Phase separation, percolation and giant isotope effect in manganites

D.Khomskii

Laboratory of Solid State Physics, Groningen University, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Abstract

Phase separation and a tendency to form inhomogeneous structures seems to be a generic property of systems with strongly correlated electrons. After shortly summarising the existing theoretical results in this direction, I concentrate on the phenomena in doped manganites. I discuss general theoretical results on the phase separation at small doping and close to the doping $x = 0.5$. The “global” phase diagram in this region is constructed. These general results are illustrated on the example of the particular system with rich and complicated properties—$(\text{LaPr})_{1-x}\text{Ca}_x\text{MnO}_3$ in which there exist a ferromagnetic metallic (FM) phase and a charge ordered (CO) insulating one. The experimental situation in this system is discussed and the interpretation is given in the framework of the model with competition of FM and CO, and the indications of phase separation and percolative nature of this system are given. Giant isotope effect observed in this situation is shortly discussed.

Keywords: phase separation; phase diagrams; CMR manganites; charge ordering

The systems with correlated electrons present quite specific class of compounds, many properties of which differ markedly from those with ordinary band electrons. Recently yet another specific feature of these materials came to a forefront and attracts now considerable attention—the often present in them tendency to phase separation and creation of inhomogeneous states. This tendency was first studied theoretically in a number of models ($s$-$d$, or double exchange model [1–5]), Hubbard model [6], $t$-$J$ model [7,8] and was invoked to explain properties of many real systems: magnetic semiconductors (see e.g. [9]), cuprates [10] etc.

Depending on the specific situation the instability of homogeneous state and the tendency to phase separation may result in a formation of different structures: either random, percolation-like networks [11–13] or regular structures, e.g. stripes [14,15]. Many properties in this situation differ markedly from those of homogeneous states, and it has to serve as a basis of the explanation of experimentally observed phenomena in them.

There appear at present more and more indications that the formation of inhomogeneous states with concomitant percolation behaviour is an intrinsic feature of manganites with the colossal magnetoresistance (CMR): percolation picture quite naturally explains many features of manganites in a wide concentration range, and may even lie at the core of the very phenomenon of CMR [16,17]. In this article I will give a short summary of the theoretical situation with the phase separation in manganites and of some of the experimental con-
sequences and evidences of it, based mostly on the experimental results of Moscow groups (Babushkina, Balagurov, Fisher et al.)—see [18–21] and also other papers in these Proceedings [22,23]. In particular, giant isotope effect which is characteristic of this situation was studied in details in these works and will be discussed shortly at the end of this paper.

The electronic state of typical band-like systems like ordinary metals or semiconductors is usually homogeneous. This is to a large extent caused by the Fermi pressure of electrons: the increase of the Fermi energy with increasing electron density gives large positive contribution to the bulk modulus of the system and thus stabilizes homogeneous state.

However if due to strong electron correlation the electrons become localized (Mott–Hubbard localization), this positive contribution to the bulk modulus disappears or is strongly reduced, and some other factors may appear instead driving the system towards inhomogeneous state. As mentioned in the introduction, this instability of the homogeneous state and the resulting tendency to phase separation seems to be a generic feature of systems with strong electron correlation; the homogeneous states are rather an exception than a rule, existing formally only at rare isolated points of the phase diagram, such as exactly half-filled case for Hubbard or $t$–$J$ model or charge-ordered state $x = 0.5$ in manganites (see below).

The traditional model applied for manganites is the double-exchange model [24,25]

$$H = -t \sum_{(ij)} c^\dagger_{i\sigma} c_{j\sigma} + J \sum_{(ij)} S_i S_j - J_H \sum S_i c^\dagger_{i\alpha} \sigma c_{i\sigma}$$  \hspace{1cm} (1)

which describes conduction electrons $c^\dagger_{i\sigma}$, $c_{i\sigma}$ interacting by the Hund’s rule coupling $J_H$ with localized spins $S_i$ which by themselves would form an antiferromagnetic state due to exchange interaction $J$.

Standard quasiclassical treatment of this situation [25] leads to the conclusion that for $J_H \gg t > J$ doping of the insulating antiferromagnetic state (the increase of the concentration of conduction electrons $x$) leads to a gradual canting of antiferromagnetic sublattices until at critical concentration $x_c \sim J/t$ the system becomes ferromagnetic. This is due to the fact that for large $J_H$ the hopping of electrons is hindered by the antiferromagnetic ordering, $t_{\text{eff}} = t \cos \frac{\theta}{2}$, where $\theta$ is the angle between spins of the sublattices, and to gain kinetic energy it is favourable to make the angle $\theta$ smaller. Simple calculations (minimization of the total energy in $\theta$) give for $J_H \gg t$ $\cos \frac{\theta}{2} = \frac{x}{x+1}$, from which we get the condition for ferromagnetism induced by doping ($\theta = 0$ for $x \geq x_c$).

However one immediately sees that in this treatment the homogeneous canted state is absolutely unstable [4,5]; the electron energy in this approximation is

$$E = E_0 - \frac{t^2}{2} x^2$$  \hspace{1cm} (2)

so that $\partial^2 E/\partial x^2 < 0$, i.e. the compressibility of the system is negative which signals the instability towards phase separation. This tendency survives in a more elaborate quantum treatment [4], this is confirmed by the numerical calculations [3].

Thus the homogeneous canted state of double exchange systems is absolutely unstable at low doping, and the system would phase separate into regions of undoped antiferromagnet and region with higher electron (or hole) concentration—ferromagnetic or strongly canted metallic (FM) droplets. These FM droplets may form percolative network, which can explain transport and other properties of manganites in this region [16,11,12].

In reality other factors also play an important role in this effect—notably the long-range Coulomb forces which oppose charge segregation on a large scale. Nevertheless the tendency to phase separation survives even in this case [7,9], Coulomb interaction limiting the size of FM clusters.

It is well established [26,27] that besides antiferro- and ferromagnetic states, also charge-ordered states are realized in manganites, especially at commensurate doping $x = 0.5$ (one elec-
tron or hole per two Mn’s). This state with simple checkerboard charge ordering (CO) is an exact ground state for \( x = 0.5 \), but often it extends to other values of \( x \), e.g. in \( \text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3 \)—down to \( x = 0.3 \) [26]. For these cases an interesting phase diagram was found in [27]: strong enough magnetic field renders system metallic, but with an unusual reentrant behaviour in \((H, T)\)-plane (see fig. 1) (insulating CO state (COI) exists at intermediate temperature range, but is transformed into FM state at lower temperatures; this transition is accompanied by large hysteresis).

The answer is apparently that the low-temperature FM state is not an ordinary disordered liquid, as compared to a CO “crystal”, but a Fermi-liquid with a unique ground state (Fermi-surface) and consequently with zero entropy. On the contrary, the CO insulating state for \( x < 0.5 \) is not fully ordered: as follows from the neutron data [26] the overall CO periodicity in this state is the same as for \( x = 0.5 \) (superlattice peaks at \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\)) but one has to accommodate somewhere the extra electrons (or Mn\(^{3+}\) ions) present for \( x < 0.5 \)—and this is apparently done in a random fashion which gives an extra entropy of the CO state and drives the system into this state with increasing temperature.

What is the exact nature of this partially ordered CO state? There are in general two options. Either these extra electrons (Mn\(^{3+}\)) are distributed randomly in one sublattice of the checkerboard CO state typical for \( x < 0.5 \), or there again exists phase separation, with the electron-rich regions forming percolation—again random!—network on a CO background. One can give arguments that most probably it is the latest situation which is realized in practice. Thus the situation close to doping \( x = 0.5 \) resembles that at small \( x \): the system away from particular commensurate doping tends to phase separate into a commensurate (here charge-ordered) state and FM droplets. As we will see below this picture permits to explain many experimental results in the system (La\(_{1-y}\text{Pr}_y\)\(_{1-x}\text{Ca}_x\)\(_3\text{MnO}_5\) and is confirmed by direct experiments [11,19–21].

Qualitative arguments supporting this conclusion can be drawn using the pseudospin description of the charge ordering and corresponding analogy with magnetic systems. The simplest model describing the formation of a CO state is that of spinless fermions with \( nn \) repulsion

\[
H = -t \sum_{\langle ij \rangle} c_i^\dagger c_j + V \sum_i n_i n_j - \mu \sum_i n_i, \tag{3}
\]

where we introduced also chemical potential \( \mu \) to be able to describe the situation with arbitrary doping.

One can easily show [28,19] that for \( V > 2t \) the ground state of a system with one electron per two sites \( (n_{el} = x = \frac{1}{2}) \) is the checkerboard CO state. By introducing the pseudospin variables \( \sigma_i \) such that \( n_i = \frac{1}{2} + \sigma_i^z \) \( (\sigma^z = +\frac{1}{2} \quad \text{corresponds to an occupied site and} \quad \sigma_i^z = -\frac{1}{2} \quad \text{to an empty one}) \) one can model our system by the Hamiltonian

\[
H = -t \sum_i (\sigma_i^+ \sigma_j^- + \text{h.c.}) + V \sum_i \sigma_i^z \sigma_j^z - \mu \sum_i \sigma_i^z + \text{const.} \tag{4}
\]

(Actually the model (4) is not exactly equivalent to (3) due to different commutation relation of op-
erators, but the qualitative behaviour of both systems is very similar.) The CO state at \( n = \frac{1}{2} \) corresponds to an “antiferro” state with total \( \langle \sigma^z \rangle = 0 \).

One can easily see that the situation with nonzero net “magnetization” \( \langle \sigma^z \rangle \neq 0 \) which corresponds to \( \langle n \rangle \neq \frac{1}{2} \) would describe the state with some of the pseudospins of one sublattice reversed.

As is well known, the increase of the “magnetic field” \( \mu \) causes metamagnetic transition—a jump of magnetization, which is actually the I order phase transition, see fig. 2. Consequently, the situation with fixed net magnetization \( 0 < \langle \sigma^z \rangle < \frac{1}{2} \) (which corresponds to a net electron density \( \frac{1}{2} < n < 1 \) or hole concentration \( x = 1 - n \) between 0 and \( \frac{1}{2} \)) corresponds to coexistence of two phases: “antiferro” (CO) one with \( \langle \sigma^z \rangle = 0 \), and “ferro” one (all extra electrons forming one big cluster with \( \langle \sigma^z \rangle = 1 \) or \( n = 1, x = 0 \)). The vertical line in fig. 3 may be viewed as a Maxwell construction with unstable regions shown by dashed lines in fig. 3. Thus these qualitative arguments show that the system with doping close but different from \( x = \frac{1}{2} \) may indeed phase separate into CO state with \( x = \frac{1}{2} \) and another phase, presumably metallic, with some \( x < \frac{1}{2} \).

One comes to essentially the same conclusions from quite different point of view. As recently noticed in [29], with the account of the CE-type magnetic structure of CO phase in manganites at \( x = 0.5 \) [26] the motion of charge carrier is essentially one-dimensional, along the ferromagnetic zigzag chains in CE-structure. Corresponding band structure consists of bonding and antibonding bands and nonbonding band in between [29,30]. For \( x = 0.5 \) the bonding band is full and the other two bands are empty. For \( x > 0.5 \) the lower band becomes gradually depopulated, with corresponding gradual change in band energy. However the situation is highly asymmetric around \( x = 0.5 \); for \( x < 0.5 \) (more electrons in the system) it is the dispersionless nonbonding electron band which becomes populated. As a result the total band energy is constant for certain range of concentrations < 0.5 which again leads to the phase separation.

The resulting “global” phase diagram of manganites for \( x \leq 0.5 \) takes the form shown schematically in fig. 3. Maxwell construction is shown there by dashed lines. We see that there exists two regions of phase separation: for \( 0 < x < x_1 \) the system phase separates into undoped antiferromagnetic insulator (\( x = 0 \)) and ferromagnetic metallic phase with \( x = x_1 \). Close to half-filling the system is again unstable and for \( x_2 < x < 0.5 \) it separates into the mixture of the CO insulating antiferromagnetic phase with \( x = x_1 \), and a FM phase with \( x = x_2 \). The inclusion of Coulomb interaction would modify the parameters of these phases and would prevent full phase separation but rather stabilize “fine-grained” mixture of phases, but would not change the situation qualitatively. The question whether these exists a “window” \( x_1 < x < x_2 \) at which a homogeneous FM state would be
realized, is open: it may depend on parameters of the specific system etc. Thus e.g. such homogeneous FM state may exist for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (although it is actually not known for certain at present); but such window is definitely absent for $\text{Pr}_{1-x}\text{CaMnO}_3$ [26] which is insulating for all $x$.

The conclusions reached above show that the phase separation is a generic property of manganites and probably also of many other systems with correlated electrons. What form the final state takes depends on many specific details ignored in our general treatment, such as specific type of magnetic structure, possible orbital effects, Coulomb and electron–lattice interaction etc. It may be random percolation network with different lengthscales, or it may even be a regular stripe-like structure.

Above we concentrated on the situation in manganites at $x \leq 0.5$. For overdoped (or electron-doped [32]) manganites the situation with respect to phase separation may be similar [31], although the details may differ significantly. In any case the treatment shortly presented above [30] definitely shows that in general the situation for $x < 0.5$ and $x > 0.5$ is highly asymmetric—the conclusion which agrees with all the experimental observations.

In the last part of the paper I will shortly discuss experimental evidences in favour of the theoretical picture described above. One of the most convenient systems to study these effects, especially the interplay of CO insulating and FM states, is the system $(\text{La}_{1-y}\text{Pr}_y)_{1-x}\text{Ca}_x\text{MnO}_3$ studied in details in [11,12,18–23]. As already mentioned above, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ has a ferromagnetic metallic state with the colossal magnetoresistance for $0.16 \leq x \leq 0.5$. $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ however is a charge-ordered insulator in this concentration range. Thus by changing the ratio La/Pr in a mixed compound we can go from FM to COI phases, even with fixed doping $x$. It turns out that close to the crossover from one phase to another which is characterized by strong hysteresis, all the properties very strongly depend on isotope composition: one can even induce a metal–insulator transition by only substituting $^{18}\text{O}$ instead of $^{16}\text{O}$ [18,19,34]. The schematic phase diagram for this system which follows from all these experiments has the form shown in fig. 4 where the borderline between FM and COI phases is marked for both $^{16}\text{O}$ and $^{18}\text{O}$ systems.

Quite characteristic for this case, besides the very specific form of the phase diagram, with the reentrant behaviour and with giant isotope effect, are many properties which signal an intrinsic inhomogeneity in this situation. Many properties in this regime find natural explanation in the percolation picture. Such are e.g. the magnetic properties [22], strongly nonlinear $I$–$V$ characteristics of these samples [11], many other transport properties [12]. The inhomogeneous nature of these samples was visualized directly in [12].

I will discuss here only one extra spectacular effect which finds natural explanation in the picture of phase separation. The behaviour of the magnetization of these systems with external field shows very unusual “shifted hysteresis” behaviour shown in fig. 5 [23]. $M(H)$ curves are symmetrical for $H < 0$. Similar but less spectacular behaviour was also seen in [35,36]. Simultaneously with this unusual $M(H)$ curves the magnetization shows marked relaxation behaviour, with characteristic times reaching tens of minutes.

The most natural explanation of all these facts can be obtained in a picture of inhomogeneous
state, with ferromagnetic droplets immersed in the charge ordered antiferromagnetic matrix (neutron studies directly confirm this interpretation [20]). The first part of $M(H)$ curves is explained in this picture by the conventional orientation of the moments in ferromagnetic regions (an ordinary hysteresis close to $H = 0$ is also seen but apparently it is a very soft magnet, and the coercive force is very low).

Starting from the fields $\sim 1-2$ T the ferromagnetic regions start to grow, “eating up” the antiferromagnetic ones, until at $H \simeq 4-5$ T they occupy the whole sample, and the magnetization reaches saturation.

At the reverse change of field there exists marked hysteresis, seen also in resistivity and in other properties. One can successfully model this behaviour, including also time dependence, by assuming the existence of two locally stable states, FM and CO antiferromagnetic one, with certain energy barriers between them. Thus this experiment gives yet another clear indication of an inhomogeneous state at least of this particular system but most probably present also in many other situations.

The last comment concerns the nature of giant isotope effect in this situation. As follows from the theoretical considerations based on model (3) [28,19] the balance between COI and FM state strongly depends on the ratio of the electron (or hole) bandwidth $\sim t$ and effective $nn$ repulsion $V$: CO state exists only for $V > V_c \sim 2t$. By changing isotope composition we in principle modify electron hopping $t$, either because of the polaron band narrowing

$$t \rightarrow t^* = t \exp \left( -\frac{E_{pol}}{\omega} \right)$$

where $E_{pol}$ is the polaron binding energy and $\omega$ is the typical phonon frequency; or, in the absence of polaron effects, the effective hopping decreases simply due to the averaging of $t(r)$ over lattice vibrations (both thermal and zero-pont ones) [19]. Both these effects work in the right direction, reducing the bandwidth for heavier $^{18}$O ions and shifting the equilibrium in the direction of the CO state. However the estimates show that the changes of $t_{eff}$ are still rather small, and it is not completely clear what is the real nature of this strong isotope dependence. (Actually this problem is the same as the one encountered in the whole class of manganites where relatively small changes in crystal structure caused e.g. by going from La$_{1-x}$Ca$_x$MnO$_3$ to Pr$_{1-x}$Ca$_x$MnO$_3$ change all the properties drastically.) One possible explanation of this strong sensitivity of the behaviour of e.g. (La$_{1-x}$Pr$_x$)$_{0.7}$Ca$_{0.3}$MnO$_3$ to oxygen isotope composition [18–23] may again lie in the behaviour close to percolation threshold where as is well known relatively minor change of parameters may lead to a drastic modification of the properties of the system.

In conclusion, we presented above theoretical arguments which show that the instability towards phase separation and formation of inhomogeneous states is an intrinsic tendency of many systems with correlated electrons, in particular CMR manganites. Such phase separation should exist both at low doping level and close to $x \simeq 0.5$. Whether the optimally doped phase with CMR is homogeneous or it is also inhomogeneous at small scale (with possible dynamic phase separation) is not clear at present. In any case the tendency to phase separation and the resulting percolation picture should be taken into account in the interpretation of many experiments in manganites. In many cases this is the most natural and possibly the only explanation of experimental observations. Some of them were shortly discussed or mentioned in our paper; there exist now many other indications of the same phe-
nomenon which we had no chance to discuss (e.g. neutron [37] or NMR [38] results). All these data, together with the theoretical arguments presented above, point to the crucial role played by the phase separation and percolation in the physics of CMR manganites and presumably in many other systems with correlated electrons.

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