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Phase separation in strongly correlated electron systems with spin-state transitions

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Abstract. In some transition metal compounds, in particular in those with Co\textsuperscript{3+} and Fe\textsuperscript{2+} having the \textit{d}\textsuperscript{6} configuration, these ions can exist in different spin states, with the possibility of spin-state transitions between them. We demonstrate on a simple model that in doped compounds of such type there typically occurs a phase separation with the formation of inhomogeneous states, one of which corresponds to an undoped material with the low-spin state of Co\textsuperscript{3+}, and the other one with intermediate-spin state and delocalized \textit{e}_\textit{g} electrons. The generic phase diagram of such systems is constructed.

1. Introduction
Complex cobalt-based oxides with perovskite structure (cobaltites), such as La\textsubscript{1-x}Sr\textsubscript{x}CoO\textsubscript{3}, can undergo the transitions between different spin states of cobalt ions (spin-state transitions - SST), which can occur with the change of temperature, pressure, and doping \textit{x}. They are often accompanied by the metal-insulator transition. The Co\textsuperscript{3+} ion having six electrons at the 3\textit{d} shell can exist in three different spin states: low-spin (LS) state with \(S=0\) (\(t^6_{2g}e^0_{g}\)), intermediate-spin (IS) state \(S=1\) (\(t^5_{2g}e^1_{g}\)), and high-spin (HS) state \(S=2\), see e.g. Ref. [1]. Thus, cobaltites, in addition to quite common charge, orbital, and spin degrees of freedom with the possibility of respective orderings, have an “extra dimension”: the possibility of spin-state (or, in other words, multiplet) transitions. Correspondingly, if doping of materials like manganites can cause phase separation due to an interplay of the motion (kinetic energy) of doped holes with the underlying magnetic and orbital structure [2], in systems with SST one can expect similar phenomena due to an interplay with the spin state of the matrix.

Let \(\Delta\) be the energy difference between \(t_{2g}\) and \(e_g\) levels in Co\textsuperscript{3+} and Co\textsuperscript{4+} ions. Then, the energies of IS and HS states will differ from the energy of LS Co\textsuperscript{3+} by \(\Delta - J_H\) and \(2(\Delta - 2J_H)\), respectively, where \(J_H\) is the Hund’s rule coupling constant. The corresponding energies for Co\textsuperscript{4+} are \(\Delta - 2J_H\) and \(2(\Delta - 3J_H)\). For \(\Delta > 3J_H\) and \(\Delta < 2J_H\), the ground state of both Co\textsuperscript{3+} and Co\textsuperscript{4+} is LS and HS, respectively. At \(2J_H < \Delta < 3J_H\), we have LS Co\textsuperscript{3+} and HS Co\textsuperscript{4+}. Thus, for isolated Co ions, the IS state is always unfavorable in energy.

The situation becomes more complicated if there exists a charge transfer between cobalt ions. First, note that the hopping integrals between the \(t_{2g}\) states in cobaltites are as a rule much

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smaller than for the $e_g$ states. In the treatment below, we ignore the $t_{2g} - t_{2g}$ hopping and take into account only the hopping of $e_g$ electrons. The inclusion of $t_{2g} - t_{2g}$ hoppings will not modify qualitative results, introducing only minor numerical changes. Second, the states with the number of electrons per ion larger than six are unfavorable due to the strong on-site Coulomb repulsion. Third, the transitions of electrons between the lattice sites corresponding to the changes of spin by more than one half are strongly suppressed since they involve the simultaneous change of a state for two or more electrons. As a result, in hole-doped cobaltites there remain only two most probable hopping processes: (i) the transitions of electrons between the IS Co$^{3+}$ and LS Co$^{4+}$ and (ii) transitions between the HS Co$^{3+}$ and IS Co$^{4+}$.

Thus, to facilitate the kinetic energy gain due to the electron transfer, one should create a ground state with intermediate spins. Such a situation can arise if in the ground state for isolated ions we have either LS Co$^{4+}$ or HS Co$^{3+}$. The former, more realistic case corresponds to $\Delta > 3J_H$ when some of LS Co$^{3+}$ can be promoted to the IS state. In the latter case corresponding to $\Delta < 2J_H$, Co$^{4+}$ would be HS, and some Co$^{3+}$ ions can be transformed to the IS state. In the intermediate situation, $2J_H < \Delta < 3J_H$, the electron transfer can occur if we promote both ions, Co$^{3+}$ and Co$^{4+}$, to some excited states, which seems to be less probable. Below we restrict our treatment to the first, the most realistic case. The other possibility can be treated in a similar fashion [3].

2. The model Hamiltonian

We study the systems with spin-state transitions in the framework of a simple model similar to that used in the case of doped manganites, where the competition between the localized and band states can lead to the nanoscale electronic phase separation [4]. Here we restrict ourselves to the consideration of zero temperature. We assume also a ferromagnetic alignment of all spins of cobalt ions at $T = 0$. In the case of cobaltites, the role of the localized level is played by the ground state of Co ions, LS Co$^{3+}$ and the delocalized (band) charge carriers are electrons promoted to the $e_g$ levels.

When $\Delta > 3J_H$, we can assume that only LS Co$^{3+}$, IS Co$^{3+}$, and LS Co$^{4+}$ ions exist in the system. Treating LS Co$^{3+}$ state as a vacuum state, we introduce creation operators (spinless fermions) for an electron at the $e_g$ level and a hole at the $t_{2g}$ level at site $\mathbf{n}$, $a^\dagger_\mathbf{n}$ and $c^\dagger_\mathbf{n}$ respectively, according to the following rules

$$0 = |\text{Co}^{3+}_{LS}\rangle (E^{\text{vac}} = E_0), \ a^\dagger_\mathbf{n}|0\rangle = |\text{Co}^{2+}\rangle (E^{(2+)} = U'), \ c^\dagger_\mathbf{n}|0\rangle = |\text{Co}^{4+}_{LS}\rangle (E^{(h)} = E_1), \ (1)$$

where we introduce the reference energies, $E_0$ and $E_1$, for LS states of Co$^{3+}$ and Co$^{4+}$ ions, respectively, and the on-site Coulomb repulsion energy $U'$ of two $e_g$ electrons. In terms of these operators, the IS state of Co$^{3+}$ ions can be constructed as

$$|\text{Co}^{3+}_{IS}\rangle = c^\dagger_\mathbf{n}a^\dagger_\mathbf{n}|0\rangle \ (E^{(3+)}_{IS} = E_0 + \Delta - J_H = E_2). \ (2)$$

Using these operators, we can write the following single-site Hamiltonian

$$H_\mathbf{n} = [E_0 + (E_1 - E_0)(n^e_\mathbf{n} - n^h_\mathbf{n})] + (\Delta - J_H)n^e_\mathbf{n} + Un^e_\mathbf{n}(1 - n^h_\mathbf{n}), \ (3)$$

where $U = U' + E_1 - \Delta + J_H$ and $n^e_\mathbf{n} = a^\dagger_\mathbf{n}a_\mathbf{n}$ and $n^h_\mathbf{n} = c^\dagger_\mathbf{n}c_\mathbf{n}$ are the operators describing the numbers of electrons at in $e_g$ levels and holes at $t_{2g}$ levels, respectively. Taking the sum over all lattice sites and introducing the intersite hopping term, we get

$$H = \sum_\mathbf{n} [E_0 + (E_1 - E_0 - \mu)(n^e_\mathbf{n} - n^h_\mathbf{n})] + \Delta_1 \sum_\mathbf{n} n^e_\mathbf{n} + U \sum_\mathbf{n} n^e_\mathbf{n}(1 - n^h_\mathbf{n}) - t \sum_{\langle \mathbf{nm} \rangle} (a^\dagger_\mathbf{n}a_\mathbf{n} + h.c.), \ (4)$$

where $\Delta_1 = \Delta - J_H$ and $\mu$ is the chemical potential. The mean values $n^e$ and $n^h$ obey the equality $n^e - n^h = x$, where $x$ is the doping level.
3. Homogeneous states

Hamiltonian (4) is quite similar to that of the Falicov-Kimball model [5]. Here we have, in fact, an interplay between the electron localization in the LS state and the itinerancy in the IS state. This kind of interplay was analyzed in detail both analytically [4] and numerically [6], and a tendency for a nanoscale phase separation was demonstrated. We analyze Hamiltonian (4) using the Hubbard I decoupling [7] in the equation of motion for the one-electron Green function $G^e(n, n_0; t - t_0) = -i(T_{un}(t) a^\dagger_{un}(t_0))$ for the $e_g$ electrons. In the frequency-momentum representation, we get

$$G^e(k, \omega) = -\frac{\omega + \mu - \Delta_1 - Un^h}{(\omega + \mu - \Delta_1 - E_1(k))(\omega + \mu - \Delta_1 - E_2(k))},$$

where $E_{1,2}(k) = \{U + \epsilon(k) \pm [(U - \epsilon(k))^2 + 4U\epsilon(k)(1 - n^h)]^{1/2}\}/2$ are energy spectra for two Hubbard subbands and $\epsilon(k)$ is the energy spectrum at $U = 0$. We choose $\epsilon(k)$ in the simplest tight-binding form, ignoring orbital degeneracy and the specific features of the hopping integrals of $e_g$ electrons, $[\epsilon(k) = -2t(cos k_x + cos k_y + cos k_z)$ for the simple cubic lattice]. The mean values $n^e$ and $n^h = x + n^e$ are found then by solving the equation

$$n^e = -i \int \frac{d^3kd\omega}{(2\pi)^4} G^e(k, \omega)e^{i\omega\eta},$$

where the Green function $G^e(k, \omega)$ implicitly depends on $n^e$ and $n^h$. We solve this equation in the limit $U \to \infty$. In this case, the number of IS Co$^{3+}$ ions is $n_{IS,Co^{3+}} = \langle n^e_n n^h_n \rangle = n^e$, and the number of LS Co$^{3+}$ ions is $n_{LS,Co^{3+}} = 1 - x - n^e = 1 - n^h$ (here we use the equality $\langle n^e_n(1 - n^h_n) \rangle = 0$, when $U \to \infty$).

The typical dependence of $n_{LS,Co^{3+}}$ and $n_{IS,Co^{3+}}$ on $x$ are shown in Fig. 1. In general case, there are two solutions to Eq. (6), corresponding to $n^h \neq 1$ and $n^h = 1$ ($n_{LS,Co^{3+}} = 0$), where all Co$^{3+}$ ions are promoted to IS state. When $x < x_2$ the solution with $n^h \neq 1$ corresponds to the minimum of the system energy. At $x > x_2$, the solution with $n^h = 1$ becomes favorable in energy (see the inset to Fig. 1), and the jump-like transition in the numbers $n^e$ and $n^h$ occurs. When $x > x_3(> x_2)$, both these solutions coincide. Note also, that Co$^{3+}$ ions in IS state appear in the system starting from some doping level $x_1(< x_2)$.

4. Inhomogeneous states and the phase diagram

In the previous section, we considered a possible homogeneous states of the system. Note, however, that in the wide doping range ($0 < x \lesssim x_3$ when $\Delta > 3J_H$), a homogeneous state turns out to be unstable toward a phase separation, as it can be seen in the inset to Fig. 1. Namely, it
is more favorable in energy, if the system forms inhomogeneous state with two phases: one phase with undoped LS Co$^{3+}$ ions (insulating regions), and the second metallic (and ferromagnetic due to double exchange) phase in which Co$^{3+}$ ions are promoted to the IS state. We take this fact into account in construction the phase diagram of the model in $\Delta/J_H$–$x$ plane by comparison of system energies in different states. The phase diagram of the system calculated at $t/J_H = 1$ is shown in Fig. 2. In this phase diagram, we also show corresponding results for the parameter range $\Delta < 3J$, which is obtained in a way similar to the case $\Delta > 3J_H$, considered in the previous section [3].

Note that the differences of the system energies in different states do not depend on the references energies $E_0$ and $E_1$. Thus, the structure of the phase diagram in $\Delta/J_H$–$x$ plane depends only on the value of the hopping integral. At rather small $t$ ($t/J_H \leq 1$), we have an intermediate region in the phase diagram, where the charge carries are localized at any doping level with LS Co$^{3+}$ and HS Co$^{4+}$ ions (see Fig. 2). This intermediate region gradually disappears with the growth of $t$.

The presence of inhomogeneous states with different spin states of Co is indeed seen in many experiments for doped LaCoO$_3$, see e.g. [8, 9].

5. Conclusions
Based on a simplified model of a strongly correlated electron system with spin-state transitions, we demonstrated a tendency to the phase separation for doped perovskite cobaltites in a wide range of doping levels. The phase diagram including large regions of inhomogeneous states was constructed in the plane of parameters doping $x$ versus $e_g - t_{2g}$ energy splitting $\Delta$. The form of the phase diagram turns out to be strongly dependent on the value of the hopping integral $t$.

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