PHYSICAL REVIEW B VOLUME 62, NUMBER 1 1 JULY 2000-I

Phase separation and enhanced charge-spin coupling near magnetic transitions

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(Received 12 July 1999; revised manuscript received 19 January 2000)

The generic changes of the electronic compressibility in systems which show magnetic instabilities are studied within a mean-field approach. It is shown that, when going into the ordered phase, the inverse compressibility is reduced by an amount comparable to its original value, making charge instabilities also possible. We discuss, within this framework, the tendency towards phase separation of the double-exchange systems, the pyrochlores, and the magnetic transitions of the Hubbard model.

I. INTRODUCTION

The theoretical possibility of phase separation (PS) in magnetic systems was first discussed in connection with the Hubbard model for itinerant magnetism.[1] The work of Emery and Kivelson[2] has since established that PS should be ubiquitous in doped antiferromagnets. Recent arguments suggest that PS is also likely in other magnetic materials, such as those in which magnetism is due to double-exchange interactions.[3–8] Spin polarons, which can be viewed as a manifestation of PS on a small scale, have been analyzed in relation to the pyrochlores.[10] Finally, there is an extensive literature on PS in two-dimensional (2D) doped antiferromagnets (see, for instance Refs. 11–16), although there is no definitive consensus on its existence.

A variety of different experiments show features which are compatible with electronic phase segregation, at least on small scales, near magnetic transitions. For instance, near an antiferromagnetic transition there is ample evidence for the formation of charged stripes, both in the cuprates[17] and in the nickelates.[18] In the ferromagnetic manganites, various experiments suggest the existence of polarons near the Curie temperature,[19] which, as mentioned above, can be viewed as phase separation on small scales. In addition and also in the ferromagnetic manganites (i.e., $\mathrm{La}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$, $x\approx 1/3$), inhomogeneous textures[20] and hysteretic effects[21] have been reported near T_c. Note that we are discussing the relatively simple case of the optimally doped, *ferromagnetic* compounds, avoiding the complications which arise between the competition between antiferromagnetism, charge ordering, and double exchange in these materials. Finally, there is evidence for inhomogeneous textures in ferromagnetic pyrochlores.[22] The purpose of this paper is to show the theoretical foundations which make likely the existence of electronic phase segregation near magnetic transitions. We do not pretend to give an exhaustive list of the experimental evidence which supports this view.

In the following, we analyze how a magnetic transition influences the electronic compressibility. Although most of the paper is restricted to a mean-field treatment, we expect the main conclusions concerning PS to survive in the presence of critical fluctuations, at least in three dimensions. In the systems we study at zero temperature (Hubbard model), the effective dimensionality is increased (by 2 or 3, depending on the dynamical critical exponent). This means that, in three dimensions, we are safely above the critical dimension. Therefore, we do not expect major problems from the mean-field approach. For those models we study at finite temperature (double-exchange systems and pyrochlores), critical fluctuations can be important. Nevertheless, phase separation can be considered as a diverging charge fluctuation at the macroscopic scale. Therefore, it is not unreasonable to expect an increase in the PS tendency due to the enhancement of charge fluctuations caused by their coupling to the critical fluctuations of the magnetic order parameter (not included in the mean-field analysis).

The paper is organized as follows. A general framework is presented in the next section. Simple applications to the Hubbard model are considered in Sec. III. Then it is shown that the same approach predicts the existence of PS in the pyrochlores (Sec. IV). Section V studies PS in double-exchange models, including some improvements over the standard mean-field approach. Section VI analyzes the role of long-range interactions. Finally, the main conclusions of our work are summarized in Sec. VII.

II. GENERAL FEATURES OF THE ELECTRONIC COMPRESSIBILITY NEAR A MAGNETIC PHASE TRANSITION

The formation of an ordered phase induces a decrease in the free energy of the material, usually called the condensation energy. Because of it, quantities which depend on the variation of the free energy with temperature, such as the specific heat, show anomalous, nonanalytic behavior at the critical temperature. For instance, the specific heat shows an

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abrupt reduction at T_c in mean-field theories. The phase transition can also be tuned by varying n, the electronic content (per unit cell), in many systems, leading to phase diagrams like those shown in Figs. 2–4. Thus one expects an anomalous dependence of the free energy on the electronic density as the phase boundary is crossed by changing the electronic concentration.

A standard Ginzburg-Landau expansion of the free-energy density[23] yields a simple estimate of such an effect:

$$\mathcal{F}(m)=\frac{c}{2}(\nabla m)^2+\frac{a[T-T_c(n)]}{2}m^2+\frac{b}{4}m^4+\mathcal{F}_n(n), \tag{1}$$

where m is the electronic magnetization and $\mathcal{F}_n(n)$ stands for a regular contribution to the free energy. We now neglect spatial fluctuations and obtain a mean-field approximation to $\mathcal{F}$:

$$\mathcal{F}_{\mathrm{MF}}=\frac{a[T-T_c(n)]}{2}m^2+\frac{b}{4}m^4+\frac{(n-n_0)^2}{2\tilde{\kappa}_0}, \tag{2}$$

where we have expanded the dependence of the free energy of the paramagnetic phase on n. Here $\tilde{\kappa}_0$ is the (scaled) electronic compressibility in the paramagnetic phase, and n_0 defines the equilibrium density in the absence of magnetism. We will use the name inverse scaled compressibility and the symbol $\tilde{\kappa}^{-1}(\tilde{\kappa}_0^{-1})$ to describe the derivative of the chemical potential with respect to n, that is $\tilde{\kappa}^{-1}=\partial^2\mathcal{F}/\partial n^2$. Notice that our scaled compressibility coincides with the standard definition except for trivial factors of density. When $T<T_c$, the magnetization is $m^2=a[T_c(n)-T]/b$, and the free energy becomes

$$\mathcal{F}_{\mathrm{MF}}=-\frac{a^2[T_c(n)-T]^2}{4b}+\frac{(n-n_0)^2}{2\tilde{\kappa}_0}, \tag{3}$$

while above T_c the magnetization vanishes and only the last addend survives on the right-hand side (RHS) of both Eqs. (2) and (3). Let us now fix the temperature T and expand this expression around the density n_c such that $T=T_c(n_c)$. We obtain

$$\mathcal{F}_{\mathrm{MF}}\approx-\frac{a^2}{4b}\left(\frac{\partial T_c}{\partial n}\right)^2(n-n_c)^2+\frac{(n-n_0)^2}{2\tilde{\kappa}_0}. \tag{4}$$

And by taking derivatives, we have

$$\tilde{\kappa}^{-1}\equiv\frac{\partial^2\mathcal{F}_{\mathrm{MF}}}{\partial n^2}=\begin{cases}\dfrac{1}{\tilde{\kappa}_0}, & T_c<T,\\[2ex] -\dfrac{a^2}{2b}\left(\dfrac{\partial T_c}{\partial n}\right)^2+\dfrac{1}{\tilde{\kappa}_0}, & T<T_c.\end{cases} \tag{5}$$

The compressibility has a jump at the transition. The origin of this discontinuity is the same as that in the specific heat.

Alternatively and keeping T fixed close to $T_c(n_0)$, one can first find the density n which minimizes $\mathcal{F}_{\mathrm{MF}}$. By expanding $T_c(n)$ around n_0, we find

$$n=\begin{cases}n_0, & T_c<T,\\[1ex] n_0+\dfrac{a\tilde{\kappa}_0 m^2}{2}\dfrac{\partial T_c}{\partial n}, & T<T_c.\end{cases} \tag{6}$$

Then, by expanding $T_c(n)$ around n_0 and inserting the above value of n in the free energy when $T<T_c$, we find

$$\mathcal{F}\approx\frac{a[T_c(n_0)-T]}{2}m^2+\frac{b}{4}m^4-\frac{a^2\tilde{\kappa}_0}{8}\left(\frac{\partial T_c}{\partial n}\right)^2m^4. \tag{7}$$

The dependence of T_c on the density leads to a negative quartic term in the dependence of the free energy on the magnetization. When $b/4-(a^2\tilde{\kappa}_0)(\partial T_c/\partial n)^2/8<0$, the magnetic transition becomes first order. This condition is equivalent to saying that the effective compressibility, defined in Eq. (5), becomes negative. Thus PS near the transition can be thought of as arising from the transmutation of a continuous phase transition into a first-order one by the introduction of an additional field, the density n, which is a well-known possibility in statistical mechanics.[24] The new feature found in a magnetic transition is that the correction to the compressibility can easily be comparable to the initial compressibility. The latter is determined by the density of states at the Fermi level in the paramagnetic phase. In typical magnetic systems, the transition is driven by a coupling constant which is of the order of the inverse of the density of states. Finally, the dependence of the critical temperature on the electronic density depends on the change of the coupling constant with variations in the density of states, which is of the same order (see examples below). Thus no fine-tuning of parameters is required to obtain corrections to the compressibility of the order of the compressibility itself.

III. PHASE SEPARATION IN HUBBARD-LIKE MODELS

A. Ferromagnetic transitions

Let us consider a one-band Hubbard model:

$$\mathcal{H}=\sum_{k,\sigma}\epsilon_k c_{k,\sigma}^{\dagger}c_{k,\sigma}+\sum_i Un_{i,\uparrow}n_{i,\downarrow}, \tag{8}$$

where i is a site index, σ is a spin index ($\sigma=\uparrow,\downarrow$), and $n_{i,\sigma}=\langle c_{i,\sigma}^{\dagger}c_{i,\sigma}\rangle$. This model (with appropriate additions) has been invoked as a reasonable starting point for the study of itinerant ferromagnetism.[25] Within a mean-field approximation, the Stoner criterion gives a ferromagnetic instability for $U\mathcal{D}(\epsilon_F)\geqslant 1$, where $\mathcal{D}(\epsilon)$ is the density of states per spin at energy ϵ. Let us assume that in the paramagnetic phase there are n_0 electrons per site, with chemical potential μ_0:

$$n_0=2\int^{\mu_0}\mathcal{D}(\epsilon)d\epsilon. \tag{9}$$

If we shift the two spin bands by $\pm\delta$, the induced polarization $m=n_{i,\uparrow}-n_{i,\downarrow}$ satisfies

$$\delta=\frac{m}{2\mathcal{D}(\mu_0)}+\frac{\mathcal{D}'^2(\mu_0)m^3}{16\mathcal{D}^5(\mu_0)}-\frac{\mathcal{D}''(\mu_0)m^3}{48\mathcal{D}^4(\mu_0)}, \tag{10}$$

where $\mathcal{D}'$ and $\mathcal{D}''$ stand for the derivatives with respect to energy of the density of states. Because of the lack of electron-hole symmetry when these derivatives are finite, the chemical potential in the polarized state is shifted:

$$\mu-\mu_0=-\frac{\mathcal{D}'(\mu_0)\delta^2}{2\mathcal{D}(\mu_0)}+\frac{\mathcal{D}'(\mu_0)\mathcal{D}''(\mu_0)\delta^4}{4\mathcal{D}^2(\mu_0)}-\frac{\mathcal{D}'^3(\mu_0)\delta^4}{8\mathcal{D}^3(\mu_0)}-\frac{\mathcal{D}'''(\mu_0)\delta^4}{24\mathcal{D}(\mu_0)}. \tag{11}$$

The ground-state energy, at zero temperature, can be written as

$$\mathcal{E}=E_0+\frac{m^2}{4\mathcal{D}(\mu_0)}+\frac{\mathcal{D}'^2(\mu_0)m^4}{64\mathcal{D}^5(\mu_0)}-\frac{\mathcal{D}''(\mu_0)m^4}{192\mathcal{D}^4(\mu_0)}+U\frac{n^2-m^2}{4}, \tag{12}$$

where $E_0=2\int^{\mu_0}\epsilon\,\mathcal{D}(\epsilon)d\epsilon$. This is the Ginzburg-Landau expansion needed to study the phase transition as function of electronic density at zero temperature. The system becomes ferromagnetic when $\mathcal{D}(\mu_c)U\geqslant 1$. We can expand the quadratic term in the magnetization around $n_c=2\int_0^{\mu_c}\mathcal{D}(\epsilon)d\epsilon$ as

$$\frac{1}{4}\left[U-\frac{1}{\mathcal{D}(\mu)}\right]\approx\frac{\mathcal{D}'(\mu_c)(n-n_c)}{8\mathcal{D}^3(\mu_c)}, \tag{13}$$

which leads to the following scaled inverse compressibility, as the transition is approached from the ordered side:

$$\tilde{\kappa}^{-1}=\tilde{\kappa}_0^{-1}-\frac{1}{2\mathcal{D}(\mu_c)}\left[1-\frac{\mathcal{D}''(\mu_c)\mathcal{D}(\mu_c)}{3\mathcal{D}'^2(\mu_c)}\right]^{-1}, \tag{14}$$

where $\tilde{\kappa}_0^{-1}=[2\mathcal{D}(\mu_c)]^{-1}+(U_c/2)$ and $U_c=[\mathcal{D}(\mu_c)]^{-1}$ is the critical coupling for the transition to take place. The compressibility is negative if $\mathcal{D}''(\mu_c)\mathcal{D}(\mu_c)/[3\mathcal{D}'^2(\mu_c)]>1/2$. In particular, near a saddle point in the 3D dispersion relation, we have $\mathcal{D}(\epsilon)=\mathcal{D}_0-c\sqrt{|\epsilon-\epsilon_{SD}|}$. This implies $\lim_{\epsilon\to\epsilon_{SD}}\{\mathcal{D}''(\epsilon)\mathcal{D}(\epsilon)/\mathcal{D}'^2(\epsilon)\}\to+\infty$, and the system is always unstable versus PS.

It is interesting to note that, using a different formalism, phase separation has been shown to appear near ferromagnetic phases of the Hubbard model in two dimensions,[26] in good agreement with the picture presented here.

B. Doped antiferromagnets

It is well known that the Hubbard model [Eq. (8)] at half-filling, in a bipartite lattice and with nearest-neighbor hopping only, has an antiferromagnetic (AF) ground state, except in one dimension. The main physical features of this state, a charge gap, long-range magnetic order, and low-energy spin waves, are well described using standard mean-field techniques and the random phase approximation (RPA). Recent work shows that, in the presence of a static magnetization, the opening of a charge gap occurs, while the quasiparticle residues remain finite, at least in the infinite-dimension limit,[27] further supporting the validity of a mean-field ansatz. Alternatively, a calculation of the ground-state energy in the limit of large dimensions and small values of U/t can be obtained by standard perturbation theory around a mean-field symmetry breaking state.[28] This approach does suggest the existence of PS near half-filling.[11]

The mean-field solution at half-filling is straightforward to extend to finite fillings. Hartree-Fock calculations show that there are self-consistent homogeneously doped solutions for a finite range of fillings around half-filling, in two and three dimensions.[29–31] As reported earlier, these solutions acquire a negative contribution to the electronic compressibility near the transition boundaries, making PS possible. In the following, we analyze the stability of the homogeneous mean-field solution in arbitrary dimensions, following a different approach from that used in Ref. 11.

The AF distortion shifts the mean-field levels, $\epsilon\to\mathrm{sgn}(\epsilon)\sqrt{\epsilon^2+\Delta^2}$, opening a gap and leading to the following staggered magnetization:

$$\overline{s}\equiv\sum_{\sigma=\pm1}\sigma c_{i,\sigma}^{\dagger}c_{i,\sigma}=-2\int_{-W_0}^{\tilde{\mu}}d\epsilon\,\mathcal{D}(\epsilon)\frac{\mathrm{sgn}(\epsilon)\Delta}{\sqrt{\epsilon^2+\Delta^2}}, \tag{15}$$

where $\mathcal{D}(\epsilon)=\mathcal{D}(-\epsilon)$ and $\tilde{\mu}$ are, respectively, the density of states (per spin) and Fermi level in the paramagnetic phase, with filling factor $n=2\int_{-W_0}^{\tilde{\mu}}d\epsilon\,\mathcal{D}(\epsilon)$ and half-bandwidth W_0. The energy is given by

$$\mathcal{E}=2\int_{-W_0}^{\tilde{\mu}}d\epsilon\,\mathcal{D}(\epsilon)\mathrm{sgn}(\epsilon)\sqrt{\epsilon^2+\Delta^2}+\Delta\overline{s}+\frac{U}{4}(n^2-\overline{s}^2), \tag{16}$$

with the order parameter satisfying the following self-consistency requirement:

$$\frac{1}{U}=-\int_{-W_0}^{\tilde{\mu}}d\epsilon\,\mathcal{D}(\epsilon)\frac{\mathrm{sgn}(\epsilon)}{\sqrt{\epsilon^2+\Delta^2}}. \tag{17}$$

Both the energy and self-consistency equation can be obtained from the minimization of the following functional of the order parameter $\mathcal{F}(\Delta)$, which we take as the starting point for the stability analysis:

$$\mathcal{F}(\Delta)=2\int_{-W_0}^{\tilde{\mu}}d\epsilon\,\mathcal{D}(\epsilon)\mathrm{sgn}(\epsilon)\sqrt{\epsilon^2+\Delta^2}+\frac{U}{4}n^2+\frac{\Delta^2}{U}. \tag{18}$$

Away from half-filling, a critical value U_c is required for the instability to take place, with $U_c(n)=-1/\int_{-W_0}^{\tilde{\mu}}d\epsilon\,\mathcal{D}(\epsilon)/\epsilon$. Close to the transition line $U_c(n)$, a Ginzburg-Landau analysis is straightforward, leading to

$$\mathcal{F}(\Delta)=f_0+f_2\Delta^2+f_4\Delta^4, \tag{19}$$

with

$$f_0=2\int_{-W_0}^{\tilde{\mu}}d\epsilon\,\epsilon\mathcal{D}(\epsilon)+\frac{U}{4}n^2, \tag{20}$$

$$f_2=1/U-1/U_c(n), \tag{21}$$

$$f_4=-\frac{1}{4}\int_{-W_0}^{\tilde{\mu}}d\epsilon\frac{\mathcal{D}(\epsilon)}{\epsilon^3}. \tag{22}$$

The scaled inverse compressibility satisfies

$$\tilde{\kappa}^{-1}=\frac{\partial^2\mathcal{E}}{\partial n^2}=\begin{cases}\dfrac{1}{2\mathcal{D}(\tilde{\mu})}+\dfrac{U}{2}, & U\to U_c^-\\[2ex] \dfrac{1}{2\mathcal{D}(\tilde{\mu})}+\dfrac{U}{2}-\dfrac{(\partial_n f_2)^2}{2f_4}, & U\to U_c^+\end{cases}. \tag{23}$$

Following the transition line on the AF side to the limit of small doping, one has $(\partial_n f_2)^2/2f_4 \to 1/\mathcal{D}(\tilde{\mu})$, leading to $\tilde{\kappa}^{-1} \to -1/2\mathcal{D}(\tilde{\mu})$. Therefore, we have proved the existence of PS in the vicinity of $U_c(n)$, at least close to half-filling.

In fact, PS is not restricted to the previous region. It is also present around half-filling, $n \to 1^{\pm}$, for *all* values of U, as we now show. Close to half-filling and at finite U, the compressibility satisfies

$$\tilde{\kappa}^{-1} = U/2 - = \left[2\Delta^2 \int_{-W_0}^{0} d\epsilon \frac{\mathcal{D}(\epsilon)}{(\epsilon^2+\Delta^2)^{3/2}} \right]^{-1} \tag{24}$$

and, given the inequality [see Eq. (17)]

$$2\Delta^2 \int_{-W_0}^{\tilde{\mu}} d\epsilon \frac{\mathcal{D}(\epsilon)}{(\epsilon^2+\Delta^2)^{3/2}} < 2 \int_{-W_0}^{\tilde{\mu}} d\epsilon \frac{\mathcal{D}(\epsilon)}{\sqrt{\epsilon^2+\Delta^2}} = \frac{2}{U}, \tag{25}$$

one obtains

$$\tilde{\kappa}^{-1} < 0, \tag{26}$$

proving PS around half-filling for all values of U, as previously stated. This analysis indicates that PS is a very robust feature of the AF instability at the mean-field level. In fact, for a flat model density of states, numerical results suggest that the entire AF region has negative compressibility.

The study of this section can be extended to the case of a diverging density of states at half-filling: $\mathcal{D}(\epsilon) \sim |\epsilon|^{\alpha}$ $(0 \leqslant \alpha < 1)$. The existence of PS is also proved in this case, at least around the transition line $U_c(n \to 1)$. In particular, this includes the mean-field solution of the Hubbard model in the square lattice, where the density of states has a van Hove logarithmic singularity. The conclusions of our analysis are consistent with the tendency towards inhomogeneous solutions found in mean-field studies of the Hubbard model.[32–35]

IV. PYROCHLORES

The pyrochlores are metallic oxides, $Mn_2Tl_2O_7$, which show various anomalous transport and magnetic properties, including colossal magnetoresistance. The magnetism is mostly due to the spins of Mn ions. The electronic carriers are assumed to come from a wide s band from TI orbitals, with a very low occupation. These electrons are coupled ferromagnetically to the Mn spins.[36,22] We can describe the coupled system by the Hamiltonian[10]

$$\mathcal{H} = \sum_{k,\sigma} \epsilon_k c^{\dagger}_{k,\sigma} c_{k,\sigma} - J \sum_{ij} \vec{s}_i \cdot \vec{s}_j - J' \sum_{i,\sigma,\sigma'} c^{\dagger}_{i,\sigma} \vec{\sigma}_{\sigma\sigma'} c_{i,\sigma'} \vec{s}_i \,, \tag{27}$$

where J and J' are positive (ferromagnetic), σ represents the carrier spin index $(\sigma = \uparrow, \downarrow)$, $\vec{s}_i$ is the Mn spin (assumed classical) of site i, and $\vec{\sigma}_{\sigma\sigma'}$ are Pauli spin matrices. The model undergoes a transition to an ordered phase where the local spins have a finite magnetization, $s = |\langle \vec{s} \rangle| \neq 0$, and the electron gas is polarized, $m = |\Sigma_{\sigma} \langle c^{\dagger}_{i,\sigma} \vec{\sigma}_{\sigma\sigma'} c_{i,\sigma'} \rangle| \neq 0$.

In principle, the entire issue of PS in the pyrochlores could be settled using results of Majumdar-Littlewood (ML).[10] These authors have shown that magnetic polarons (i.e., self-trapped, polarized electrons in a magnetic bubble of core spins embedded in a paramagnetic environment) are the stable configuration of carriers in the paramagnetic phase at low densities. Now we will show that the existence of polarons in the paramagnetic phase is a sufficient condition for the thermodynamic instability of the uniform phase of the standard mean-field analysis.

Let us consider a low concentration (n) of carriers in the polaronic configuration. The free energy at fixed temperature is proportional to the number of carriers (polarons):

$$\mathcal{F}_{\rm pol}(T,n) = \delta f_{\rm pol}(T) n, \tag{28}$$

where $\delta f_{\rm pol}(T) < 0$ is the free-energy reduction per carrier due to its polaronic bubble. The preference for polarons implies that the homogeneous (paramagnetic) phase $\mathcal{F}_{\rm hom}$ is above $\mathcal{F}_{\rm pol}$ in the limit $n \to 0$. Consider now that the carrier density reaches the value $\tilde{n}$ at which all volume is filled with polarons, each one with its confined carrier. It is obvious that, allowing carriers to delocalize (keeping the core magnetization and temperature constant), their kinetic energy diminishes. This implies the existence of a homogeneous phase (with finite core magnetization and total carrier polarization) with energy below the polaronic phase at finite carrier concentration. A variational reasoning guarantees that the true homogeneous solution of the mean-field treatment is even below in free energy. In conclusion, if the single polaron is stable, the free energy of the homogeneous phase must satisfy

$$\mathcal{F}_{\rm pol}(T, n \to 0) = \delta f_{\rm pol}(T) n < \mathcal{F}_{\rm hom}(T, n \to 0),$$

$$\mathcal{F}_{\rm pol}(T, \tilde{n}) = \delta f_{\rm pol}(T) \tilde{n} > \mathcal{F}_{\rm hom}(T, \tilde{n}).$$

Remember that $\mathcal{F}_{\rm pol}$ is linear in n, and both $\mathcal{F}_{\rm pol}$ and $\mathcal{F}_{\rm hom}$ start from the same point. Then the previous inequalities can only happen if the curvature of $\mathcal{F}_{\rm hom}$ changes sign with concentration, leading to a negative compressibility and PS. Therefore, we have proved our original assertion: stable polarons imply thermodynamic instability towards PS. Notice that this is a sufficient condition, but not necessary: PS can exist (see below) even if the ML polarons are not the stable configuration in the paramagnetic phase. A graphical description of the previous argument comparing polaronic- and homogeneous-phase free energies for $kT = 0.115t$ is shown in Fig. 1 (two upper curves). In addition, we also show the free energy of the correct treatment, including carrier entropy (see below).

There is, however, a source of concern with the previous conclusion. In the ML analysis, carriers in the homogeneous phase enter with energy but no entropy. This would be correct for the usual case of degenerate fermions. But the temperature is finite and the interesting region corresponds to very low carrier concentration, making the degenerate assumption questionable. For the parameters expected to apply in the pyrochlores,[10] the classical limit would be a more appropriate starting point. In fact, in the limit of zero concentration at finite temperature, the chemical potential $(\mu = \partial_n \mathcal{F}_{\rm hom})$ corresponds to classical particles, and diverges: $\mu(n \to 0) \sim \ln(n)$. This implies that, in that limit, the homogeneous paramagnetic phase (including carriers entropy) is *always* more stable than the ML polaronic ansatz. It could be argued that the entropy does not appear explicitly in the ML treatment because it is the same in both the polaronic and

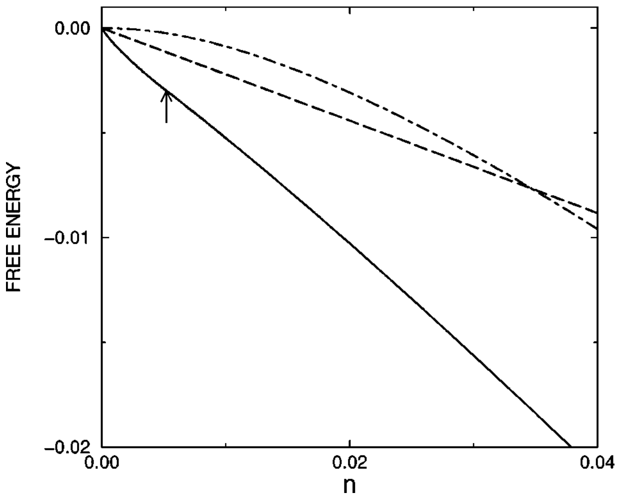

FIG. 1. Free energy vs electron concentration for the exact mean-field treatment (solid line), the polaronic ansatz (dashed straight line), and the degenerate approximation for electrons (dash-dotted line), for $kT=0.125t$ and parameters explained in the text. The arrow marks the onset of negative curvature.

homogeneous phases. This would remove any doubt about the ML analysis, but we see no obvious reason for such a cancellation to take place.

Given the previous ambiguities, we study the existence of PS in the pyrochlores with the standard thermodynamic analysis of the homogeneous phase, without relying on polaronic arguments. We perform the usual mean-field calculation *without* simplifying hypothesis for the carriers. The Helmholtz free energy $\mathcal{F}$ contains the core $\mathcal{F}_s$, carrier $\mathcal{F}_m$, and core-carrier contributions $\mathcal{F}_{sm}$, with expressions

$$\mathcal{F}_s=-\frac{Jz}{2}s^2-kT\left[\ln\left(\frac{\sinh(h)}{h}\right)-hs\right],$$

$$\mathcal{F}_m=-kT\sum_{\sigma=\uparrow\downarrow}\int d\epsilon\,\mathcal{D}(\epsilon)\ln\left[\exp\left(\frac{\mu_\sigma-\epsilon}{kT}\right)+1\right]+\sum_{\sigma=\uparrow\downarrow}\mu_\sigma n_\sigma, \tag{29}$$

$$\mathcal{F}_{sm}=-J'sm, \tag{30}$$

where $m=n_\uparrow-n_\downarrow$ is the carrier magnetization, z is the number of nearest neighbors, $\mathcal{D}(\epsilon)$ represents the paramagnetic density of states (per spin), and h describes the effective field characterizing the mean-field distribution of core spins, assumed to be classical vectors of unit length, therefore, $s=\coth(h)-h^{-1}$.

Minimization of $\mathcal{F}$ leads to the following equations:

$$\mu_\uparrow-J's-\mu-0, \tag{31}$$

$$\mu_\downarrow+J's-\mu=0, \tag{32}$$

$$-Jzs+kTh-J'm=0, \tag{33}$$

with the occupation constraint

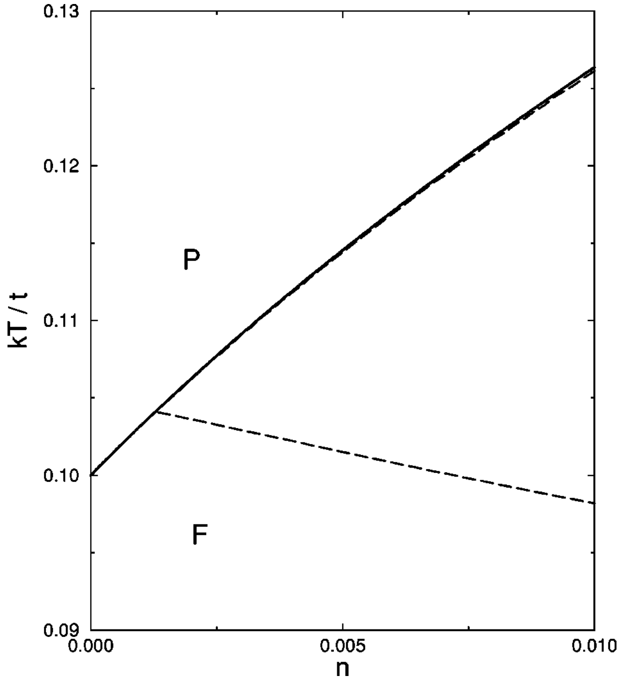

FIG. 2. Phase diagrams for the mean-field theory of Eqs. (31)–(33) for the parameters explained in the text. The solid line is the (scaled) critical temperature vs carrier concentration. The region of negative compressibility is bound by the dashed line and the critical temperature.

$$n=\sum_{\sigma=\uparrow\downarrow}n_\sigma=\sum_{\sigma=\uparrow\downarrow}\int d\epsilon\frac{\mathcal{D}(\epsilon)}{\exp\left(\frac{\epsilon-\mu_\sigma}{kT}\right)+1}. \tag{34}$$

We have solved the previous equations for parameters expected to apply in the case of pyrochlores: $kT_0=Jz/3=0.1t$, and $J'=t$, where t, a measure the electronic energy scale, is taken to be the kinetic energy of an electron confined to a unit cell volume. Searching for negative values of $\partial^2\mathcal{F}/\partial n^2$, we arrive at the phase diagram plotted in Fig. 2 for small carrier concentration. We see that, beyond a carrier concentration, a region of negative compressibility opens around the ferro-para transition. Therefore, we confirm the existence of PS as suggested by the general arguments of Sec. II. Notice that in Fig. 2 we show the area of intrinsic instability: the standard Maxwell construction would increase this PS region even into the paramagnetic phase. We have plotted (Fig. 1) the free energy of the exact solution (solid line), compared to the ML polaron ansatz (dashed, straight line) and the solution ignoring the electron entropy (dash-dotted line) for $kT=0.115t$. As explained at the beginning of this section, the correct homogeneous phase (including entropy) has the lowest free energy even at low concentration. In contrast, having ignored the electronic entropy would have led to the prediction that polarons are the preferred configuration (see two upper curves of Fig. 1). Nevertheless, PS *does* exist, and the onset of negative curvature (hardly visible to the bare eye) is marked with an arrow in that figure.

For the parameters corresponding to Fig. 2, electrons are strongly *nondegenerate*, and the numerical results almost coincide with the classical limit for the carriers, whose

Ginzburg-Landau analytic treatment we now present for completeness. Assuming the electrons to be a classical ideal gas and performing an expansion in the core *s* and carrier magnetization *m*, one obtains the following expressions for the contributions to the free energy:

$$\mathcal{F}_s=\left(\frac{3}{2}kT-\frac{Jz}{2}\right)s^2+\frac{9}{20}kTs^4, \tag{35}$$

$$\mathcal{F}_m=-nkT+nkT\ln\left(\frac{n}{n_Q}\right)+\frac{kT}{2n}ms^2+\frac{kT}{12n^3}m^4, \tag{36}$$

$$\mathcal{F}_{sm}=-J'sm, \tag{37}$$

where n_Q is a reference density marking the onset of the quantum regime.

Minimization of the free energy leads to the following transition temperature:

$$kT_c=\frac{kT_0}{2}+\sqrt{\left(\frac{kT_0}{2}\right)^2+\frac{J'^2n}{3}}. \tag{38}$$

In the vicinity of T_c, core and electron magnetization are related by

$$m=s\,\frac{J'n}{kT}\left[1-\frac{J'^2s^2}{3(kT)^2}\right] \tag{39}$$

and the scaled inverse compressibility at $T\rightarrow T_c^-$ is given by

$$\tilde{\kappa}^{-1}\equiv\frac{\partial^2\mathcal{F}}{\partial n^2}=\tilde{\kappa}_0^{-1}-\frac{15kT_ck'^4}{54(kT_c)^4+10J'^4n}, \tag{40}$$

where $\tilde{\kappa}_0^{-1}=kT_c/n$ is the inverse compressibility of the paramagnetic phase. $\tilde{\kappa}$ becomes negative beyond $n_{\mathrm{PS}}=54(kT_c)^4/(5J'^4)=1.266\times10^{-3}$, for the parameters used here, very close to the exact results of Fig. 2.

As a final remark, it is important to realize that the precise configuration of the coexisting phases in the real material will be complicated by effects beyond the present treatment (disorder, domain boundary contributions, etc.). The final picture could well be that of an arrangement of polaroniclike structures. The associated spatial inhomogeneity will certainly affect the behavior of these compounds in an important way. This suggests that, even if the original polaron argument deserves further scrutiny, the associated physics explored by ML might well apply to the pyrochlores.

V. DOUBLE-EXCHANGE SYSTEMS

The double-exchange (DE) model describes systems with local spins and itinerant electrons, in the limit where the Hund coupling between the electrons and the spins is much larger than other scales.[37] The electrons are always polarized in the direction of the local spins, and hopping (*t*) to neighboring ions is modulated by the relative orientation of these spins, leading to the following Hamiltonian:

$$\mathcal{H}=-t\sum_{\langle ij\rangle,\sigma}[z_{i\sigma}\tilde{z}_{j\sigma}c_i^\dagger c_j+\mathrm{H.c.}], \tag{41}$$

where $z_{i\sigma}$ is the spinor describing the orientation of the core at site *i*: $z_{i\uparrow}=\cos(\frac{1}{2}\theta_i)$, $z_{i\downarrow}=\sin(\frac{1}{2}\theta_i)\exp(-i\phi_i)$.

The model, put forward by Zener,[37] has received great attention in recent times as the building block needed to explain the physics of Mn perovskites. We will restrict ourselves to its simplest one-band version, leaving aside further features such as orbital degeneracy, antiferromagnetic couplings, or Jahn-Teller distortion, probably required for a more realistic description of manganites.

PS in double-exchange models has been extensively studied.[3–9] It was originally observed in numerical studies of the DE model with AF couplings between core spins, raising doubts about its existence in the bare version.[4,6,7] However, we have recently shown that the PS tendency is an intrinsic feature of the simplest DE model without additional terms.[8] For completeness, we include here an analysis of the compressibility using the Ginzburg-Landau expansion outlined in the preceding sections. The approach is a direct extension of that used in Ref. 38. We leave out the study of PS at zero temperature due to the competition between direct antiferromagnetic interactions and the double-exchange mechanism,[5] which also can be case in terms of a Ginzburg-Landau expansion.

The model is determined by the polarization of the localized spins *s*, the density of states of the itinerant electrons in the absence of spin disorder, $\mathcal{D}_0(\epsilon)$, and the temperature *T*. The free energy of the spins comes from the entropy due to their thermal fluctuations only and coincides with Eq. (35), except for the absence of the direct-exchange term. We assume that the electron gas is degenerate, an excellent approximation for temperatures in the range of T_c, and replace its free energy by the ground-state energy in a background of fluctuating spins. The bandwidth of the electrons is reduced by a factor $f=\langle\cos(\vartheta ij/2)\rangle$, where ϑij is the angle between neighboring spins. Thus, the electronic energy can be written as

$$E=fK_0=f\int_{-W_0}^{\mu_0}\epsilon\,\mathcal{D}_0(\epsilon)d\epsilon, \tag{42}$$

where μ_0 denotes the chemical potential in the absence of spin disorder and W_0 is the lower band edge (note that $-W_0\leqslant\mu_0\leqslant W_0$). We can now expand *f* in terms of the magnetization *s*, to obtain

$$E=\frac{2}{3}K_0+\frac{2}{5}K_0s^2-\frac{6}{175}K_0s^4, \tag{43}$$

which completes the required Ginzburg-Landau expansion. The Curie temperature of the model is given by $T_c=-\frac{4}{15}K_0$ (K_0 is negative). The magnetization is

$$s^2=\begin{cases}0, & T\geqslant T_c,\\ -(\frac{3}{2}kT+\frac{2}{5}K_0)/(\frac{9}{10}kT-\frac{12}{175}K_0), & T<T_c\end{cases}, \tag{44}$$

which leads to

$$\mathcal{F}=\begin{cases}\dfrac{2}{3}K_0, & T\geqslant T_c,\\ \dfrac{2}{3}K_0-kT\mathcal{R}\left(\dfrac{K_0}{kT}\right), & T<T_c\end{cases}, \tag{45}$$

where $\mathcal{R}(u)=\frac{7}{6}(u+\frac{15}{4})^2/(\frac{105}{5}-u)$.

Finally, the scaled inverse compressibility is

$$\tilde{\kappa}^{-1}=\begin{cases}\dfrac{2}{3\mathcal{D}_0(\mu_0)}, & T\to T_c+0,\\[2ex] \dfrac{2}{3\mathcal{D}_0(\mu_0)}-\dfrac{14\mu_0^2}{27|K_0|}, & T\to T_c-0\end{cases}. \tag{46}$$

The compressibility below T_c is negative when

$$\frac{|K_0|}{\mathcal{D}_0(\mu_0)}\leqslant\frac{7}{9}\mu_0^2. \tag{47}$$

This result is independent of the initial bandwidth $2W_0$. In general, there is always PS at low fillings, because $\mu_0\to -W_0$ while $K_0/\mathcal{D}_0(\mu_0)\to 0$. At half-filling, $\mu_0\to 0$, and there is no PS.

If we use

$$\mathcal{D}_0(\epsilon)=\frac{2}{\pi}\frac{\sqrt{W_0^2-\epsilon^2}}{W_0^2}, \tag{48}$$

we find that there is PS if

$$|\mu_0|\geqslant W_0\sqrt{\frac{3}{10}}, \tag{49}$$

which corresponds to a number of electrons per site, ~0.2.

The previous expansion in powers of the order parameter is not necessary, and the complete mean-field equations can be written as follows:[8]

$$x-\frac{1}{2}=\frac{1}{2}\int_{-1}^{1}d\gamma\,\mathcal{D}_0(\gamma)\tanh\left(\frac{\alpha+f\gamma}{2\Theta}\right), \tag{50}$$

$$2\Theta\frac{fQ}{s}=\frac{1}{2}\int_{-1}^{1}d\gamma\,\gamma\mathcal{D}_0(\gamma)\tanh\left(\frac{\alpha+f\gamma}{2\Theta}\right), \tag{51}$$

where $s=\coth(Q)-Q^{-1}$ is the magnetization, x describes the doping level (electron/hole), and $f=\sqrt{\frac{1}{2}(1+s^2)}=\langle\cos^2(\vartheta ij)\rangle^{1/2}$. The energy, temperature, and chemical potential are scaled in units of the half-bandwidth in the absence of spin disorder by $\gamma\equiv\epsilon/W_0$, $\alpha\equiv\mu/W_0$, and $\Theta\equiv kT/W_0$.

If $\mathcal{D}_0$ is taken to be the density of states of the original crystal lattice, neglect of the Berry phase[40] collected by the hopping electron is implicit. More appropriately, we can assume that spin disorder cancellations favor retraced paths,[39] leading to a Bethe lattice density of states, with Eq. (48) as the infinite coordination limit. In Fig. 3 (upper panel) we show the phase diagram (scaled temperature versus hole concentration x) for the density of Eq. (48). Notice that the PS region corresponds to the intrinsic instability (negative compressibility). Global stability (Maxwell construction) would increase this region.

The simple DE model offers a clear example of the general mechanism for PS in the presence of an ordering process. In fact, the mean-field treatment is intrinsically unstable versus PS in the limit of low carrier density. To see this, notice that the energy scale of the magnetic order is the electronic energy, proportional to the carrier concentration in the dilute limit. Doubling, for instance, the carrier concentration close to the Curie temperature produces a finite increase of the bandwidth. The chemical potential is pinned at the band edge, and it decreases with increasing electron density, leading to a thermodynamic instability. In our electron-hole symmetric model, the same would apply to the dilute hole limit.

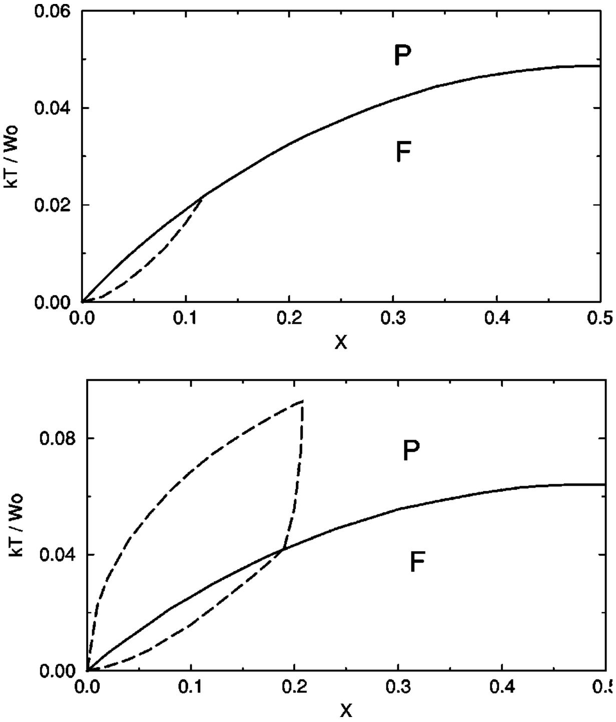

FIG. 3. Phase diagrams (upper panel) for the mean-field theory of Eqs. (50) and (51) and (lower panel) for that of Eqs. (52) and (53), both computed using an elliptic density of states. The solid line is the (scaled) critical temperature vs hole concentration. The dashed line marks the boundary of the region of negative compressibility.

Although we do not expect the mean-field approximation to be a serious drawback, certain limitations are clear. For instance, the inability to distinguish between short-range correlations and long-range order confines the negative compressibility region to the ferromagnetic phase, for only there does the bandwidth change with magnetic order. In what follows, we will show that PS is a robust feature that survives several improvements of this basic mean-field approach.

A. Schwinger bosons

An improved mean-field theory can be implemented using the Schwinger boson[41,8] method. A nondynamical field λ_i enforces the constraint $\overline{z_{i\sigma}}z_{i\sigma}=1$ at every site. The core spins are quantized according to $[z_{i\sigma},\overline{z_{j\sigma'}}]=\delta_{ij}\delta_{\sigma\sigma'}/2S$. The mean-field Hamiltonian is obtained through a Hartree decoupling of the bosonic $z_{i\sigma}\overline{z_{j\sigma}}$ and fermionic $c_i^\dagger c_j$ hopping terms:

$$\mathcal{H}_{MF}=N(ztfK-\lambda)-\mu\sum_i c_i^\dagger c_i+\lambda\sum_{i\sigma}\overline{z_{i\sigma}}z_{i\sigma}$$
$$-tf\sum_{\langle ij\rangle}(c_i^\dagger c_j+c_j^\dagger c_i)-tK\sum_{\langle ij\rangle,\sigma}(\overline{z_{i\sigma}}z_{j\sigma}+\overline{z_{j\sigma}}z_{i\sigma}), \tag{52}$$

where $K=\langle c_i^\dagger c_j\rangle$ and $f=\langle z_{i\sigma}\overline{z_{j\sigma}}\rangle$. Such a model was introduced by Sarker,[42] who identified a Curie transition and found that the e_g fermion band becomes incoherent above T_c. Accounting for the possibility of condensation of Schwinger bosons, we write $\Psi_{k\sigma}\equiv\langle z_{k\sigma}\rangle$. Assuming condensation only at $k=0$, we define $\rho\equiv|\Psi_{k=0,\sigma}|^2$. The mean-field equations are then

$$1+\frac{1}{2S}=\rho+\frac{1}{2S}\int_{-1}^{1}d\gamma\,\mathcal{D}(\gamma)\coth\left(\frac{\Lambda-K\gamma}{4S\Theta}\right),$$

$$f=\rho+\frac{1}{2S}\int_{-1}^{1}d\gamma\,\gamma\,\mathcal{D}(\gamma)\coth\left(\frac{\Lambda-K\gamma}{4S\Theta}\right),$$

$$x-\frac{1}{2}=\frac{1}{2}\int_{-1}^{1}d\gamma\,\mathcal{D}(\gamma)\tanh\left(\frac{\alpha+f\gamma}{2\Theta}\right),$$

$$K=\frac{1}{2}\int_{-1}^{1}d\gamma\,\gamma\,\mathcal{D}(\gamma)\tanh\left(\frac{\alpha+f\gamma}{2\Theta}\right), \tag{53}$$

where $\gamma=\epsilon/W_0$, $\Lambda=\lambda/W_0$, $\Theta=kT/W_0$, and $\alpha=\mu/W_0$, W_0 being the half-bandwidth in the absence of spin disorder.

Two aspects distinguish this treatment from that of the previous section. First, core spins are quantum objects with intrinsic dynamics: a minute correction close to the Curie temperature. Second and more important, long-range magnetic order (condensation of Schwinger bosons) is not a requisite for short-range correlations: the latter exist and change with temperature even in the paramagnetic phase.

We have solved the mean-field equations for a semielliptic density of states and $S=3/2$.[8] Several features of the solution are shown in Fig. 3 (lower panel). While the critical temperature is hardly affected, the region of negative compressibility enters now into the paramagnetic phase, an expected physical feature not present in the previous approximation. In this approach, the fermion bandwidth collapses to zero at high temperature. Although this is likely an artifact of the approximations, it takes place well above the Curie temperatures to be a source of concern.

B. Critical spin fluctuations

The PS region is tied to the magnetic transition, where the magnetic order (and therefore the bandwidth) changes rapidly with temperature and/or density [see, for instance, Eq. (44)]. Therefore, one can worry about the importance of critical spin fluctuations, neglected in the molecular field approximation. Assuming a nearest-neighbor, tight-binding lattice with hopping amplitude $t_{ij}=-t\cos(\theta_{ij}/2)$ and expanding the half-angle between spins in the usual manner $\cos(\theta/2)\simeq a_0+a_1\cos(\theta)$, the standard virtual crystal decoupling of the electron-spin system allows integration of the charge degrees of freedom. This produces an effective Heisenberg model for the core spins (assumed classical for simplicity), and the total free energy (charge and core spins) is given by

$$\mathcal{F}=K_\infty(x)+\mathcal{F}_H(J,T), \tag{54}$$

where x is the hole concentration and K_∞ is the electron energy (degenerate limit assumed) of the fully disordered limit $t_{ij}=a_0 t$. Here $\mathcal{F}_H$ describes the free energy of the classical Heisenberg model, with coupling constant $J=2a_1|\langle c_i^\dagger c_j\rangle|t$. A lengthy but simple calculation permits the following connection between the stability criterion and thermal properties of the Heisenberg model (cubic lattice):

$$\frac{\partial^2\mathcal{F}}{\partial n^2}=\frac{1}{\mathcal{D}(\mu)}[1-g(x)f_H(T)], \tag{55}$$

with

$$g(x)=\frac{2a_1\tilde{\mu}^2\tilde{\mathcal{D}}(\tilde{\mu})}{6|\langle c_i^\dagger c_j\rangle|}, \tag{56}$$

where the tilded symbols $\tilde{\mu}$ and $\tilde{\mathcal{D}}(\tilde{\mu})$ are the chemical potential and density of states scaled to unit half-bandwidth and

$$f_H(T)=\frac{TC(T)}{J[a_0+a_1\langle\cos(\theta_{ij})\rangle]}. \tag{57}$$

$C(T)$ represents the specific heat of the Heisenberg model. The expected increase of $C(T)$ near the critical temperature T_c links the tendency towards instability with magnetic ordering. In any case, for a fixed value of T/T_c, the system is bound to exhibit PS, $(\partial\mu/\partial x)<0$, owing to the diverging behavior of $g(x\rightarrow 0)$. Extracting the temperature dependence of $f_H(T)$ from published Monte Carlo data[43] for the cubic lattice, we estimate PS to follow the ordering transition up to $x\simeq 0.11$. The resulting phase diagram and intrinsic instability region are shown in Fig. 4 (upper panel). Notice that no approximate treatment is assumed for the criticality of the

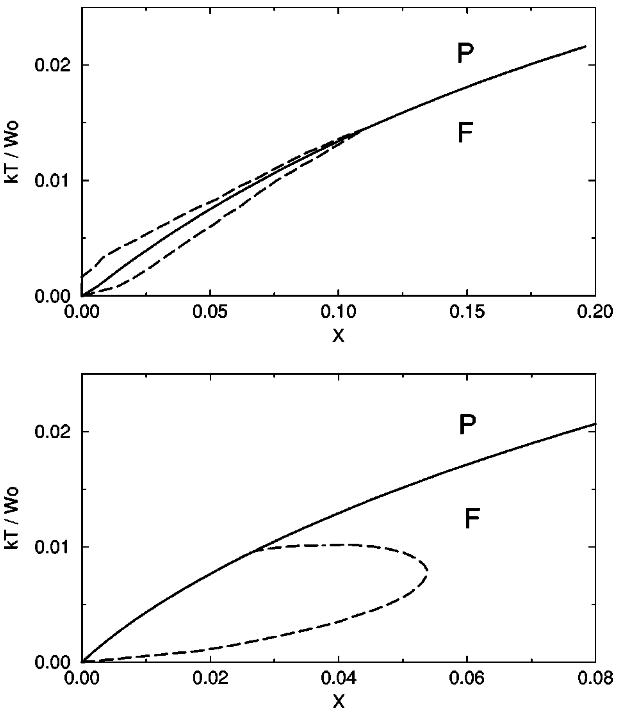

FIG. 4. Phase diagrams (upper panel) for the cubic lattice in the virtual crystal approach, including Monte Carlo data for the Heisenberg model (Sec. V B) and (lower panel) for the Bethe lattice of infinite coordination. The solid line is the (scaled) critical temperature vs hole concentration. The dashed line marks the boundary of the region of negative compressibility.

effective magnetic Hamiltonian, the only (major) surviving approximation being the virtual crystal (mean-field) decoupling of mobile carriers and core spins.

C. Infinite dimension

The mean-field decoupling of charge and core spins fluctuations remains in all the previous analysis. This manifests itself in a mere rescaling of the electronic density of states with magnetic order. Given that the PS instability can be seen as a manifestation of correlation between charge and spin at a macroscopic level (the only possibility left in a mean-field approach), concern might arise about its fate when charge-spin coupling is properly considered. Although in the general case a numerical approach would be necessary to answer this question, there is a limit in which the problem is solvable but the charge-spin coupling remains nontrivial: infinite coordination (dimension). The relevance of this limit for the understanding of correlated systems in 3D has been recognized in recent years.[44,45]

In the DE case, this problem has been considered by Furukawa,[46] and indeed PS has been observed.[6,7] In those works, the DE model included a large though finite Hund coupling, leading to AF correlations between core spins that certainly increase the tendency towards PS. Accumulated experience from numerical studies of doped antiferromagnets also seemed to suggest that antiferromagnetism is required for PS to exist (see Sec. III B and references therein). We now show that, in spite of recent suggestions on the contrary, the simple DE model without AF additions indeed exhibits PS close to the ordering temperature, according to the general mechanism explained in this paper.

The average density of states for electrons moving in an infinitely coordinated Bethe lattice according to the DE Hamiltonian is given by

$$\langle \mathcal{D}(\epsilon)\rangle_{\vec{\Omega}} = -(1/\pi)\mathrm{Im}\langle g(\epsilon,\vec{\Omega})\rangle_{\vec{\Omega}}, \tag{58}$$

where the local Greens function satisfies

$$g(\epsilon,\vec{\Omega}) = [\epsilon - \Sigma(\epsilon,\vec{\Omega})]^{-1} \tag{59}$$

and the self-energy is determined by

$$\Sigma(\epsilon,\vec{\Omega}) = (W_0/2)^2 \left\langle \frac{1+\vec{\Omega}\cdot\vec{\Omega}'}{2}[\epsilon - \Sigma(\epsilon,\vec{\Omega}')]^{-1} \right\rangle_{\vec{\Omega}'}, \tag{60}$$

where $\vec{\Omega}$ is the unit vector describing the orientation of the local core (classical) spin, W_0 represents the half-bandwidth for the fully aligned case, and angular averages are taken with the probability distribution $\mathcal{P}(\vec{\Omega})$. Notice that, though the probability distribution for spins in different sites factorizes (confining PS to the ferromagnetic phase), charge and spin fluctuations remain coupled at the same site, and the density of states is not merely rescaled by magnetic order [Eq. (60)].

The complete thermodynamic problem is solved by finding the probability distribution that minimizes the total free energy:

$$\mathcal{F} = \mathcal{F}_{\mathrm{el}} - T\mathcal{S}, \tag{61}$$

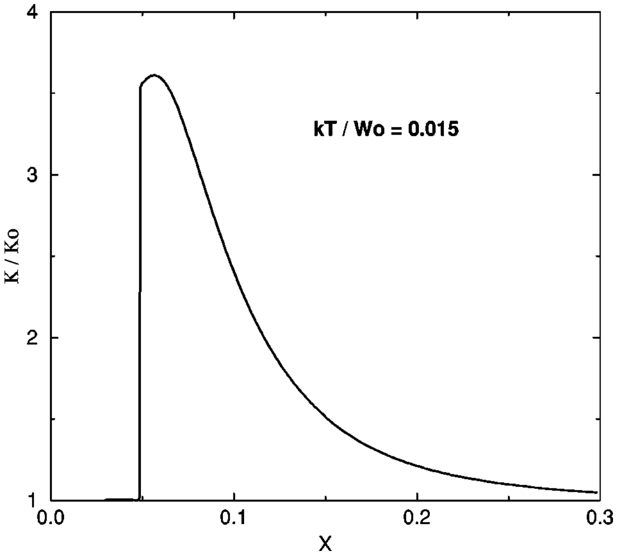

FIG. 5. Compressibility of the DE model for the (infinitely coordinated) Bethe lattice, in units of the compressibility of a free-fermion system with identical density of states, vs hole concentration at constant temperature.

where $\mathcal{F}_{\mathrm{el}}$ is the free energy of fermions for the average density of states and $\mathcal{S}$ is the core spin entropy, both depending on $\mathcal{P}(\vec{\Omega})$.

For computational convenience, we have solved the problem with two additional features: degenerate limit for carriers and a core spin distribution parametrized by an effective magnetic field (detailed analysis of the exact solution for a few temperatures shows the previous simplifications to introduce only minute corrections). The generic results of previous treatments are reproduced here. This is shown in Fig. 4 (lower panel), where the phase diagram presents the expected region of intrinsic instability (negative compressibility) at low carrier density. The inclusion of a finite Hund coupling will certainly increase the PS region, as observed in previous works.[6,7] All these studies support the view that the general scheme for PS presented in this paper applies to the simple DE model with features which are robust and not an artifact of approximations.

As mentioned before, PS can be thought of as a long-range instability caused by the coupling between carriers and core spins. Such a mechanism is operative even in the region where the system does not phase separate, and the carriers compressibility can be much enhanced close to the Curie temperature. This statement does not contradict the fact that the density of states at the Fermi level is featureless and shows no major change around the Curie temperature.[47] Remember that, if the bandwidth were not affected by the spin order, the compressibility would be merely proportional to the density of states at the Fermi level, which means featureless. It is the bandwidth change with magnetic order that produces this enhancement in the region close to the onset of magnetic order. This is shown in Fig. 5, where the compressibility of the infinitely coordinated Bethe lattice is measured in units of the compressibility of a *free*-fermion system (that is, no carrier-spin coupling) with the same density of states. This behavior of the compressibility close to the transition temperature is not a peculiarity of the infinite-dimension

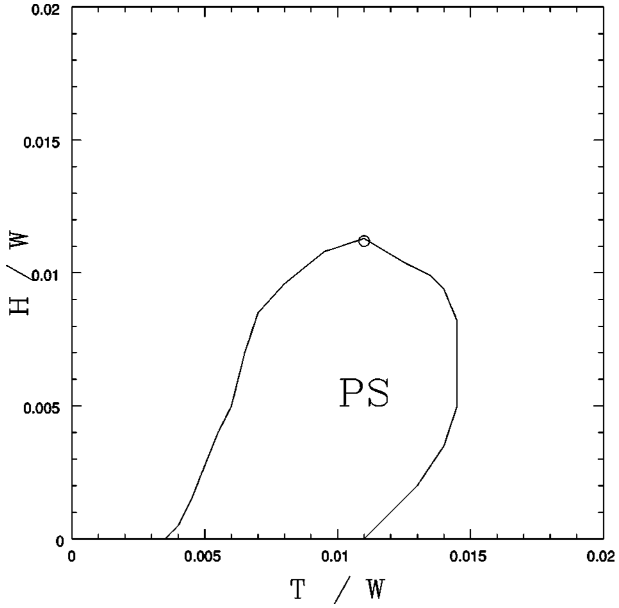

FIG. 6. Region of phase separation, as a function of magnetic field, in the double-exchange model, for a hole density $x=0.10$. The temperature and magnetic field are normalized to the electron bandwidth.

limit, but rather a general feature of all systems studied in this paper. In the case of manganites, the possible connection between this enhancement and the unusual properties of these materials remains an open and intriguing question.[9]

VI. INFLUENCE OF A MAGNETIC FIELD

So far, we have considered the existence of phase separation near a ferromagnetic- (or antiferromagnetic-) paramagnetic transition, at zero magnetic field. When a field is applied, the features associated with the transition are smoothed, at sufficiently large fields the magnetic moments are aligned, and the magnetization has a weak temperature dependence.

The increase in the compressibility which leads to phase separation is associated with the strong coupling between magnetic and charge fluctuations, as measured by the dependence of the critical temperature on electronic concentration. The magnetic field suppresses magnetic fluctuations, leading to a smaller increase in the compressibility near T_c. Phase separation should disappear at sufficiently large fields, when the temperature no longer induces significant magnetic fluctuations.

A generic case which shows the dependence of the region where phase separation occurs on magnetic field, at fixed nominal electronic concentration, is shown in Fig. 6. The calculations have been done for the double-exchange model of the previous sections, using the mean-field equations (43) and (44), plus an applied field. The region of negative compressibility is shown. As in previous examples, a Maxwell construction gives a somewhat larger region.

In a small applied field, phase separation takes place above the Curie temperature. This is due to the rounding of the discontinuity at T_c of the compressibility induced by the field. The region of phase separation lies between a high-magnetization and a low-magnetization phase, in close analogy with the phase diagram of an ordinary liquid-vapor transition. At high fields, phase separation is completely suppressed. At the highest possible field, we find a critical point.

VII. PHASE SEPARATION AND DOMAIN FORMATION

The analysis in the previous sections suggests that PS should be a frequent feature of magnetic transitions. PS on a macroscopic scale, however, cannot occur, as it requires an infinite amount of electrostatic energy. The mean-field analyses used in the previous sections may be augmented by the following argument[48,8] to include effects of Coulomb interactions. Neglecting interactions, the charge susceptibility obeys

$$\lim_{q\to 0} \chi_0(q) = -\mathcal{V}^{-1}\frac{\partial n}{\partial \mu} = -\mathcal{V}^{-1}\tilde{\kappa}, \qquad (62)$$

where $\mathcal{V}$ and n are the volume and carrier content of the unit cell, respectively. A charge fluctuation induces an electrostatic potential, which, in turn, induces more charge polarization. The standard self-consistent treatment leads to the following RPA equation for the charge polarizability:

$$\lim_{q\to 0} \chi(q) = \frac{\chi_0(q)}{1-\dfrac{4\pi e^2}{\epsilon q^2}\chi_0(q)} = \frac{-\mathcal{V}^{-1}\tilde{\kappa}}{1+\dfrac{4\pi\epsilon^2}{\epsilon q^2}\mathcal{V}^{-1}\tilde{\kappa}}, \qquad (63)$$

where ϵ is the dielectric constant of bound electrons. For $\tilde{\kappa} < 0$ (which, in the absence of Coulomb repulsion, represents the onset of the instability), the denominator has a pole at

$$q_* = \sqrt{-\frac{4\pi e^2}{\epsilon \mathcal{V}}\tilde{\kappa}}, \qquad (64)$$

and charge fluctuations of shorter wavelengths remain unstable, whereas the long-range nature of the Coulomb term prevents the formation of larger charge inhomogeneities. Thus we expect the formation of domains at length scales comparable to q_*^{-1}. As mentioned previously, this analysis takes into account neither the cost in magnetic energy associated with the formation of domain walls nor the effect of impurities. In addition to macroscopic charge neutrality, these are expected to be among the major factors affecting the spatial coexistence pattern in real materials.

VIII. CONCLUSIONS

We have discussed a general framework which shows that PS is likely to occur near magnetic phase transitions. The dependence of the critical temperature, or critical couplings, on electronic density leads to a reduction of the inverse compressibility in the ordered phase. This reduction can be of the same order as the value of the inverse compressibility in the disordered phase. The existence of PS typically depends on numerical constants of order unity, related to the electronic structure. The coupling constants do not require a special fine-tuning for PS to take place. The analysis presented here can be relevant to understand a variety of experimental findings in the manganites, pyrochlores, and doped antiferromagnets.

We have studied PS mostly within a conventional mean-field framework. For the systems studied at zero temperature, the effective dimensionality should be increased by the dynamical critical exponent, and, therefore, we do not expect major problems from the mean field study. Corrections due to critical fluctuations of the magnetic order parameter will be present for the models considered at finite temperature. Nevertheless, just as critical fluctuations tend to increase the specific heat (divergence of the second derivative of the free energy with respect to temperature), it is not unreasonable to expect a similar enhancement of charge fluctuations (i.e., the PS tendency) due to its coupling to the ordering field. Our analysis also shows that, even in the absence of phase separation, an enhanced coupling between charge and magnetic fluctuations is expected close to the transition temperature, due to the reduction of the inverse compressibility. The relevance of this enhancement for the anomalous properties exhibited by some of the systems studied here remains an open question.

Finally, we have discussed the way in which electrostatic effects frustrate the formation of macroscopic domains and have provided a scheme to calculate the scales at which domain formation is expected. Due to the neglect of major factors affecting the coexistence pattern in real materials (domain walls, impurities, etc.), our approach should be considered as a first approximation.

ACKNOWLEDGMENTS

We are thankful to D. Khomskii for many illuminating discussions. Financial support through Grant Nos. PB96-0875 (MEC, Spain) and 07N/0045/98 (C. Madrid) and the Commission for Scientific Exchange between Spain and the U.S. is gratefully acknowledged.

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