CO state with 3+ and 4+ ions. However, recently, evidence is accumulating that this picture is too drastic and it is possible that the differences in the charge of the checkerboard arrangement are far smaller than previously believed (i.e. $3.5 \pm \delta$, where δ is a small number). A proper review of this issue, which is still in a fluid state, would require an entire paper and here just [21] is cited, while readers can search for further references. The point of this subsection is to bring to the attention of readers the little-known fact that the CE state (with antiferromagnetically ordered zigzag chains) already appears in the limit of zero JT distortion (see the phase diagram figure 10) and, as a consequence, it is indeed conceivable that the experimentally observed insulating state at half-doping does not show charge and orbital ordering. The key observation, pioneered by Hotta and collaborators, is that kinetic energy arguments and the band structure of a zigzag chain at this particular doping are sufficient to understand the CE stability. There is no need to invoke huge JT couplings or huge Coulombic repulsions at nearest neighbours to stabilize the CE state. This is the only way this author knows to rationalize the close proximity in energy of an FM

metallic state. If the electron–phonon or Coulomb interactions were huge, a metallic state should have a much higher energy.

7. Two rapidly emerging areas of investigations for the future

7.1. Complexity in transition metal oxides

Although the term complexity is mainly associated with soft matter such as polymers and liquid crystals, the tendency towards inhomogeneous states and, e.g., the existence of rapid changes in transport upon the application of small perturbations (such as small magnetic fields), suggest that manganites and probably also other oxides can be labelled as representative of 'complex' matter. This is a rapidly growing area of investigation, pioneered by our group, as well as Bishop's group at Los Alamos and by others. This author believes this subject has tremendous potential for expansion in the near future.

7.2. Applications in real devices

There are many papers circulating, mainly by the Houston, Tokyo and Augsburg groups—but surely there are others—reporting exotic behaviour in thin films involving manganites, such as the existence of two resistance states depending on the sign of gate voltages, when current circulates perpendicular to the films. This is a very unexpected result and at least one theory has already been proposed based on the phase separation scenario [22]. This area will rapidly evolve and it may lead to applications of complex oxides, which will represent a tremendous boost to the field of strongly correlated electrons in general.

8. Even more general open questions

At the risk of sounding naive, here are very general issues that, in my opinion, should also be addressed by the experts.

- Can quasi 1D manganites be prepared experimentally? Perhaps chemists may already know that this is impossible, but here let us just say that, in the area of cuprates, it was quite instructive to synthesize copper oxides with chain or ladder structures. These quasi-1D systems can usually be studied fairly accurately by theorists, and concrete quantitative predictions can be made, both for static as well as dynamical properties. Regarding the CMR effect, there are already calculations (see figure 11, taken from [23]; see also [24]) that show a very large MR effect in 1D models. In a 1D system, a single perfectly AF link is sufficient to block the movement of charge (since its effective hopping in the large Hund coupling limit is zero), creating a huge resistance. Small fields can slightly bend those AF-oriented spins, allowing for charge movement and decreasing rapidly the resistivity by several orders of magnitude, as shown in the figure.
- Should we totally exclude superconductivity (SC) as a possibility in manganites? Naively, the presence of SC in transition metal oxides of the $n = 3$ shell should not be necessarily restricted to the cuprates. In the Cu oxide context, SC appears when the insulator is rendered unstable by hole doping. AF correlations are among the leading candidates to explain the d-wave character

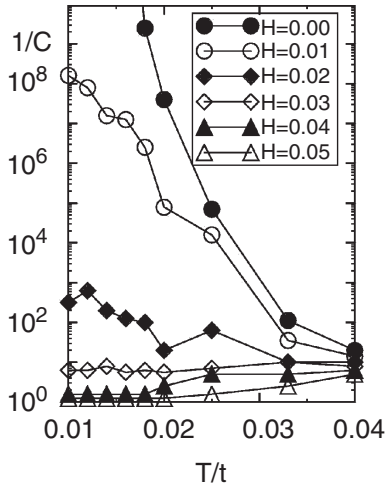

Figure 11. Inverse conductivity of the half-doped one-orbital model on a 64-site chain at several values of the magnetic field H (in units of the hopping) as indicated. Note the enormous changes in conductivity with increasing fields. Couplings and details can be found in the original work by Mayr and collaborators [23].

of the superconducting state. In the high-doping side of the superconducting region, a Fermi liquid exists even at a low temperature. Is there a doped-manganite compound, likely a large bandwidth one, that does not order at low temperatures and maintains a metallic character? Alternatively, can a metallic manganite compound become paramagnetic upon the application of, e.g., high pressure, at low temperatures? Searching for metal–insulator transitions near these quantum critical points, if they exist, may lead to surprises. If it is confirmed that, even in these circumstances, no SC is found, then the $S = 1/2$ spins of cuprates (as opposed to higher spins of other materials) is likely to play a key role in the process. Early studies by Riera and collaborators [25] have shown that the prominent presence of FM and phase separation as the spin grows, may render SC unstable in Mn oxides.

- Technical applications of manganites remain a possibility. This comment has overlap with the one expressed before in section 7.2, but some redundancy will not hurt. There are two areas of technologically motivated investigations in manganites. One is based on materials with high T_C, at or above room temperature, which may be useful as nearly half-metals in the construction of multilayer spin-valve-like devices. Fert's group has made progress in this area recently, and there are several other groups working on the subject. Another area is the investigation of thin films, exploiting CMR as an intrinsic property of these materials. Special treatments of those films may still lead to a large MR at high temperatures and small fields, as needed for applications. Of course, there is a long way before CMR even matches the remarkable performance of the giant-MR (GMR) devices.

9. Is the tendency to nanocluster formation present in other materials?

We end this informal paper with a description of materials that present properties similar to those of the Mn oxides, particularly regarding inhomogeneities, phase competition and the occurrence

of a T^* (for a detailed, long list of materials, see [1]). It is interesting to speculate that all of these compounds share a similar phenomenology. Then, by investigating one particular system, progress could be made in understanding the others as well. We start with the famous high-T_c compounds, continue with diluted magnetic semiconductors—of much interest these days due to spintronic applications—and finish with organic and heavy-fermion materials.

9.1. Phase separation in cuprates

Considerable effort has recently been devoted to the study of inhomogeneous states in cuprates. In this context, the issue of stripes as a form of inhomogeneity was raised several years ago after experimental work by Tranquada and collaborators and theoretical work by Kivelson, Zaanen, Poilblanc and others. However, recent results obtained with STM techniques by Davis, Pan and collaborators have revealed inhomogeneous states of a more complex nature. They appear in the surface of one of the most studied superconductors Bi2212 (but they may be representative of the bulk as well), at low temperatures in the superconducting phase, both in the underdoped and optimally doped regions. In the figures presented by the authors of these STM investigations, the spatial distribution of d-wave superconducting gaps were notoriously inhomogeneous. Indications of similar inhomogeneities have been observed using a variety of other techniques as well. (The list of relevant experiments is simply too large to be reproduced here. For a partial list see [1].) Currently, this is a much debated area of research in high-critical-temperature superconductors, and it is unclear whether cuprates are intrinsically inhomogeneous in all their forms or whether the inhomogeneities are a pathology of only a fraction of the Cu oxides. It is also unclear to what extent the notion of stripes, with at least partial order in its dynamical form, survives the Bi2212 evidence of inhomogeneities where the patches are totally random.

Note that recent NMR work on YBCO by Bobroff *et al* has not reported inhomogeneities, suggesting that phase separation may not be a generic feature of the cuprates. Similar conclusions were reached by Yeh and collaborators through the analysis of quasi-particle tunnelling spectra. Clearly, more work is needed to clarify the role of inhomogeneities in the cuprate compounds.

The results discussing the general aspects of the competition between two ordered phases in the presence of quenched disorder (see for instance the phase diagram in section 2) can in principle be applied to the cuprates as well, where SC competes with an AF state (the latter perhaps including stripes). In fact, the phase diagram of the single-layer high-T_c compound $La_{2-x}Sr_xCuO_4$ contains a regime widely known as the 'spin-glass' region. In view of the results in [1, 10], it is possible, that this spin glass region could have emerged, due to the influence of disorder, from a clean-limit first-order phase transition separating the doped AF state (again, probably with stripes) and the superconducting state. This hypothesis was recently tested [37] in a toy model Monte Carlo simulation and the results indeed show a glassy state separating the AF from the SC states once quenched disorder is introduced. In fact, the reported phase diagram—that arises from a very simply simulation—is remarkably similar to that of the real cuprates! (see figure 12, left panel). In this context, the 'PG' simply emerges from a mixture of two states that have gapped features such as those in AF and d-wave SC states. A cartoon representing the proposed mixed state in the deep underdoped limit is shown in the right panel. The arrows in the SC islands represent the U(1) phase of the SC order parameter, but the similarity to the state proposed for the cuprates in figure 1 is remarkable. This SC island state was probably

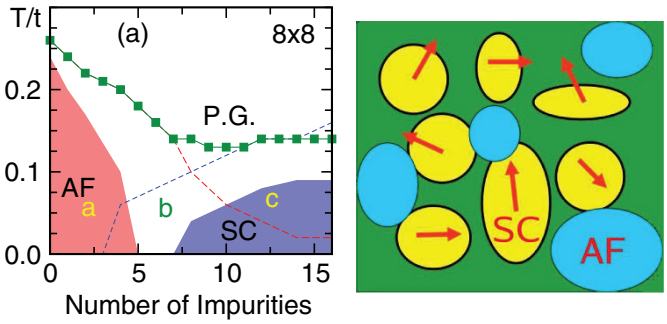

Figure 12. (Left panel) Phase diagram of a phenomenological model for cuprates reported in [37], where more details can be found. The 'P.G.' line denotes the region where a PG in the density-of-states appears upon cooling. The 'number of impurities' is equivalent to hole doping, namely, for each Sr added in the simulation ('impurity' that causes quenched disorder), a hole carrier is donated. (Right panel) A cartoon representing the state proposed for the SC–AF competition in the underdoped regime, when quenched disorder opens a gap between the AF and SC states. This state is the one proposed to show 'giant' effects, as explained in the text.

already observed by Iguchi *et al* [27]. The results of Ong *et al* on the Nernst effect may also find an explanation with this scenario.

9.2. Colossal effects in cuprates?

If preformed superconducting regions are indeed present in underdoped cuprates (figure 12, right), then the 'alignment' of their order parameter (i.e. alignment of the local phases ϕ that appear in the complex-number order parameter $\Delta = |\Delta|e^{i\phi}$ for different islands) should be possible upon the influence of suitable small external perturbations. This is similar to the presence of preformed FM clusters in manganites, which align their moments when a relatively small external magnetic field is applied (see [10] and also Cheong and collaborators). Could it be that 'colossal' effects occur in cuprates and other materials as well? This is an intriguing possibility raised by Burgy *et al* [10]. There are already experiments by Decca and collaborators [28] that have reported an anomalously large 'proximity effect' in underdoped $YBa_2Cu_3O_{6+\delta}$. In fact, Decca *et al* referred to the effect as 'colossal proximity effect'. Very recent and careful investigations by Bozovic *et al* [29] have also reported a 'giant proximity effect' compatible with the ideas expressed here. The actual calculations and details can be found in our recent publication [37]. Perhaps, colossal-type effects are more frequent than previously expected, and they are prominent in manganites simply because one of the competing phases is a ferromagnet which can be favoured by an easily available uniform magnetic field. If a simple external perturbation would favour CO, AF or SC states, large effects may be observed in the region of competition with other phases. If this scenario is correct, several problems should be percolative, and studies by Mayr [10] suggest that a resistor network mixing superconducting and insulating islands could roughly mimic results for cuprates. However, obviously, more work is needed to test these very sketchy challenging ideas. Note that this scenario for cuprates is totally different from the 'preformed Cooper pairs' ideas of Kivelson and Emery, and Randeria and collaborators where the

state above the critical temperature is homogeneous, but contains pairs that have not condensed. Here, the superconducting regions can be fairly large, containing probably hundreds of pairs, and are expected to move very slowly with time.

Even at a phenomenological level, the order of the transition between an antiferromagnet and a superconductor is still unknown. Mayr, Alvarez and collaborators are carrying simulations of toy models with both phases which hopefully will clarify these matters. The possibilities for the phase diagrams of two competing phases—according to general argumentations based on Landau free energies—involve bi-, tri- and tetracritical order. In the context of manganite models, the first two appear to be favoured for the AF–FM competition since first-order transitions at low temperatures have been found. However, in cuprates, the tetracritical possibility in the clean limit has been proposed by Sachdev and collaborators as well. This would lead to local coexistence of AF and d-wave SC in the underdoped region. Some experiments support this view [30]. Recent theoretical work also favours the emergence of tetracriticality from this competition [31], although a first-order transition is not excluded. More work is needed to clarify this elementary aspect of the problem. See section 9.4 for a proposed revised phase diagram of cuprates.

9.3. Cuprates are in the dirty limit?

The results for manganites and cuprates have also similarities with the physics of superconductivity in granular and highly disordered metals [32]. In this context, a critical temperature is obtained when the phases of the order parameters in different grains lock. This temperature is much smaller than the critical temperature of the homogeneous system. In manganites, the Curie or charge-ordering temperature may also be much higher in a clean system than in the real system, as discussed here and in [1, 2]. Section 9.4 deals with these ideas.

Very recently, an exciting result has been unveiled in the context of high-temperature superconductors. This is a scaling relation linking the superfluid density ρ_s, the critical temperature T_c and the dc conductivity of the normal state σ_{dc} (figure 13). The actual relation [33] is $\rho_s \propto \sigma_{dc} T_c$. The implications of this relation has been discussed in [34]: since Nb and Pb also satisfy the same relation and they are believed to be dirty BCS superconductors, it is reasonable to assume that the cuprates two belong to the same class. This result is compatible with the nanoscale phase-separated picture proposed in the previous subsections. Adding this to the evidence of stripes in some cuprates [35], and of *tiles* in some others [36], it becomes apparent that the high-T_c cuprates are not homogeneous superconductors.

9.4. A revised 'menu' for cuprates

In view of these recent studies, our group believes that the widely accepted phase diagram for cuprates (with an AF insulator that leads to a glass and then to a superconductor upon increasing hole doping) needs revision. In the picture proposed in [37], this phase diagram arises only in the case where quenched disorder is sufficiently strong to open a window between the SC and AF phases, as shown in figure 14(d). However, 'cleaner' compounds, such as possibly YBCO, should have a more direct transition, AF–SC, as sketched in figures 14(a)–(c), where local AF + SC coexistence, first-order AF–SC transition and stripes are shown. The latter has been widely mentioned in the cuprate literature, particularly after the pioneering work of Zaanen, Kivelson and others. In our framework, this represents just one possible intermediate state to move from the AF to the SC upon doping, but there are other possibilities.

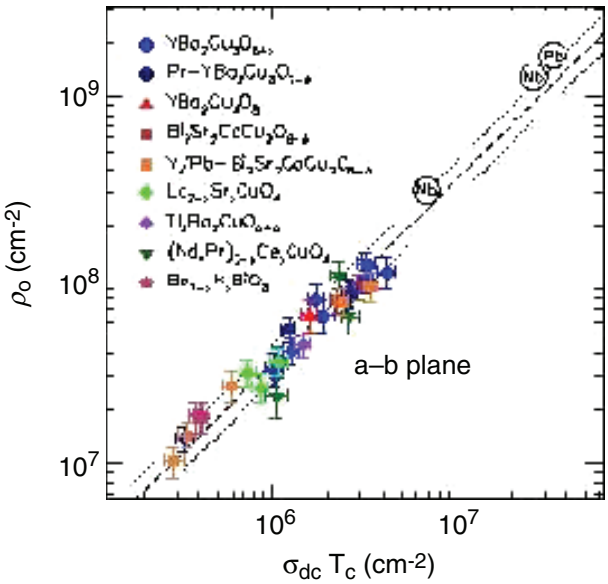

Figure 13. The Homes' scaling relation recently unveiled in [33, 34]. Dirty BCS superconductors also satisfy this scaling law [34], implying that the high-T_c cuprates are in the dirty limit. This is compatible with the nanoscale phase separation picture for cuprates.

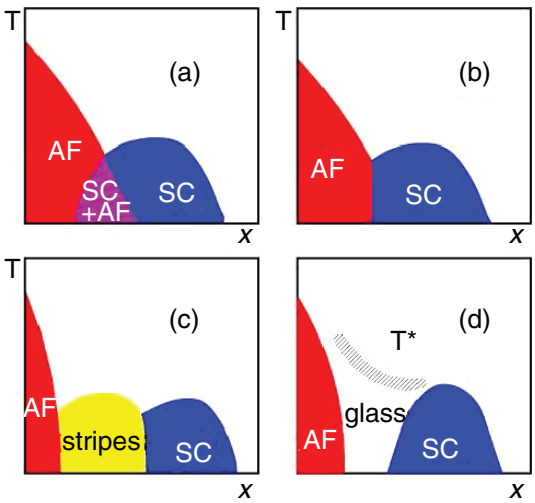

Figure 14. Possible phase diagrams when AF and SC are competing. (a), (b) and (c) emerge in the clean limit, while (d) needs quenched disorder. Details can be found in [37].

*9.5. Relaxor ferroelectrics and T**

The so-called *relaxor ferroelectrics* are an interesting family of compounds having ferroelectric properties and diffuse phase transitions [38]. The analogies with manganites are notorious. Representative cubic materials, such as $PbMg_{1/3}Nb_{2/3}O_3$, exhibit a glass-like phase transition at a freezing temperature $T_g \sim 230$ K. Besides the usual features of a glassy transition,

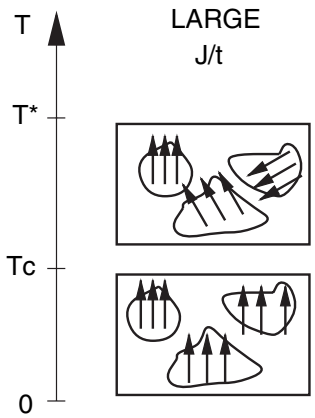

Figure 15. Schematic representation of the clustered state proposed for diluted magnetic semiconductors in [41]. At T^*, uncorrelated FM clusters are formed. At T_C, their moments are oriented in the same direction.

a broad-frequency-dependent peak in the dielectric constant has been found. The transition does not involve long-range ferroelectric order, providing a difference with most manganites that tends to have some form of long-range order at low temperature (although there are several with glassy behaviour). However, a remarkable similarity is the appearance of another temperature scale, the so-called Burns temperature [39], which is ∼650 K in $PbMg_{1/3}Nb_{2/3}O_3$. Below this temperature, polar nanoregions are formed. The Burns temperature appears to be the analogue of the T^* temperature of manganites discussed here. These analogies between ferroelectrics and Mn oxides should be explored further. For example, is there some sort of 'colossal' effect in the relaxor ferroelectrics? Are there two or more phases in competition? Can we alter the chemical compositions and obtain phase diagrams as rich as in manganites, including regimes with long-range order?

9.6. Diluted magnetic semiconductors (DMS) and T^*

DMS based on III–V compounds are recently attracting considerable attention due to their combination of magnetic and semiconducting properties, and this may lead to spintronic applications [40]. $Ga_{1-x}Mn_xAs$ is the most studied of these compounds with a maximum Curie temperature $T_C \approx 110$ K at low doping x, and with a carrier concentration $p = 0.1x$ [40]. The FM is carrier-induced, with the holes introduced by doping mediating the interaction between $S = 5/2$ Mn^{2+} spins. Models similar to those proposed for manganites, with coupled spins and carriers, have been used for these compounds. Recently, the presence of a T^* has also been proposed by Mayr *et al* and Alvarez *et al* [41], using Monte Carlo methods quite similar to those discussed in the manganite context. The idea is that in the random distribution of Mn spins, some of them spontaneously form clusters (i.e., they lie close to each other). These clusters can magnetically order by the standard Zener mechanism at some temperature, but different clusters may not correlate with each other until a much lower temperature is reached. This situation is illustrated in figure 15. Naively, we expect that above the true T_C, the clustered state will lead to an insulating behaviour in the resistivity, as it happens in Mn oxides (recent work by Alvarez has

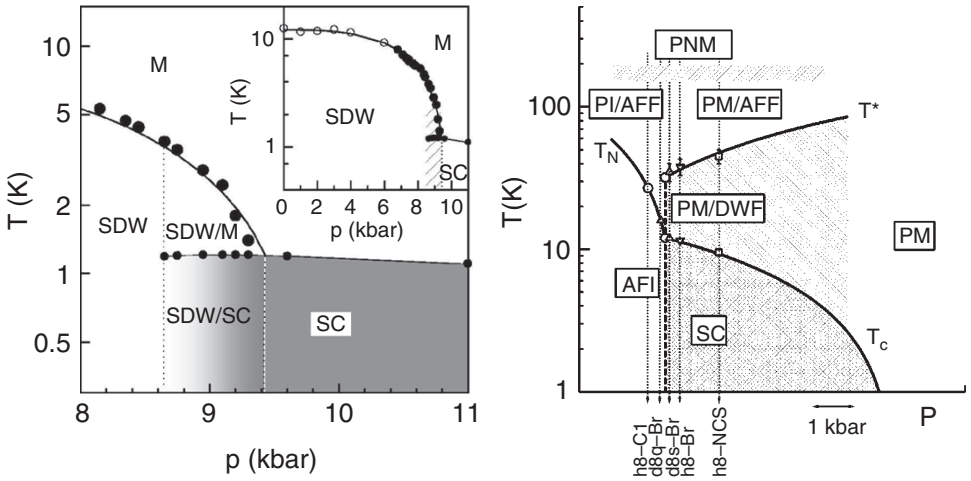

Figure 16. Left panel, phase diagram of $(TMTST)_2PF_6$ [44]. the SDW, M and SC indicate the SDW, metallic and superconducting regimes, respectively. The gradient in shading indicates the amount of SC phase. Right panel, phase diagram of κ-$(ET)_2X$ [45]. PNM stands for paramagnetic non-metallic, AFF is a metallic phase with large AF fluctuations, and DWF is a density wave with fluctuations. Note the first-order SC–AF transition (broken lines), as well as the presence of a T^* scale. Further details can be found in [45].

confirmed this hypothesis). This, together with the Zener character of the FM, unveils unexpected similarities between DMS and Mn oxides that should be studied in more detail.

9.7. Cobaltites

Recent work has shown that cobaltites, such as $La_{1-x}Sr_xCoO_3$, also present tendencies towards magnetic phase separation [42]. NMR studies have established the coexistence of FM regions, spin-glass regions and hole-poor low-spin regions in these materials [43]. This occurs at all values of x from 0.1 to 0.5. There are interesting similarities between these results and the NMR results of Papavassiliou and collaborators for the manganites, clearly showing a tendency towards mixed-phase states. Analysis of the common features (and differences) between manganites and cobaltites should be pursued in the near future.

9.8. Organic superconductors, heavy fermions and T^*

There are other families of materials that also present a competition between superconductivity and AF as the cuprates do. One of them is the group of organic superconductors [46].[2] The large field of organic superconductivity will certainly not be reviewed here, but some recent references will be provided to guide manganite/cuprate experts into this interesting area of research. In figure 16 (left panel), the phase diagram [44] of a much studied material known as $(TMTST)_2PF_6$ is shown. In a narrow region of pressures, a mixture of spin-density-wave (SDW) and SC (superconductivity) is observed at low temperatures. This region may result

[2] Phase diagrams of relevance for our discussion can be found, e.g., in figures 3.14, 3.15, 3.19, 3.23, 4.14, 5.67, and 7.6.

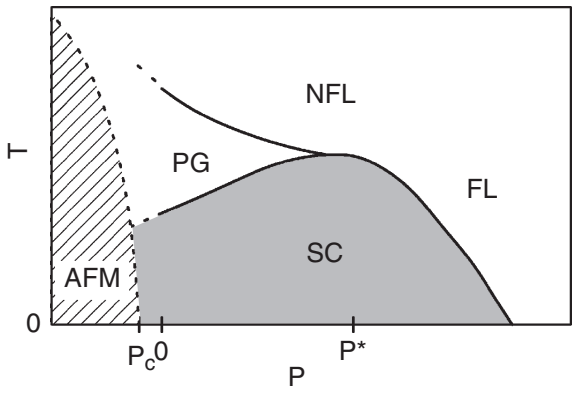

Figure 17. Schematic temperature–pressure phase diagram of some Ce-based heavy fermions, taken from [50].

from coexisting domains of both phases, as in the FM–CO competition in manganites. The two competing phases have the same electronic density and the domains can be large. Alternatively, the coexistence of the two order parameters can be local, as in tetracritical phase diagrams. The layered organic superconductor κ-$(ET)_2Cu[N(CN)_2]Cl$ has also a phase diagram with coexisting SC and AF [47]. In addition, other materials of the same family present a first-order SC–AF transition at low temperatures, according to the phase diagram recently reported in [45]. This result is reproduced in figure 16 (right panel), where a characteristic scale T^* produced by charge fluctuations is also shown. The similarities to the results for manganites are strong: first-order transitions or phase coexistence, and the presence of a T^*. It remains to be investigated whether the similarities are accidental or reveal the same phenomenology observed in competing phases of manganites. Recent results by Inagaki *et al* [48] provide important information that reveals giant effects in organic compounds. Also Sasaki *et al* [49] have reported phase separation near the Mott boundary in an organic superconductor stressing once again the similarities to oxides discussed above.

Another family of materials with competing SC and AF is the heavy fermions. As in previous cases, just a few references are provided here to illustrate the similarities to other compounds. In figure 17, a schematic phase diagram of Ce-based heavy fermions is shown [50]. Note the presence of a PG region, with NFL behaviour at higher temperatures. The PG phase is reminiscent of the region between ordering temperatures and T^*, discussed in manganites and cuprates, and it may arise from phase competition. In addition, clusters in U- and Ce-alloys were discussed in [51], and spin glass behaviour in $CeNi_{1-x}Cu_x$ was reported in [52]. Recently, Takimoto *et al* [53] found some interesting formal analogies between models for manganites and *f*-electron systems that deserve further studies.

9.9. Other materials with CMR?

The list of other materials with large magnetoresistance is not short enough to be included here. But the author would like to mention a recent work by Mira *et al* [54] where 'colossal-like' magnetoresistance is reported in a commercially available material, MnAs. The ideas discussed here and in the many references, and in [1] appear to be very general and they should apply to materials well beyond those of the Mn oxide family.

10. Conclusions

In recent years, a large effort has been devoted to the study of manganese oxides. Considerable progress has been achieved. Among the most important aspects unveiled is the presence of tendencies towards inhomogeneous states, both in experiments and in simulations of models. However, considerably more work is needed to fully understand these challenging compounds and confirm the relevance of nanoclusters to the CMR effect.

Considering a more global view of the problem, recent years have brought a deeper understanding of the many analogies among a large fraction of materials belonging to the correlated-electron family. Analogies between organic, cuprate and heavy-fermion superconductors are strong. The SC–AF phase competition with the presence of a T^*, PGs, phase coexistence and first-order transitions is formally similar to analogous phenomena unveiled in the FM–CO competition for manganites. In addition, all of these compounds share a similar phenomenology above the critical temperature, with nanoclusters formed. This phenomenon occurs even in diluted magnetic semiconductors, relaxor ferroelectrics and other families of compounds. The self-organization of clustered structures in the ground state appears to be a characteristic of many interesting materials, and work in this promising area of investigations has just started. This 'complexity' seems to be a common feature of correlated electron systems, particularly in the regime of colossal effects where small changes in external parameters lead to a drastic rearrangement of the ground state.

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