Giant dielectric permittivity and magneto-capacitance effects in low doped manganites

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Received 2 April 2014, revised 21 May 2014
Accepted for publication 30 May 2014
Published 8 July 2014

New Journal of Physics 16 (2014) 073011
doi:10.1088/1367-2630/16/7/073011

Abstract
The effect of giant dielectric permittivity due to phase separation accompanied by charged inhomogeneities in low-doped manganites is discussed. The effect appears in the vicinity of the second-order magnetic phase transition and is caused by long-range Coulomb forces. The long-range Coulomb interaction is responsible for the formation of inhomogeneous charged states and determines their characteristic length scales. We derive the phase diagram of the inhomogeneous charged states in the framework of the phenomenological theory of phase transitions. The large value of the static dielectric function reduces the characteristic value of the Coulomb energy of the inhomogeneous state and makes the appearance of the magnetoelectric effect possible. We discuss the formation of a state with giant dielectric permittivity and magneto-capacitance effects in that case.

Keywords: manganites, phase separation, dielectric permittivity, magneto-capacitance effect

The importance of the inhomogeneous phase-segregated states in the explanation of the anomalous transport and magnetic properties in manganites [1–10] and in high-temperature superconductors (HTS) [11–13] has been widely discussed. In doped manganites, the complex interactions between different degrees of freedom lead to unusual magnetic and transport
properties. Moreover, it has been suggested [14] that the spiral magnetic order observed in undoped manganites \( \text{ReMnO}_3 \) may lead to multiferroic behavior. It has also been suggested [15] that the charge ordering in magnetic systems may cause the magnetoelectric effect. Here, we propose that the magnetoelectric effect may appear not due to charge ordering but due to charge segregation, which appears near the Coulomb-frustrated second-order phase transition. In this paper, we discuss the tendency and conditions of the formation of inhomogeneous states with spatial charge localization and phase separation within the phenomenological theory, and we clarify the role of the Coulomb interaction in this phenomenon. We demonstrate the possibility of magnetoelectric behavior in low-doped manganites and clarify the role of the Jahn–Teller interaction in that behavior.

The problem of Coulomb-frustrated phase separation in different charged systems is the subject of ongoing discussion [3–6, 11–13, 16–22]. Numerous studies have focused on first-order phase transitions where the charge density is coupled linearly to the order parameter (as an external field) [18, 19] or to the square of the order parameter (local temperature) [21].

The importance of the Coulomb interaction in the formation of inhomogeneous charged states in doped manganites has been emphasized [23–28]. In many cases [23–28], in order to describe the phase-separated state near the magnetic phase transition, an interaction with additional degrees of freedom was considered. The interaction with these degrees of freedom leads to an energy gain compared to the case of the purely magnetic phase separation. This energy gain is relatively small (about \( 3kT_c \approx 0.03–0.1 \text{ eV per one unit cell} \)). Therefore, this type of phase separation is not plausible. It follows from the fact that the characteristic energy of the magnetic interaction \( kT_c \approx 0.01–0.03 \text{ eV} \) is less than the Coulomb energy \( V_c \approx 0.10–0.13 \text{ eV} \). Here, we use the static dielectric constant for manganites \( \varepsilon = 30–40 \). In order to justify the existence of the phase segregation near the magnetic phase transition in the presence of the long-range Coulomb interaction, some authors [23–28] have underlined the important role of the Jahn–Teller effect, which is characterized by the Jahn–Teller energy \( J_{JT} \). According to [23–28], the main contribution to the energy of the low-temperature phase is due to Jahn–Teller distortions. For example, in [23, 24], nanoscale electronic inhomogeneities are discussed for \( J_{JT} \approx 0.5 \text{ eV} \). In our view, in [23–25], the characteristic value of the Coulomb energy is underestimated—\( V_c \approx 0.02 \text{ eV} \) (for \( \varepsilon = 20 \))—at least by an order of magnitude. But what is more important is that in manganites, a phase separation in the vicinity of the magnetic phase transition is observed. Therefore, in order to come to the correct conclusions about the phase-separated state, we should compare the contribution of the relevant interactions to the total energy of the inhomogeneous state rather than the different coupling constants. In this paper, we demonstrate that the phase-separated state accompanied by charged inhomogeneities in manganites arises naturally near the magnetic phase transition frustrated by the long-range Coulomb forces without coupling with any additional degrees of freedom like Jahn–Teller distortions. We underline that for the existence of this effect, it is important to have a relatively strong interaction between the electrons and the magnetic degrees of freedom. Another important conclusion is that the phase separation becomes plausible due to the self-screening of the space-charge inhomogeneities, provided that the screening due to the lattice charges is strong, leading to large values of the dielectric permittivity \( \varepsilon = 30–40 \). We show that in the absence of percolation between phase segregated regions there exists a large contribution to the dielectric constant that is connected with the displacements from the equilibrium positions of the charged clusters. This contribution to the dielectric function is magnetic-field dependent and
leads to the magnetoelectric effect. Therefore, we expect giant dielectric permittivity and magnetocapacitance effects in low-doped manganites.

We accurately analyze the total energy of the system and treat Coulomb interaction exactly because it is the key factor that determines the characteristics of inhomogeneous states. The idea of phase segregation and inhomogeneous charge distribution in manganites was successfully applied for the description of the magnetoresistive effect in the limit of the percolating charged regions [2–6]. In this paper, we emphasize the possibility of the magnetocapacitance effect due to polarization of the non-percolated nano-regions in an external electric field in the inhomogeneous state in the low-doped systems.

The phenomenological approach to the theory of Coulomb-frustrated phase transition emphasizes that the properties the system are universal and are determined by the closeness to the phase transition point and by the dependence of the critical temperature of the phase transition on doping. This approach is essentially independent of other properties of the system. Therefore, the results demonstrate that the properties of the inhomogeneous states are determined by the proximity to the phase transition and the strength of the Coulomb interactions but are independent of other microscopic interaction in manganites.

Our approach indicates that phase separation with the formation of charged inhomogeneities is quite a common phenomenon inherent to various systems with different types of phase transitions, such as manganites and HTS materials. Our estimates show that the Coulomb energy in the charged separated states is relatively small.

We consider a doped system in the vicinity of a second-order magnetic phase transition. We assume that the free carrier density \( \rho \) is proportional to the dopant concentration \( x = \rho / \rho_0 \), where \( \rho_0 = e/a^3 \) is the characteristic carrier density, \( e \) is elementary charge and \( a \) is the lattice parameter. The thermodynamic potential \( \Phi = \int \phi(\eta, \rho)d^3r \) describes the behavior of the magnetic order parameter \( \eta \) near the second-order phase transition, and the coupling between the order parameter and the charge density reads:

\[
\begin{align*}
\phi(\eta, \rho) &= \phi_0 + \phi_\eta + \phi_{int} + \phi_e \\
\phi_\eta(\eta) &= \frac{\alpha}{2} \eta^2 + \frac{\beta}{4} \eta^4 + \frac{\xi}{2} (\nabla \eta)^2 - \eta H \\
\phi_{int}(\eta, \rho) &= -\frac{\sigma}{2} \eta^2 \frac{\rho(\rho_0 - \rho)}{\rho_0^2} \\
\phi_e(\rho) &= \frac{\gamma (\rho(r) - \bar{\rho})}{2\rho_0^2} \int \frac{\rho(r') - \bar{\rho}}{|r - r'|} dV' + \frac{\theta (\rho(r) - \bar{\rho})^2}{2\rho_0^2}
\end{align*}
\] (1)

where \( \phi_0 \) is the density of the thermodynamic potential in the high-temperature phase, \( \phi_\eta \) is the density of the thermodynamic potential of the low-temperature phase, \( \alpha, \beta \) and \( \xi \) are coefficients in the expansion of the thermodynamic potentials in powers of the order parameter \( \alpha = \alpha'(T - T_c) \), where \( T_c \) is critical temperature in the absence of doping, \( \alpha' = 1/C \), \( C \) is the Curie constant) and \( \xi \) is proportional to the co-called diffusion coefficient of the magnetization \( \eta \) and is defined by the exchange interaction. It defines the characteristic length \( \xi^{1/2} \) where the order parameter changes. \( H \) is the external magnetic field. \( \phi_{int} \) describes the interaction of the order parameter with the charge density and \( \sigma \) is the constant of the interactions. In order to provide a global stability of the system, we require that \( \sigma > 0 \) [16]. \( \phi_e \) describes the charging effects due to the Coulomb interaction between the charge carriers, and \( \bar{\rho} \) is the average charge.
density. The spatial distribution of the charge density $\rho$ and the order parameter $\eta$ are
determined from minimization of the thermodynamic potential. Therefore the effects of
screening are calculated self-consistently during minimization of the thermodynamic potential
(1). The inclusion of the gradient term for the charge density is not necessary, because the
spatial distribution of the charge density is determined by the minimization of the Coulomb
energy. We assume that the Coulomb contribution is the strongest: $\theta \ll a^2 \gamma$, where $\theta$ is the
constant that describes the strength of the local electron–electron interaction, different from the
Coulomb repulsion. The effect of the average dopant concentration $\bar{\rho}$ on the thermodynamic
potential in the high-temperature phase is included in $\phi_0$. The coefficient $\gamma$ is inversely
proportional to the static dielectric constant $\varepsilon$, $\gamma = \rho_0^2 / \varepsilon$. The expression for $\gamma$ takes into account
the effect of the local excess positive charge of the lattice explicitly via the static dielectric
constant. Indeed, the direct Coulomb repulsion between electrons in crystals is reduced due to
electronic polarizability by the factor $\varepsilon_\infty$. If we take into account polaronic effects, the effective
interaction between electrons is renormalized and $\varepsilon_\infty$ should be replaced by the static dielectric
function (for details see the [29]). As a result, the coefficients in the thermodynamic potential
depend on the charge density $\rho$, and the term $\sigma \rho (\rho_0 - \rho)$ determines the shift of the critical
temperature $T_c$ due to variation of the local charge density:

$$T_{\text{cp}}(x) = T_{c0} + \frac{\sigma x (1 - x)}{\alpha'}.$$ (2)

Here $x = \rho / \rho_0$ and $\bar{x} = \bar{\rho} / \rho_0$ are dimensionless carrier densities. In the uniform case, we have
$x = \bar{x}$ ($\rho = \bar{\rho}$) and $\eta_\alpha = H/2a\bar{\alpha}(\bar{x}, T)$ for $T > T_{c0}$ and $\eta_\alpha = -\bar{\alpha}(\bar{x}, T)/\beta - H/\bar{\alpha}(\bar{x}, T)$ for $T < T_{c0}$
($\bar{\alpha}(x, T) = \alpha(T) - \sigma x (1 - x)$).

Note that we consider the inhomogeneous states, which appear near the second-order
phase transition to the ferromagnetic phase. Therefore, we do not consider any effect of
antiferromagnetic phase or charge ordering. We believe that the influence of the
antiferromagnetic or the charge-ordered states to the formation of the charge-segregated state
is not important. We assume that magneto–dipole coupling between bubbles is small in
comparison with the exchange interaction. The tunnelling of the carriers is important because it
leads to the exchange interaction between bubbles. This leads to the magnetic ordering of
different bubbles, the divergence of the correlation radius and the appearance of macroscopic
magnetization in the sample. Therefore, we consider the temperature $T_{\text{cp}}(x_i)$ (2) as the
temperature of the phase transition in the system of bubbles.

In figure 1, we plot the free energy as a function of the carrier density $x$ for the case of the
uniform phases. In the region of density where the second derivative of the free energy on $x$ is
negative, the uniform state becomes metastable. The phase segregated nonuniform states have
lower energy as demonstrated in figure 1. Therefore, there is a tendency to phase separation into
domains with a different carrier density $x$ (for details see [22]). In the equilibrium state the order
parameter is determined as a steady-state solution of the Landau–Khalatnikov equation
$\partial \eta / \partial t = \Gamma \delta \phi(\eta, x) / \delta \eta$ [30]: $\delta \phi(\eta, x) / \delta \eta = 0$. The carrier density is determined from the
following equation: $\delta \phi(\eta, x) / \delta x = \mu$, where $\mu$ is the chemical potential, which can be found
from the conservation of the total number of carriers. The second equation reads:

$$-\frac{\sigma}{2} \eta^2 (1 - 2 x(r)) + \gamma \int \frac{(x(r') - \bar{x})}{|r - r'|} dV' + \theta (x(r) - \bar{x}) = 0.$$ (3)
Using the formula \( r = \pi \delta |r' - r| = -|r' - r| \) and assuming that \( \vartheta \ll a^2 \), we obtain the dependence of the equilibrium charge density \( x \) on \( \eta \): \[ x(\eta) \approx \bar{x} - \frac{\sigma (1 - 2\bar{x})}{8\pi\vartheta} \left( \nabla^2 \eta^2 - \frac{\vartheta^2}{4\pi\vartheta} \nabla^2 \left[ \eta^2 \nabla^2 \eta^2 \right] \right) = -\frac{\vartheta \vartheta}{64\pi^2 \vartheta^2} \nabla^4 \eta^2. \] \( \text{(4)} \)

Substituting equation (4) into equation (1) \( (\vartheta \ll a^2) \), we obtain the expression of the density of the thermodynamic potential (1) \( \rho_{\rho} \) for the equilibrium distribution of the charge density \( x(\eta) \): \[ \rho_{\rho}(\eta) = \phi_{\rho}(\eta) - \frac{\sigma \bar{x}(1 - \bar{x})}{2} \eta^2 - \frac{\sigma^2 (1 - 2\bar{x})^2}{32\pi\vartheta} \left( \nabla \eta^2 \right)^2 \]
\[ + \frac{\vartheta \vartheta}{256\pi^2 \vartheta^2} \left( \nabla^2 \eta^2 \right)^2 + \frac{\sigma^3 (1 - 2\bar{x})^2}{128\pi^2 \vartheta^2} \eta^2 \left( \nabla^2 \eta^2 \right)^2. \] \( \text{(5)} \)

The negative sign in the third term of equation (5) indicates that the uniform state may be unstable towards inhomogeneous fluctuations.

This instability leads to spatially inhomogeneous solutions. Calculation of the total thermodynamic potential of the inhomogeneous state, including the Coulomb energy and the energy interphase boundaries, shows that the minimum of the thermodynamic potential corresponds to the phase-separated state. Local minima may correspond to different inhomogeneous states where the new phase is organized in the form of symmetric bubbles, periodic stripes or some other arrangement. The most simple solution is spherically symmetric bubbles of the low-symmetry phase separated from each other by a large distance.

This type of solution (a charged bubble of magnetic phase screened by an external charge) represents the minimum of the Coulomb energy together with the energy of the interphase
boundaries. Therefore, this phase-separated state has the lowest energy through the most part of the phase diagram and in particular in the vicinity of the upper boundary of the appearance of the inhomogeneous states [20]. Thus this equilibrium inhomogeneous state in the low-doped samples has a spherical form and the distribution of charge has the shape of an electric double-layer [31]. This solution has the characteristic size $R_0$. The characteristic average charge density inside the bubbles is $\chi_1$ and the average charge density outside of these regions is $\chi_2$. The average charge density in the system is $\bar{\chi}$. The average value of the order parameter inside the bubble, $\eta_i \approx \eta_0 + H/2(\bar{\chi}(\chi_1, T))$, is relatively large, while the order parameter outside the bubbles is much smaller, $\eta_i \approx -H/\bar{\chi}(\chi_2, T)$, where $\eta_0^2 = -\bar{\chi}(\chi_1, T)/\beta$. It is clear that the charge is concentrated near the surface of the sphere. Therefore we can apply the approximation of the double electrical layer for evaluation of the Coulomb energy. At large distances from the sphere, the order parameter and the charge density are equal to their equilibrium values $\chi = \bar{\chi}$ and $\eta = \eta_0(\bar{\chi})$ ($\eta_0 \approx \eta_2(\bar{\chi}) = H/\bar{\chi}(\chi, T)$). Therefore, the thermodynamic potential $\Phi_i$ of the volume $V_0$ in that case has the form:

$$\Phi_i(R_0, x_i) = \Phi_0 - \frac{A(x_i)}{3}R_0^3 + \frac{B(x_i)}{2}R_0^2 + \frac{C(x_i)}{4}R_0^4,$$

(6)

here $\Phi_0 = \phi_0 V_0 - H^2 V_0 (2\bar{\chi}(\chi_2, T))^{-1}$, $A(x_i) = \pi \bar{\chi}^{-2}(\chi_1, T) B^{-1} - 2\pi H^2 \bar{\chi}^{-2}(\chi_2, T) + O(H^3)$, $B(x_i) \approx 8\pi \bar{\chi}^{-1} B^{-1}(-\bar{\chi}(\chi_1, T) + Hn_0^2(\chi_1, T) + H^2(4\beta n_0^4(\chi_1, T))^{-1})$, $C(x_i) \approx \gamma d(\bar{\chi} - \chi_1)^2 F$. Here, we define the dimensionless factor $F$ ($F = 4 \int \phi d^3r / R_0^3 d(\bar{\chi} - \chi_2)^3$) in order to parameterize the distribution of charge. $F = 1/18$ in the limit of the double electrical layer, $V_0$ is the volume per one bubble ($V_0 = V/n$, where $n$ is the number of spheres) and $d$ is the interphase boundary thickness. Here, we take into account the strong screening of the localized charges and write the Coulomb energy in the double electrical layer approximation. The internal charge of the double electrical layer represents the charge near the surface of the charged bubble. The external charge is of the opposite sign and represents the charge of the region where the density of the charge carriers is reduced. This charge screens the electric field of the charged bubble. As a result, the electric field is localized in the vicinity of the charged bubble. This distribution of the electric field directly follows from the numerical minimization of the thermodynamic potential (1). In that case, it is proportional to $dR_0^3$. If the screening is absent, this energy is proportional to $R_0^3$ [11]. The parameters $A(x_1)$ and $B(x_1)$ (6) depend on temperature $T$ and magnetic field $H$, and parameter $C(x_1)$ depends on the average charge density $\bar{\chi}$. Parameters ($\bar{\chi}, T$) are external, and we find the phase diagram as a function of these parameters. Since $\bar{\chi}$ is determined by the doping, we describe the evolution of the properties of the system with doping.

The minimum of the potential $\Phi_i(R_0, x_i)$ (6) is determined by the set of equations: $\partial \Phi_i(R_0, x_i)/\partial R_0 = 0$ and $\partial \Phi_i(R_0, x_i)/\partial x_i = 0$, which define the equilibrium values of parameters: $R_0$ and $x_i$. For the equilibrium size of the charged domain $R_0$, we obtain:

$$R_0 = \frac{y \eta_0 A_0(x_1) - A(x_1)}{(y(x_1))^{-1} \eta_0 - 1) C(x_1)}.$$  

(7)
Then \( x_{s,s} \) is determined by the equation:

\[
\frac{(y(x_{s,s})A_0(x_{s,s}) - A(x_{s,s}))((y(x_{s,s})A_0(x_{s,s}) - A(x_{s,s}))}{(y(x_{s,s})^{-1} - 1)(y(x_{s,s})^{-1} - 1)B(x_{s,s})C(x_{s,s})} = 1
\]  

(8)

where we use the notations: \( \eta_1 = \eta_0 - H(\alpha(x_{s,s}, T))^{-1} \), \( A_0(x_{s,s}) = \pi \tilde{x} \tilde{y}(x_{s,s}, T) \beta^{-1} \), \( y(x_{s,s}) = 4\sigma(1 - 2x_{s,s})(x_{s,s} - \tilde{x})(-3\alpha(x_{s,s}, T))^{-1} \), \( \beta = 4\eta_1(3\eta_3) \). For computer simulation we assume that \( x_{s,s} \approx \tilde{x} - \lambda(x_{s,s} - \tilde{x}) \). Here \( \lambda \) is the ratio of the volume of the bubble \( (V_1) \) and the effective volume surrounding the bubble \( (V_2) \), where the charge density \( x \) differs from \( \bar{x} \). In order to estimate the characteristic length of the phase-segregated regions as well as the screening radius, it is necessary to perform numerical simulations. Nevertheless some estimates may be performed from equations (7), (8). Indeed, from equation (7), we estimate the typical size of the nano-regions: \( R_0 \approx 1-5 \text{ nm} \). Therefore the distance between bubbles may be estimated as: \( L_{R0} \approx 2(\lambda^{-1/3} - 1)R_0 \) (here \( \lambda \approx 0.5 \) corresponds to the condition of the compact packing). The thickness of the interphase boundary is equal to the screening length \( d \), which should be about \( L_{R0}/2 \) under the condition of the compact packing.

As a result, for the charge of the unit bubble \( Q \) we have:

\[
Q(T, H) = \rho_1(x_{s,s} - \tilde{x})\frac{4\pi}{3}R_1^3.
\]  

(9)

The average magnetization \( m \) is determined by the equation:

\[
m(T, H) = \frac{\rho_1}{3} \frac{4\pi}{3} R_1^3 V_0 + \frac{\rho_2}{3} \frac{1 - 4\pi}{3} \frac{R_1^3}{V_0}.
\]  

(10)

The temperature and magnetic field dependence of \( R(T, H), Q(T, H) \) and \( m(T, H) \) are shown in figure 2(a), (b). The magnetic susceptibility \( \chi(H, T) \) is temperature dependent \((\chi = dm(H)/dH)\), as shown in figure 3.

When the external electric field is applied, the charged bubbles shift from an equilibrium position. Since the bubbles are not bound to the lattice, they will be accelerated by the field. In real systems, the bubbles will be pinned to the lattice by lattice defects and by the Jahn–Teller distortions. Therefore, the polarization appears as a result of the shift of the positively charged
bubbles with respect to the negatively charged background in the case of hole doping. Since the bubbles are not strongly bound to the lattice, this shift and the corresponding polarization may be relatively large. Here we assume that this shift will be limited by Jahn–Teller deformation, which bounds the bubbles with the lattice. These arguments may be formulated in terms of a relatively simple formula for the effective dielectric constant:

\[ \varepsilon_{\text{eff}} = -\frac{\bar{\rho}(x) x}{\pi R} \left( \frac{x}{R} \right)^3. \] (11)

Here, \( k \) is the coefficient that determines the local lattice deformation, which appears due to charge localization and the Jahn–Teller effect. Any charge displacement causes additional local deformation of the lattice and therefore protects against large charge displacements. As a result, this local Jahn–Teller deformation may be estimated as \( d_{JT}(r) \sim k_{JT} \rho_0(x(r) - \bar{x}) \). In order to take this effect into account we introduce the phenomenological coefficient \( k \) in equation (11) \( k \sim k_{JT} \). Note that in the limit of the strong pinning (for \( k_{JT} \to \infty \)), the charged bubbles becomes strongly bound to the lattice. The coefficient \( k \) in equation (11) becomes small, leading to the relatively small contribution of the bubble displacements to the dielectric permittivity. The value of the coefficient \( k \) is very difficult to evaluate theoretically. Therefore, \( k \) should be evaluated from experiment. But we expect that the pinning is weak. The value of \( k \) should be relatively large. The effective dielectric permittivity \( \varepsilon_{\text{eff}}(T, H) \) (11) is large because of the large value of \( k \) and the large value of the polarization. Importantly, \( \varepsilon_{\text{eff}}(T, H) \) depends on the magnetic field, and therefore has magnetoelectric properties. The coefficient of the magnetocapacitance effect \( \Delta \varepsilon / \varepsilon_0(0) = (\varepsilon(H) - \varepsilon(0)) / \varepsilon(0) \) may be estimated from equations (7)–(11) and figure 2, where the dependence of the effective charge of the bubbles is plotted as a function of the field. As it follows from figure 2, in the magnetic field in the range 5–7 T, \( \Delta \varepsilon / \varepsilon_0(0) \approx 0.5 - 5 \). Note, that the magnetic field may cause the percolation of the charged regions, leading to the strong enhancement of the effect. On the other hand, our phenomenological theory is applicable only for the case when different bubbles do not overlap. The discussion of the percolation requires additional theoretical constructions and assumptions, and therefore it is out of the scope of our consideration.

The condition that the inhomogeneous phase has lower energy than the uniform state \( (\Phi_\text{R}(x_i, x_i) < \Phi_\text{eff}) \) determines the region of the stability of the inhomogeneous phase. The
equation $\Phi_\sigma(R_\alpha, x_1) = \Phi_\eta \sigma - H/2\bar{a}(\bar{x}, T)$ defines the upper boundary of the existence of the inhomogeneous state. As a result, this formula and equations (7) and (8) define the upper boundary $T_{s1}(\bar{x})$ in the recurrence form as a function of $x_1$:

$$T_{s1} = T_c + \frac{\sigma}{\alpha} x_1 (1 - x_1) - \frac{\sigma Z}{\alpha' (1 - 2x_1)^2}$$

$$\bar{x} = x_1 - \frac{2Z}{3 (1 - 2x_1)^3},$$

where $Z = \frac{16\beta_\xi y F}{\pi \sigma^3}$.

These equations determine the transition temperature $T_{s1}$ to the stable inhomogeneous phase as a function of external parameters $\bar{x}$. This condition means that the energy of this inhomogeneous phase is lower than the energy of the homogeneous state. Applying a similar procedure, we obtain the equation that defines the lower boundary of the inhomogeneous phase $T_{s2}(\bar{x})$. Note that lower boundary $T_{s2}$ will always be close to the temperature $T_{c'}(\bar{x})$, because there is no any gain in energy, when the bubble of the high-temperature phase is formed ($\Phi_\eta (\eta = 0) = 0$, and $\Phi_\eta (\eta_0) < 0$). It leads to the essential difference between the formation of the bubble of the low-temperature phase surrounded by the high-temperature phase and the bubble of the high-temperature phase surrounded by the low-temperature phase. The first one is energetically favourable, and therefore the region of the existence of these bubbles is considerably large. It is important to note that equation (11), which determine the phase diagram, do not depend on $d$. This fact allows us to avoid optimization of the thermodynamic potential with respect to $d$. A typical phase diagram of the inhomogeneous state is presented in figure 4. Phase transition to the nonhomogeneous state represents a typical first-order phase transition. A metastable inhomogeneous phase appears at the temperature $T_{c0}$, which is much higher then the temperature of the phase transition, and it is shown in the phase diagram by the dashed line. This line is determined by equations (7) and (8) and $A (x_0)^2 = 4C (x_0, \bar{x})B (x_0, \bar{x})$. The phase transition from the phase-separated state to an FM phase takes place because the thermodynamic potential of the FM phase becomes lower than the thermodynamic potential of the phase-separated state. The FM phase becomes the ground states. Moreover, below this temperature, the phase-
separated state does not exist. The minimum of the thermodynamic potential corresponding to an inhomogeneous state does not exist any longer. Therefore, this phase transition is the phase transition of the first order with the characteristic hysteresis.

Let us compare the calculated phase diagram with the experimental phase diagram of \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) [33]. The phase transition at \( T_c \) corresponds to the transition to an inhomogeneous state with the formation of the magnetic long-range order at \( T_c \) [33]. Then, with the lowering the temperature, the size of bubbles increases and at \( T_c \) \((T_c \text{ in } [33])\), the uniform magnetic state is formed. Note that experimental situation is more complicated. In \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) compound at the temperature \( T_{OO} \) (the case of manganites), \( \eta \approx 0.1 \sim 0.2 \), to equation (14) we obtain that \( u_p \) is less then 0.02 eV. Note that because of the screening, the Coulomb energy is strongly reduced and phase separation becomes possible. The energy gain due to the formation of the low-temperature phase \( u_p \) (the forth and the second terms in equation (6)) per one unit cell. For the Coulomb contribution, we obtain:

\[
u_p = \left( \frac{3e^2}{4\pi \varepsilon_0 a^3} \right) \frac{dR_0 F}{a^2}.
\]

Substituting \( \varepsilon = 30 - 40 \) (the case of manganites), \( F \approx 1/18, R_0 \approx 1 - 5 \text{ nm} \), to equation (14) we obtain that \( u_p \) is less then 0.02 eV. Note that because of the screening, the Coulomb energy is strongly reduced and phase separation becomes possible. The energy gain due to the formation of the low-temperature phase is \( u_p \approx 3k_B T_c \), \( u_p \approx a^3 \left( \bar{a}(x_1, T = 0) \right)^3/\beta = a^3 T_c \eta_0^2(x_1, T = 0)/C \), \( C = \eta_0^3(T = 0)/3k_B N_A \), where \( N_A \) is the Avogadro number. Therefore \( u_p \approx 0.03 - 0.1 \text{ eV} > u_p \), and the phase separation becomes favorable. Therefore, the typical size of the nano-regions, which was estimated from equation (7) as \( R_0 \approx 1 - 5 \text{ nm} \), represents quite a good approximation.

The analysis of the pair distribution function obtained by neutron scattering shows that the charge density in manganites is localized on the scale of 3 to 4 interatomic distances [5, 32]. The extra charge in that case is not more then \( 0.1 - 0.2 e \) per unit cell. This is consistent with our estimates. This state is characterized as the state with nano-dimensional charge and phase separation. The dynamics of these charged nano-regions may lead to a high value of the effective dielectric constant \( \varepsilon_{eff}(T, H) \) in the low frequency range [34].

We have shown that the second-order phase transition with a strong dependence of the critical temperature \( T_c(x) \) (2) on doping is unstable with respect to the formation of spatially inhomogeneous charged states. Within the phenomenological Landau theory, we have shown that these states appear at some temperature \( T_m \), which is substantially higher then the temperature \( T_c(\chi) \) (figure 4). As a result, the phase transition becomes effectively a first-order phase transition. Note that the Coulomb interaction determines the charge distribution, the screening and the characteristic length scale of the nonhomogeneous states. The spatially inhomogeneous state becomes possible in the systems with large dielectric constants and with relatively small charge density variations. We demonstrated that the effective dielectric
permittivity $\varepsilon_{\text{eff}}(T, H)$ \((11)\) is large because of the large value of polarization associated with the shift of bubbles, and the effective dielectric permittivity $\varepsilon_{\text{eff}}(T, H)$ depends on the magnetic field.

In conclusion, we underline that the localized charged states and the phase separation appear even in the case of the second-order phase transition. The properties of these states are described within the phenomenological theory of the phase transitions. The Coulomb interaction determines the spatial charge distribution, the screening and the characteristic length of charge localization. The inhomogeneous states become possible because of the large dielectric constants and relatively small spatial variation of the charge density. These states in the low-doped manganites may lead to magnetolectric behavior. The giant value of the effective dielectric permittivity and the magneto-capacitance effect in the inhomogeneous state in low-doped systems may become a powerful tool in the investigation of the inhomogeneous charge-segregated states in different materials, including low-doped cuprates near the threshold of the superconducting state.

Acknowledgments

Enlightening discussions with A P Levanyuk, B Z Malkin, and D Mihailovic are highly appreciated. We acknowledge financial support from Slovenian Ministry for Science and Technology and Ad-Futura (Slovenia).

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