

## Phase separation in inhomogeneous mixed-valence systems

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A simple alloy-analogy model for inhomogeneous mixed-valence systems is considered in the context of manganites. It is assumed that the Mn ions coexist in two magnetic configurations,  $Mn^{4+}$  and  $Mn^{3+}$ , and that they interact via a nearest-neighbor charge interaction. In addition, two nearest-neighbor ions with equal valence interact antiferromagnetically (superexchange), while ions of different valence are coupled ferromagnetically (double exchange). Assuming classical spins, we show that the system is unstable to phase separation, i.e., to the coexistence of antiferromagnetic and charge ordered ferromagnetic domains.

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### I. INTRODUCTION

The discovery of the colossal magnetoresistance<sup>1</sup> has renewed the interest in the rich phase diagram of  $La_{1-x}Ca_xMnO_3$ .<sup>2-4</sup> The end compounds  $LaMnO_3$  and  $CaMnO_3$  are antiferromagnetic insulators, while for intermediate  $x$  the system is either a ferromagnetic metal or a charge ordered antiferromagnet.<sup>3</sup> Coupling to the lattice in the form of polarons or a dynamical Jahn-Teller effect<sup>5-7</sup> and orbital order have been found. The lattice distortions manifest themselves in changes of the Mn-O-Mn bond lengths and angles.<sup>8</sup> Most attempts to theoretically explain the phenomenon invoke the double exchange mechanism within the framework of the ferromagnetic Kondo lattice.<sup>9</sup> There is some experimental evidence for phase separation in the manganites, i.e., a separation into electron rich and electron poor domains larger than the atomic scale (for a brief review see Ref. 10). For small  $x$  this question has been theoretically addressed in Refs. 11–13. Phase separation has recently also been an important issue in high- $T_c$  compounds.<sup>14</sup>

The manganese ions exist in a mixed trivalent and tetravalent state in which each of the three  $t_{2g}$  orbitals is singly occupied with their spins coupled to form a total spin  $S = 3/2$ . The  $e_g$  orbitals, on the other hand, are empty for  $Mn^{4+}$  and occupied by one  $3d$  electron in  $Mn^{3+}$ , which is ferromagnetically correlated with the localized  $t_{2g}$  electrons (Hund's rule), yielding  $S' = 2$ . The Mn-O bonds are crucial to understand the spin-exchange interactions between the Mn ions.<sup>15</sup> Two Mn of equal valence do not involve the charge transfer of an  $e_g$  electron and the interaction is an antiferromagnetic (AF) superexchange. On the other hand, if the two ions have different valence the  $e_g$  electron can hop between the sites inducing a ferromagnetic (FM) double exchange coupling.

It is useful to distinguish between homogeneous and inhomogeneous mixed valence compounds. In the former case the valence is intermediate (not integer) and typically heavy band-like states at the Fermi surface give rise to a metallic conductivity. In the case of inhomogeneous mixed valence the ionic configurations are well defined and the conductivity is semiconductor-like. Examples of this class are  $Sm_3S_4$ ,  $Eu_3S_4$ ,  $Eu_3O_4$ ,<sup>16,17</sup> and to some extent  $Fe_3O_4$ . For the manganites this means that the  $e_g$  electrons hop slowly from site

to site and their kinetic energy (other than contributing to the double exchange bond) can be neglected. This point of view, namely to consider the manganites as an inhomogeneous mixed-valence compound, was taken in Goodenough's<sup>15</sup> pioneering work. In more recent contributions<sup>6,9,13</sup> the manganites are described by a Kondo lattice with ferromagnetic exchange. The Bloch states induce a metallic homogeneous mixed-valence ground state, rather than a mixture of trivalent and tetravalent ions. The manganites are most likely in an intermediate regime between homogeneous and inhomogeneous mixed valence. The description as a homogeneous system is adequate at low temperatures where the Fermi sea is stabilized by Bloch states, while at intermediate and high temperatures the local bonds play the dominant role giving rise to semiconductor-like behavior.

In this paper we consider an inhomogeneous mixed-valence system for the manganites consisting of a distribution of nearest-neighbor bonds consistent with the concentration of tetravalent ions. Four coupling constants are involved, namely the AF couplings  $J_{33}$  and  $J_{44}$ , the ferromagnetic coupling  $J_{34}$ , and a chemical interaction  $U$ . The subindices refer to the valence of the ion, i.e.,  $J_{33}$  is the superexchange between two trivalent ions. The chemical interaction  $U$  takes into account the difference in the bond strength between the different ions. The model is described with more detail in Sec. II. In Sec. III we discuss the ground state of the model. The same properties also are valid at intermediate temperatures. In Sec. IV we discuss other mechanisms that favor or limit phase separation. It is concluded that inhomogeneous mixed valence favors small phase-separated domains. Conclusions and a discussion of the limitations of the model, in particular the lack of coherent states and simplifications to the complicated bond arrangements of  $Mn^{3+}$ , follow in Sec. V.

### II. MODEL

We assume that the manganites can be described as an inhomogeneous mixed-valence compound. The Mn ions form a simple cubic lattice, which we subdivide into two interpenetrating sublattices  $\alpha$  and  $\beta$ , with coordination number  $z$ . We limit ourselves to a probabilistic description of the local environment by defining bond probabilities of nearest-

neighbor pairs. We further assume that the spins  $S=3/2$  and  $S'=2$  are large enough to be treated as classical. We introduce the pair probabilities  $P_{ij}^{\alpha\beta}$  giving the probability of finding an ion  $i$  at a site of the sublattice  $\alpha$  and an ion  $j$  at a neighboring site on the sublattice  $\beta$ . Here  $i$  and  $j$  can take the values  $3+$ ,  $3-$ ,  $4+$ , and  $4-$ , corresponding to trivalent and tetravalent ions with upspin and downspin, respectively. There are then 16 such pair probabilities, which are normalized by the condition  $\sum_{ij} P_{ij}^{\alpha\beta} = 1$ . The single-site probabilities expressed in terms of the  $P_{ij}^{\alpha\beta}$  are given by

$$n_i^\alpha = \sum_j P_{ij}^{\alpha\beta}, \quad n_j^\beta = \sum_i P_{ij}^{\alpha\beta}, \quad (1)$$

where  $n_i^\alpha$  denotes the probability of finding the component  $i$  at a site of the sublattice  $\alpha$ . The probabilities are further constrained by the total number of  $e_g$  electrons, i.e.,  $x = \frac{1}{2}(n_{4+}^\alpha + n_{4-}^\alpha + n_{4+}^\beta + n_{4-}^\beta)$ , where  $x$  is the fraction of Ca ions substituting La ions.

Within the pair approximation the entropy of the system is given by<sup>18</sup>

$$S = \frac{N}{2}(z-1) \sum_i (n_i^\alpha \ln n_i^\alpha + n_i^\beta \ln n_i^\beta) - N \frac{z}{2} \sum_{ij} P_{ij}^{\alpha\beta} \ln P_{ij}^{\alpha\beta}, \quad (2)$$

where  $N$  is the total number of Mn ions. As mentioned in the introduction we consider a charge (chemical) and a magnetic (Ising-like) interaction between nearest-neighbor ions, given by<sup>16</sup>

$$\begin{aligned} H_c &= NzU \sum_{\sigma\sigma'} (P_{3\sigma 3\sigma'}^{\alpha\beta} + P_{4\sigma 4\sigma'}^{\alpha\beta} - P_{3\sigma 4\sigma'}^{\alpha\beta} - P_{4\sigma 3\sigma'}^{\alpha\beta}), \\ H_{ex} &= NzS^2 J_{44} \sum_{\sigma\sigma'} \sigma\sigma' P_{4\sigma 4\sigma'}^{\alpha\beta} + NzS'^2 J_{33} \sum_{\sigma\sigma'} \sigma\sigma' P_{3\sigma 3\sigma'}^{\alpha\beta} \\ &\quad - NzSS' J_{34} \sum_{\sigma\sigma'} \sigma\sigma' (P_{3\sigma 4\sigma'}^{\alpha\beta} + P_{4\sigma 3\sigma'}^{\alpha\beta}), \end{aligned} \quad (3)$$

where  $\sigma = \pm 1$ . The free energy of the system is then given by  $\mathcal{F} = H_c + H_{ex} - TS$ , which must be minimized with respect to the  $P_{ij}^{\alpha\beta}$  subject to the normalization condition and the given concentration  $1-x$  of  $e_g$  electrons. An estimate of the coupling parameters can be obtained from the phase diagram of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ :  $J_{33}$  and  $J_{44}$  are comparable corresponding to transition temperatures of about 100 K,  $J_{34}$  is about two times larger, and  $U$  is the largest energy expected to be about ten times larger than  $J_{33}$ .

### III. GROUND STATE

In the absence of an external magnetic field the model is invariant under the following transformations:<sup>19</sup> (i) change of sign of  $J_{34}$  and inversion of all spins of one magnetic component, e.g., all  $\text{Mn}^{4+}$  spins, (ii) simultaneous interchange of  $x$  with  $1-x$  and  $J_{33}$  with  $J_{44}$ , and (iii) change of sign of  $J_{33}$  and  $J_{44}$  by reinterpreting a FM phase as AF and vice versa (inversion of one sublattice).

From these symmetries it is clear that the ground state of our model does not have a phase transition as a function of  $x$ .

There is no frustration of the spins and consequently the system can be mapped onto one with only ferromagnetic interactions. Hence as a function of  $x$  the only possible changes in the ground state are crossovers or the coexistence of different phases. Below we study the ground-state energy as a function of  $x$ .

(i) For  $\text{CaMnO}_3$ , i.e.,  $x=1$ , all Mn ions are tetravalent and only  $P_{4\sigma 4\sigma'}^{\alpha\beta}$  can be different from zero. The antiferromagnetic spin interaction yields  $E_G = (U - S^2 J_{44})Nz$  and from entropy considerations we have that  $P_{4+4-}^{\alpha\beta} = 1$  while all other pair probabilities are zero. As expected the ground state is a pure AF.

(ii) For  $\text{LaMnO}_3$ , i.e.,  $x=0$ , all Mn ions are trivalent and only  $P_{3\sigma 3\sigma'}^{\alpha\beta}$  is different from zero. Minimization of the free energy in the limit  $T \rightarrow 0$  yields an AF ground state with  $E_G = (U - S'^2 J_{33})Nz$  and  $P_{3+3-}^{\alpha\beta} = 1$  while all other pair probabilities are zero.

(iii) For  $x=0.5$  the ground state is charge ordered, i.e., one sublattice contains only trivalent ions and the other only tetravalent ions. The ground state is ferromagnetic with  $P_{3+4+}^{\alpha\beta} = 1$ , while all other pair probabilities vanish, and has energy  $E_G = -(U + SS' J_{34})Nz$ .

(iv) For  $0.5 \leq x \leq 1$  the only nonvanishing pair probabilities are  $P_{3+4+}^{\alpha\beta} = 2-2x$  and  $P_{4-4-}^{\alpha\beta} = 2x-1$  and the ground-state energy is

$$E_G = -2(1-x)(U + SS' J_{34})Nz + (2x-1)(U - S^2 J_{44})Nz. \quad (4)$$

This expression interpolates linearly between the end points given by cases (i) and (iii).

(v) For  $0 \leq x \leq 0.5$ , on the other hand, the only nonvanishing pair probabilities are  $P_{3+3-}^{\alpha\beta} = 1-2x$  and  $P_{3+4+}^{\alpha\beta} = 2x$ . The ground-state energy here interpolates linearly between the end-point cases (ii) and (iii) and is given by

$$E_G = -2x(U + SS' J_{34})Nz + (1-2x)(U - S'^2 J_{33})Nz. \quad (5)$$

The linear dependence of the ground-state energy on  $x$  corresponds just to Vegard's law. In this case a homogeneously mixed system has the same energy as the separate constituents, i.e., in case (v)  $2x$  parts of the charge ordered ferromagnet and  $1-2x$  parts of  $\text{LaMnO}_3$ . The mixing energy is exactly zero.

Note that while the ground state can only have a crossover as a function of  $x$ , there are two possible phase transitions as a function of temperature. The high- $T$  phase is a disordered paramagnet. Assuming that the chemical interaction  $U$  is much larger than the magnetic ones, the system for intermediate  $x$  will undergo a second-order transition into a paramagnetic state with partial charge order, and at even lower- $T$  magnetic order will set in. The phase diagram studied with the Migdal-Kadanoff decimation procedure along the lines of Ref. 19 yields similar results.

### IV. PHASE SEPARATION

The approach outlined in the previous sections yields the same ground-state energy for a homogeneous mixture of bonds and a phase separated system. In this section we examine possible mechanisms that could stabilize either of

these phases. These mechanisms represent refinements of the model beyond the simple nearest-neighbor bond approximation. The first three favor phase separation, while the last two tend to limit phase separation.

*Next-nearest-neighbor (NNN) correlations.* For the ground-states (i), (ii), and (iii) in the previous section (corresponding to  $x=1$ ,  $x=0$ , and  $x=0.5$ , respectively), Mn ions on the same sublattice are ferromagnetically correlated. We call ferromagnetically correlated NNN bonds satisfied and those antiferromagnetically correlated unsatisfied. It is assumed that unsatisfied NNN bonds are energetically unfavorable and we assign an additional energy  $\epsilon$  to such a bond. This can be implemented by introducing three-site diagrams, i.e., the simultaneous interaction of an ion with two nearest neighbors. The eight possible three-site diagrams are obtained by assigning trivalent and tetravalent ions to the sites. The relative spin orientations in the ground state are then determined by the magnetic interactions. Four diagrams belong into the satisfied NNN bond class and the other four diagrams are unsatisfied.

It is energetically favorable to maximize the satisfied NNN bond and thereby minimize the unsatisfied ones. This leads to domains of ground states of the type (i), (ii), and (iii). In this case only the boundaries between domains have unsatisfied bonds. The additional energy is then proportional to  $\epsilon$  times the surface of the domains. Optimally there are only two large domains, one with  $x=0.5$  and the other one being an end-point compound ( $x=0$  or  $x=1$ ). This corresponds to a complete separation of phases. A refinement of this argument to more complex interactions, e.g., third- and fourth-order neighbors, does not change this conclusion. This surface energy vanishes in the thermodynamic limit.

*x dependence of  $J_{34}$ .* While the superexchange requires integer-valent Mn ions, the ferromagnetic double exchange<sup>20</sup> requires intermediate valence and depends on the fractional occupation of the  $e_g$  orbitals. Assuming the system is metallic it is easy to calculate the energy of one link at  $T=0$  joining two ferromagnetically and antiferromagnetically correlated Mn ions. The energy difference is the exchange energy, which is proportional to the hopping  $t$ . For homogeneously distributed electrons the carrier density is determined by  $x$ . Considering two  $e_g$  orbitals with directed hopping we obtain<sup>21</sup>

$$E_F - E_{AF} = -tx \left[ \frac{1}{2} + x \right] / 2 \quad \text{if } 0 \leq x \leq 0.5,$$

$$E_F - E_{AF} = -tx(1-x) \quad \text{if } 0.5 \leq x \leq 1. \quad (6)$$

This expression is maximum at  $x=0.5$  indicating that the bond is strongest for exactly one electron per link. Due to the  $x$  dependence of the exchange the ground-state energy, Eqs. (4) and (5), is no longer linear in  $x$  and again phase separation is favored. In other words, it is energetically favorable to have AF and charge ordered FM domains, in which the FM bonds have maximum strength.

*Volume changes.* The AF superexchange bonds are shorter than the FM double exchange bonds. This gives rise to a strong coupling to the lattice. Volume changes couple to the long-range order parameter  $\eta$  for the charge (chemical) interaction<sup>17</sup>

$$E_{latt}/V = c(\Delta V)^2 + \lambda(\Delta V)\eta^2,$$

$$\eta = \sum_{\sigma\sigma'} (P_{3\sigma 4\sigma'}^{\alpha\beta} - P_{4\sigma 3\sigma'}^{\alpha\beta}), \quad (7)$$

where  $c$  contains the elastic constants,  $\Delta V$  is the change in volume, and  $\lambda$  is the electron-lattice coupling constant. Minimizing with respect to  $\Delta V$  we obtain for the ground state  $E_{latt} = -(\lambda^2 \eta^4 / 4c)V = -(4\lambda^2/c)p^4 V$ , where  $p=x$  if  $0 \leq x \leq 0.5$  and  $p=1-x$  if  $0.5 \leq x \leq 1$ . The energy gain is maximum for  $x=0.5$  and zero for  $x=0$  and  $x=1$ . This mechanism again favors phase separation into AF and charge ordered FM domains.

*Coulomb interactions.* Assuming that the  $xN$  Ca ions are randomly distributed on the La sublattice, a phase separation causes a local charge imbalance, i.e., the domains have either an excess or deficiency of electrons as compared to the positive background. This gives rise to an increase of the Coulomb interaction which favors the uniform phase. Three contributions have to be considered: (a) the kinetic energy, (b) the electrostatic energy of the electrons with the background, and (c) the Coulomb energy between the electrons. We divide the system into two domains of volume  $V_{\pm}$  and electron density  $\rho_{\pm}$ , which satisfy  $V = V_+ + V_-$  and  $V_+ \rho_+ + V_- \rho_- = V \rho_0$ , where  $\rho_0$  is the density of the uniform system. We assume a screening length  $\lambda^{-1}$  (for simplicity independent of the electron density) for the metallic phase. A total phase separation ( $\rho_- = 0$ ) increases the energy by the amount

$$\Delta E_{Coul} = (3/10m)(3\pi^2)^{2/3} \rho_0^{5/3} V [(V/V_+)^{2/3} - 1] \\ + (2\pi e^2 \rho_0^2 / \lambda^2) V [(V/V_+) - 1], \quad (8)$$

where  $m$  is the effective mass of the electrons. Since  $V/V_+$  is fixed by  $x$ , subdividing the domains into many smaller domains (keeping the total  $V_+$  and  $V_-$  invariant) does not modify the energy, unless the size of the domains becomes comparable to  $\lambda^{-1}$ . In this case the above expression for  $\Delta E_{Coul}$  is an overestimate, since a sphere of radius  $\lambda^{-1}$  would contain regions with high and low electron density. Small sized domains are then energetically favored.

*Lattice mismatch.* The two coexisting phases (AF and charge ordered FM) have different lattice constants, so that there is necessarily a lattice mismatch, which introduces strain into the sample. The volume mismatch  $\delta V$  occurs at the boundaries  $S$  between domains on a shell of width  $a$ . If  $c$  is the corresponding lattice constant, the energy for  $\tilde{N}$  domains of average size  $\tilde{V}$  (i.e.,  $\tilde{N}\tilde{V} = V$ ) is

$$E_{mis} = (c/2)\tilde{N}(\delta V)^2 \approx (a^2 c/2)\tilde{N}S^2 \alpha \tilde{N}\tilde{V}^{4/3} = V(V/\tilde{N})^{1/3}. \quad (9)$$

It is then energetically favorable to have many small domains.

The above arguments suggest that the equilibrium ground state for an inhomogeneous mixed-valence system with two magnetic configurations as considered here is phase separated, consisting of small insulating AF integer-valent domains and small charge ordered FM (semiconducting or metallic-like at finite  $T$ ) regions.

## V. CONCLUSIONS

We considered an inhomogeneous mixed-valence compound of the type  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  within a simple alloy-analogy model. Assuming that all interactions can be described by pair probabilities we obtain that the ground-state energy is a linear superposition of the  $x=0.5$  charge ordered FM state and one of the AF integer-valence end points of the alloy at  $x=0$  or  $x=1$  (Vegard's law). The dependence of the double exchange mechanism on the electron density and volume changes due to the different bond lengths yield deviations from the linearity in  $x$  favoring a phase separation. On the other hand, the local charge neutrality (Coulomb interactions) and the lattice mismatch (as a consequence of the different bond lengths) limit the size of the domains. The energetically most favorable configuration is then a phase-separated alloy with relatively small regions of an integer-valent AF insulator and a charge ordered FM, which becomes a poor metal at intermediate temperatures.

Within the limitations of this model the conductivity at low and intermediate  $T$  is due to the thermally activated hopping of the  $e_g$  electrons. We assume that the conductivity is proportional to the available  $\text{Mn}^{3+}\text{-Mn}^{4+}$  pairs (preferably with parallel spin because of the double exchange) in the system, since these are the only bonds contributing to the transport. The probability for hopping is then given by  $P_{3+4+}^{\alpha\beta} + P_{4+3+}^{\alpha\beta}$ , which is maximum for  $x=0.5$ , and the activation energy corresponds to the long-range charge order gap (i.e.,  $P_{3+4+}^{\alpha\beta} \neq P_{4+3+}^{\alpha\beta}$ ).<sup>16,17</sup> To have nonzero conductivity requires in addition that the FM domains are percolating (or drift in an electrical field), since otherwise the electrons cannot travel through the sample. Hence, the carriers are localized (donor/acceptor-like bound states) close to the end points, i.e., for small  $x$  or small  $1-x$ , where the system is insulating. Note that the temperature dependence of the distribution of bonds also yields a thermal expansion (or contraction).<sup>17</sup>

Experimentally at low  $T$  the alloys are poor metals in the mixed-valence regime. This exposes the main limitation of the model. Aspects of the competition of Bloch-like states with covalent bonds have been neglected. Ideally Bloch states give rise to a Fermi surface and stabilize the system

against phase separation. The ground state is a coherent (in time and space) superposition of the two electronic configurations leading to a homogeneous state. Homogeneous vs inhomogeneous mixed valence is a well-understood issue in rare-earth compounds. Above a characteristic (Kondo) temperature the local interactions dominate and the two configurations can be distinguished. In the present case the mixing of the two configurations via a hybridization is minimal, so that the system is likely to be somewhere midway between homogeneous and inhomogeneous mixed valence. The key question in the present context is the degree of formation of the Fermi surface, i.e., the degree to which there is coherence at low  $T$ . In any case the inhomogeneous mixed-valence approach should be valid at intermediate temperatures.

In this paper we simplified the complicated nature of the  $\text{Mn}^{3+}\text{O}^{2-}$  bonds.  $\text{Mn}^{3+}$  has only one empty  $3d$  orbital, so that it hybridizes square coplanar lattice orbitals.<sup>15</sup> Hence,  $\text{Mn}^{3+}$  can only satisfy four metallic bonds and the remaining two bonds (perpendicular to the plane) are ionic.  $\text{Mn}^{4+}$ , on the other hand, has both  $e_g$  electrons missing, so that it can sustain six metallic bonds. The bonds of the  $\text{Mn}^{3+}$  ions lead to planar spin and charge arrangements, including orbital order. It may therefore be more appropriate to consider a coordination number  $z=4$  rather than  $z=6$  as for the isotropic three dimensional case. From the symmetries listed in Sec. III we concluded that the ground state as a function of  $x$  has no phase transition. This of course changes if the anisotropy of the  $\text{Mn}^{3+}\text{O}^{2-}$  bonds is properly taken into account.<sup>15</sup> Phases with more complicated magnetic order are then possible and limit the range of  $x$  over which phase separation is possible. Orbital order can be included into our model by introducing  $NNN$  interaction (between sites on the same sublattice) and by associating an orbital index to the  $\text{Mn}^{3+}$  ions. This considerably complicates the model, but does not change the quite general phase-separation arguments.

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