Magnetic inhomogeneities in materials with spin-state transitions

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Abstract

In some transition metal compounds, in particular in those with Co^{3+} and Fe^{2+} having the d^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^{3+}, and the other one with intermediate-spin sate and with delocalized e_g electrons. The generic phase diagram of such systems is constructed.

The phase separation phenomena: a key issue in the physics of strongly correlated electron systems, especially in manganites and related compounds

The simplest type: formation of nanoscale inhomogeneities such as ferromagnetic metallic droplets (magnetic polarons or ferrons) located in an insulating antiferromagnetic matrix ⇒ self-trapping of charge carriers

Usually related to an interplay between different order parameters involving magnetism: ferro *vs* antiferro, antiferro *vs* supercond., *etc*.

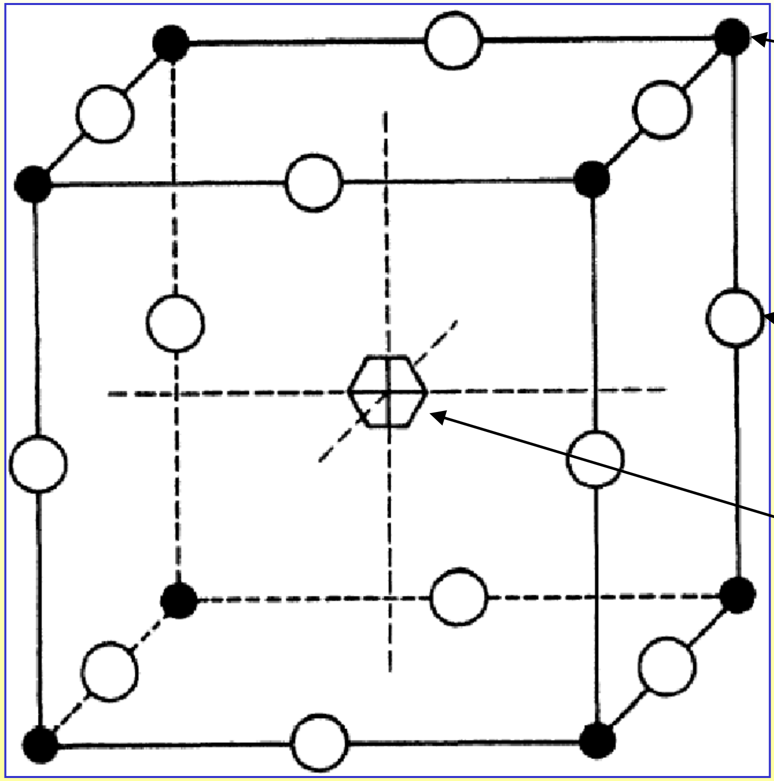
Another degree of freedom: a competition between different multiplet states of transition metal ion in magnetic oxides leading to so called spin-state transitions

⇓

The situation is characteristic of compounds with Co^{3+} and Fe^{2+} ions. Typical example: cobaltites with the perovskite structure such as $La_{1-x}Ca_xCoO_3$

Crystal structure of cobaltites
$RE_{1-x}A_xCoO_3$

ideal cubic sell, perovskite structure



Co^{3+}, Co^{4+}

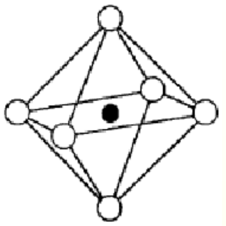
O^{2-}

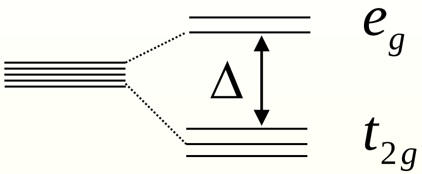
RE^{3+}, A^{2+}

RE=La, Pr, Sm, …

A=Ca, Sr, Ba, …

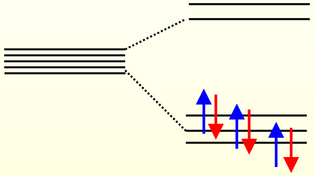
Electronic configurations of Co^{3+} and Co^{4+} ions





low-spin state

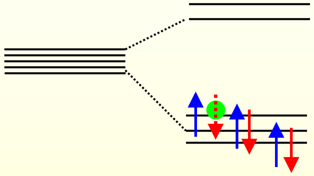
$\mathrm{Co}^{3+}_{\mathrm{LS}}$



$S = 0$

$E^{3+}_{\mathrm{LS}} = E_0$

$\mathrm{Co}^{4+}_{\mathrm{LS}}$

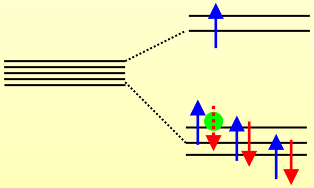


$S = 1/2$

$E^{4+}_{\mathrm{LS}} = E_1$

intermediate-spin state

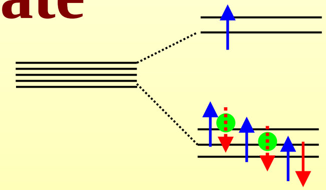
$\mathrm{Co}^{3+}_{\mathrm{IS}}$



$S = 1$

$E^{3+}_{\mathrm{IS}} = E_0 + (\Delta - J_H)$

$\mathrm{Co}^{4+}_{\mathrm{IS}}$

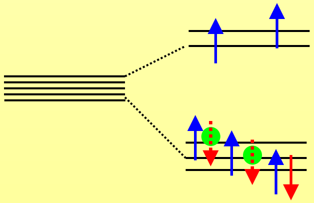


$S = 3/2$

$E^{4+}_{\mathrm{IS}} = E_1 + (\Delta - 2J_H)$

high-spin state

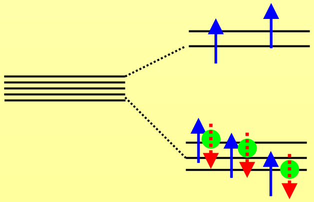
$\mathrm{Co}^{3+}_{\mathrm{HS}}$



$S = 2$

$E^{3+}_{\mathrm{HS}} = E_0 + 2(\Delta - 2J_H)$

$\mathrm{Co}^{4+}_{\mathrm{HS}}$



$S = 5/2$

$E^{4+}_{\mathrm{HS}} = E_1 + 2(\Delta - 3J_H)$

Possible ground states of Co^{3+} and Co^{4+} ions (in the absence of inter-site hopping)

1. $\boxed{\Delta > 3J_H} \longrightarrow \left(\mathrm{Re}^{3+}\mathrm{Co}^{3+}_{\mathbf{LS}}\right)_{1-x}\left(\mathrm{A}^{2+}\mathrm{Co}^{4+}_{\mathbf{LS}}\right)_x \mathrm{O}^{2-}_3$

$$\boxed{E_0^{(1)} = E_0(1-x) + E_1 x}$$

2. $\boxed{\Delta < 2J_H} \longrightarrow \left(\mathrm{Re}^{3+}\mathrm{Co}^{3+}_{\mathbf{HS}}\right)_{1-x}\left(\mathrm{A}^{2+}\mathrm{Co}^{4+}_{\mathbf{HS}}\right)_x \mathrm{O}^{2-}_3$

$$\boxed{E_0^{(2)} = E_0(1-x) + E_1 x + 2\left(\Delta - 2J_H - J_H x\right)}$$

3. $\boxed{2J_H < \Delta < 3J_H} \longrightarrow \left(\mathrm{Re}^{3+}\mathrm{Co}^{3+}_{\mathbf{LS}}\right)_{1-x}\left(\mathrm{A}^{2+}\mathrm{Co}^{4+}_{\mathbf{HS}}\right)_x \mathrm{O}^{2-}_3$

$$\boxed{E_{loc} = E_0(1-x) + E_1 x + 2\left(\Delta - 3J_H\right)x}$$

Intermediate-spin state is impossible!

Charge transfer between Co^{3+} and Co^{4+} (similar to the double exchange)

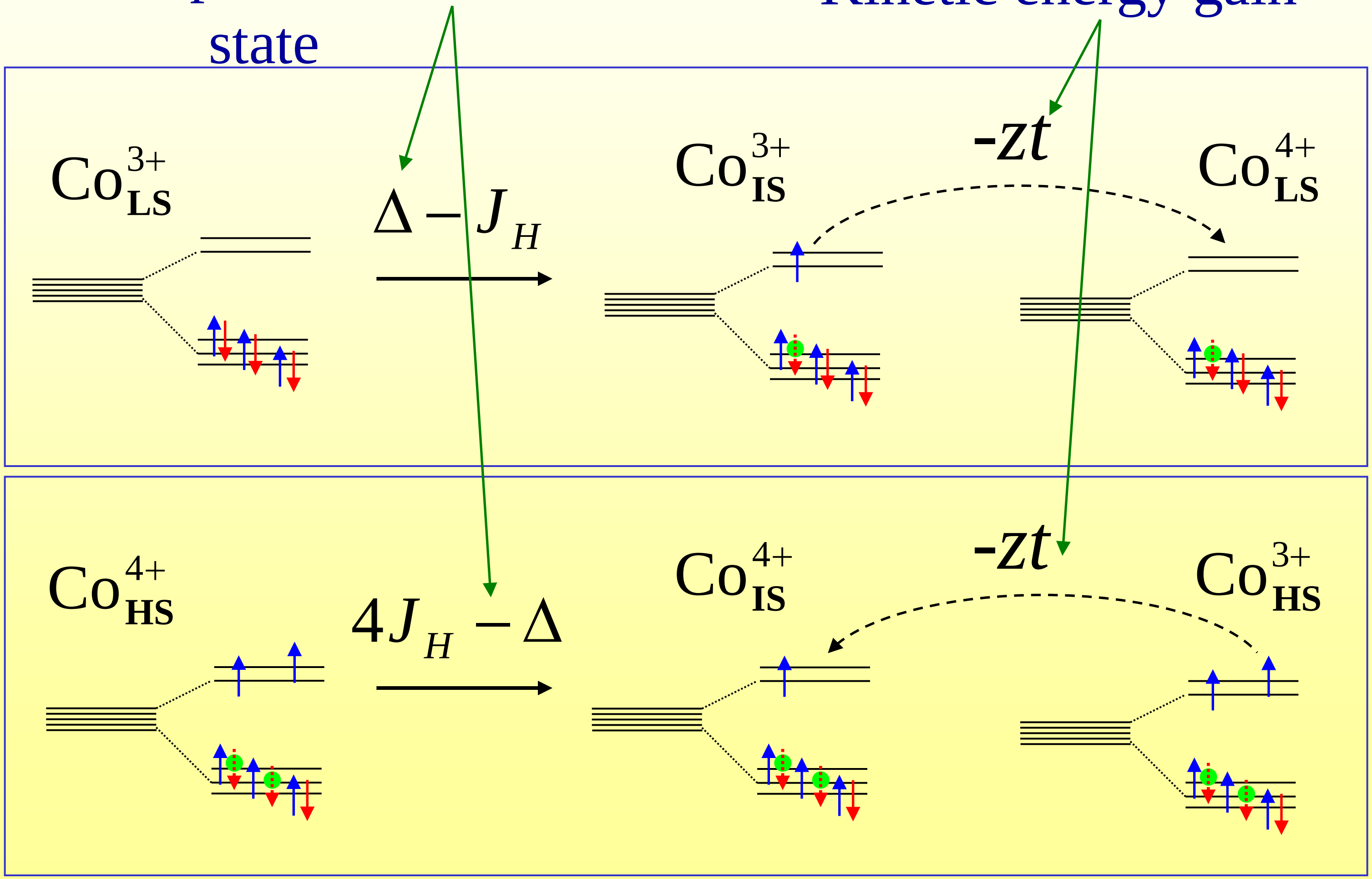
$$\mathrm{Co}^{3+}_{1\uparrow} - \mathrm{O}^{2-}_{2\uparrow,3\downarrow} - \mathrm{Co}^{4+} \Rightarrow \mathrm{Co}^{4+} - \mathrm{O}^{2-}_{1\uparrow,3\downarrow} - \mathrm{Co}^{3+}_{2\uparrow}$$

Energy cost to promote Co ion to IS state

Kinetic energy gain

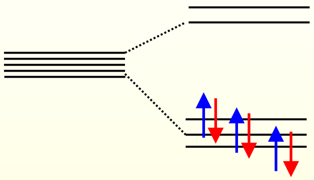
$\Delta > 3J_H$

$\Delta < 2J_H$



Model Hamiltonian at $\Delta > 3J_H$ (LS-LS case)

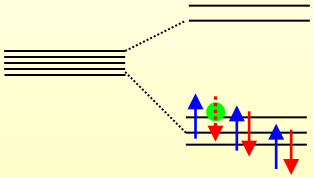
ferromagnetic spin alignment is supposed
(electrons and holes are spinless fermions)



$$\left|\mathrm{Co}^{3+}_{\mathrm{LS}}\right\rangle = \left|0\right\rangle$$

vacuum state

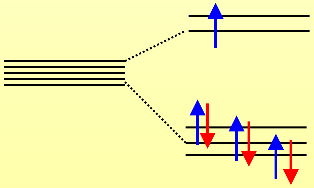
$$\boxed{E_{vac} = E_0}$$



$$\left|\mathrm{Co}^{4+}_{\mathrm{LS}}\right\rangle = c^{+}_{\mathbf{n}}\left|0\right\rangle$$

$c^{+}_{\mathbf{n}}$ creates a hole at t_{2g} level

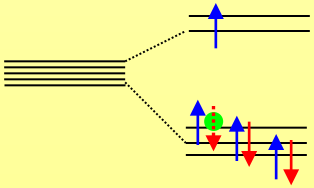
$$\boxed{E^{h} = E_1}$$



$$\left|\mathrm{Co}^{2+}\right\rangle = a^{+}_{\mathbf{n}}\left|0\right\rangle$$

$a^{+}_{\mathbf{n}}$ creates an electron at e_g level

$$\boxed{E^{e} = U'}$$



$$\left|\mathrm{Co}^{3+}_{\mathrm{IS}}\right\rangle = c^{+}_{\mathbf{n}}a^{+}_{\mathbf{n}}\left|0\right\rangle$$

intermediate spin state

$$\boxed{E^{e-h} = E_0 + \Delta - J_H}$$

One-site Hamiltonian

$$\boxed{\begin{aligned} H_{\mathbf{n}}^{0} &= E_0 + (E_1 - E_0) n_{\mathbf{n}}^{h} + (U' - E_0) n_{\mathbf{n}}^{e} + \\ &\quad + \left[(\Delta - J_H) - (E_1 - E_0) - (U' - E_0)\right] n_{\mathbf{n}}^{e} n_{\mathbf{n}}^{h} \end{aligned}}$$

$$n_{\mathbf{n}}^{e} = a_{\mathbf{n}}^{+} a_{\mathbf{n}}$$

$$n_{\mathbf{n}}^{h} = c_{\mathbf{n}}^{+} c_{\mathbf{n}}$$

Effective Hamiltonian for the LS-LS case

$$\boxed{\begin{aligned} H' &= \sum_{\mathbf{n}} \left[E_0 + (E_1 - E_0 - \mu)(n_{\mathbf{n}}^{h} - n_{\mathbf{n}}^{e})\right] + \\ &\quad + \Delta_1 \sum_{\mathbf{n}} n_{\mathbf{n}}^{e} + U \sum_{\mathbf{n}} n_{\mathbf{n}}^{e} (1 - n_{\mathbf{n}}^{h}) - t \sum_{\langle \mathbf{n},\mathbf{m} \rangle} \left(a_{\mathbf{n}}^{+} a_{\mathbf{m}} + a_{\mathbf{m}}^{+} a_{\mathbf{n}}\right) \end{aligned}}$$

$$U = U' + E_1 - \Delta + J_H - 2E_0 \qquad \boxed{\Delta_1 = \Delta - J_H} \qquad \boxed{\langle n_{\mathbf{n}}^{h} - n_{\mathbf{n}}^{e} \rangle = x}$$

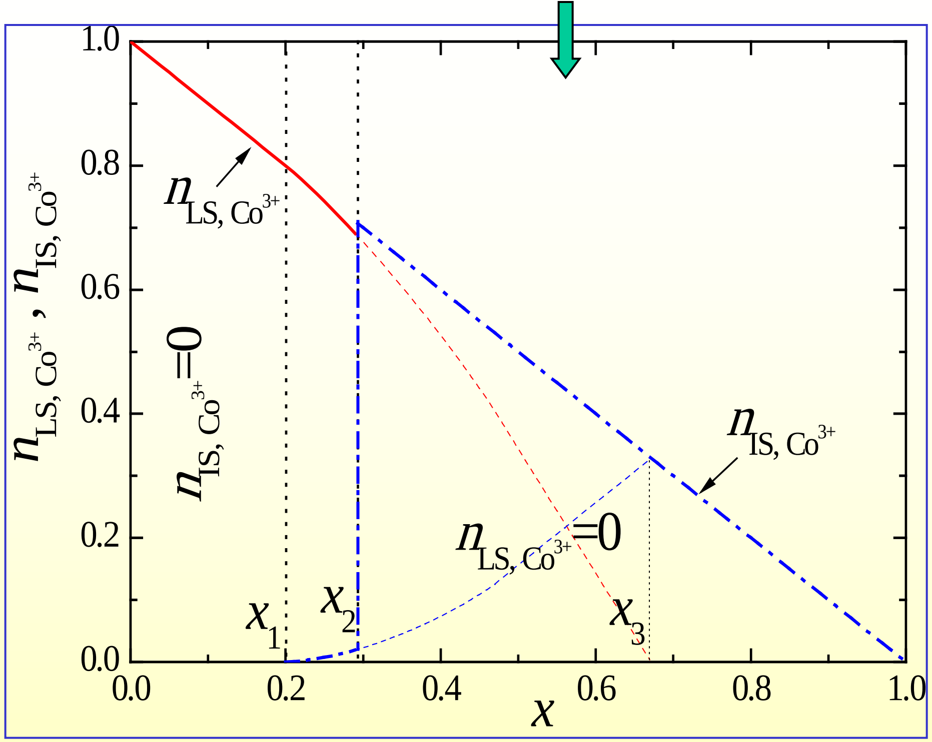
This Hamiltonian is similar to the *lb* model.

T.V. Ramakrishnan et al.PRL 2004, K. Kugel et al. PRL 2005

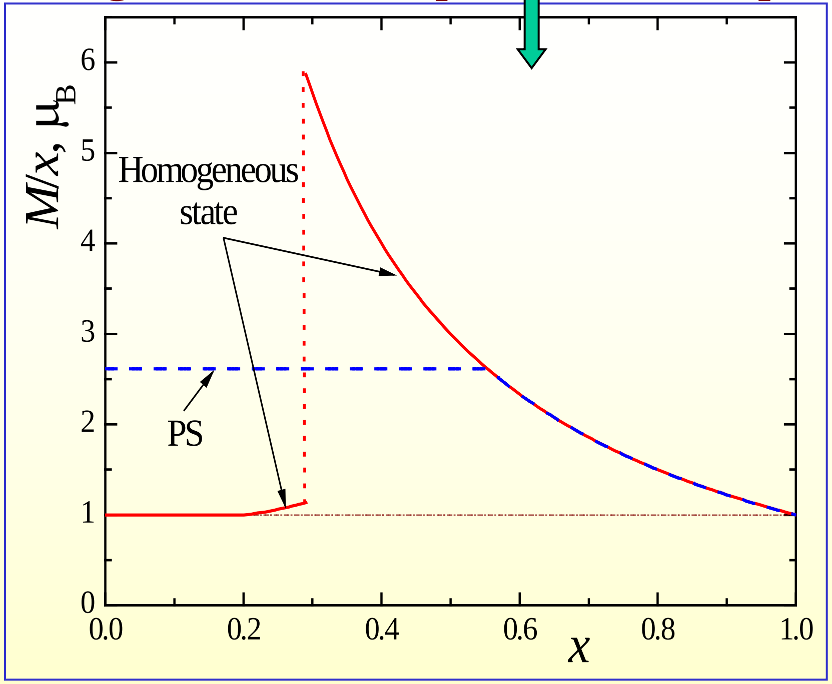
We analyze it in the Hubbard I approximation in the limit $U \to \infty$.

There are 2 solutions, corresponding to $n^h \neq 1$, and $n^h = 1$ ($n_{\mathrm{LS,\,Co}^{3+}} = 0$).

Densities of LS and IS Co^{3+} ions vs. doping x

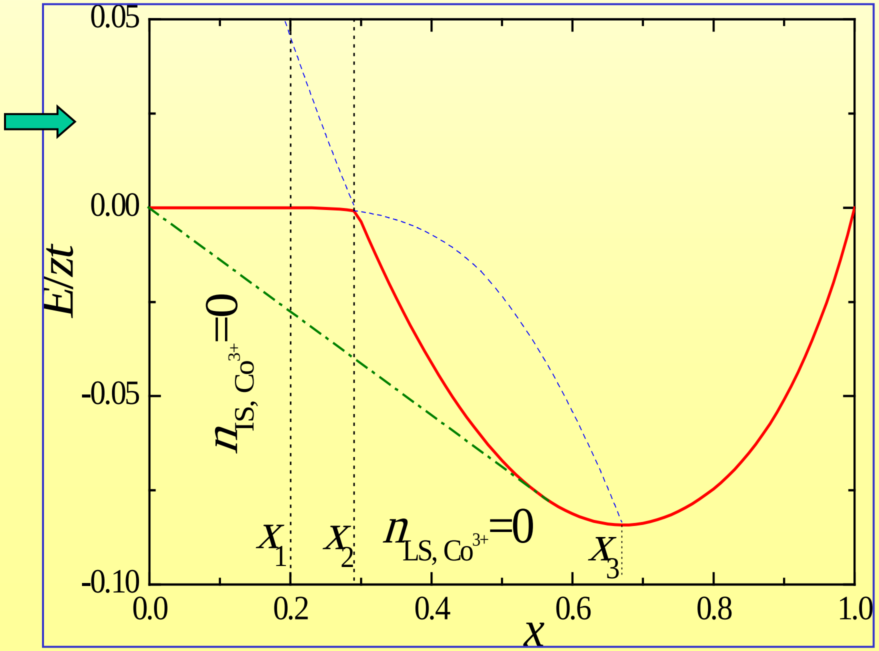


Magnetic moment per Co^{4+} vs. doping



$$n_{\mathrm{IS,Co}^{3+}} = n^e,\ n_{\mathrm{LS,Co}^{3+}} = 1 - n^h$$

Energy

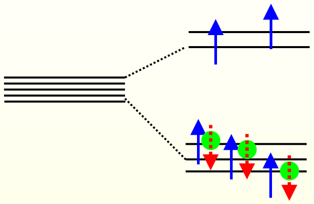


Features:

1. There exists a jump-like transition to the state with $n_{\mathrm{LS,Co}^{3+}} = 0$
2. The homogeneous state is unstable in the region $0<x<x^*\approx x_3$

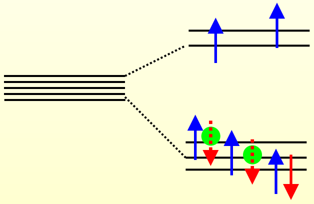
Model Hamiltonian at $\Delta<2J_H$ (HS-HS case)

ferromagnetic spin alignment is supposed



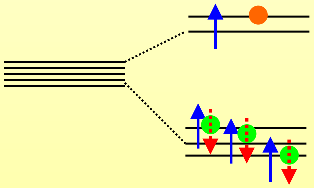
$|\mathrm{Co}^{4+}_{\mathrm{HS}}\rangle = |0\rangle$ vacuum state

$$\boxed{E_{vac} = E_1 + 2\Delta - 6J_H}$$



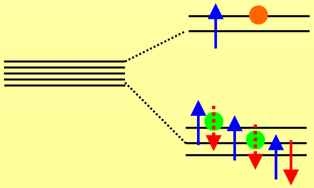
$|\mathrm{Co}^{3+}_{\mathrm{HS}}\rangle = a^+_{\mathbf{n}}|0\rangle$ $a^+_{\mathbf{n}}$ creates *an electron* at t_{2g} level

$$\boxed{E^e = E_0 + 2\Delta - 4J_H}$$



$|\mathrm{Co}^{5+}\rangle = c^+_{\mathbf{n}}|0\rangle$ $c^+_{\mathbf{n}}$ creates *a hole* at e_g level

$$\boxed{E^h = U'}$$



$|\mathrm{Co}^{4+}_{\mathrm{IS}}\rangle = a^+_{\mathbf{n}}c^+_{\mathbf{n}}|0\rangle$

intermediate spin state

$$\boxed{E^{e-h} = E_0 + \Delta - 2J_H}$$

Effective Hamiltonian for the HS-HS case

(it is derived in the way similar to the LS-LS case)

$$H' = \sum_{\mathbf{n}} \left[E_1 + 2\Delta - 6J_H + \left(E_1 - E_0 - 2J_H - \mu \right)\left(n_{\mathbf{n}}^e - n_{\mathbf{n}}^h \right) \right] + \\ + \Delta_2 \sum_{\mathbf{n}} n_{\mathbf{n}}^h + U \sum_{\mathbf{n}} n_{\mathbf{n}}^h \left(1 - n_{\mathbf{n}}^e \right) - t \sum_{\langle \mathbf{n},\mathbf{m} \rangle} \left(c_{\mathbf{n}}^+ c_{\mathbf{m}} + c_{\mathbf{m}}^+ c_{\mathbf{n}} \right)$$

$$\boxed{\Delta_2 = 4J_H - \Delta}$$

$$\boxed{\left\langle n_{\mathbf{n}}^e - n_{\mathbf{n}}^h \right\rangle = 1 - x}$$

HS-HS case ($\Delta < 2J_H$) is similar to LS-LS case ($\Delta > 3J_H$) under the following replacement:

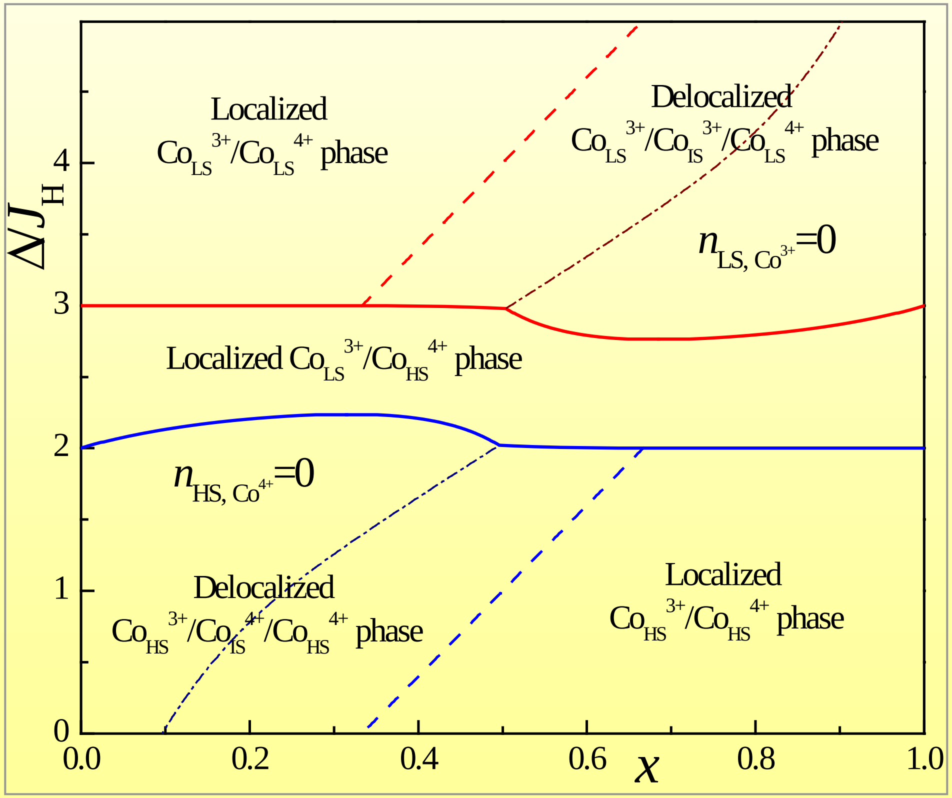
$$n^e \to n^h,\ n^h \to n^e,\ x \to 1\text{-}x,\ \Delta_1 \to \Delta_2$$

The energy differences between LS-LS ($\Delta > 3J_H$), HS-HS ($\Delta < 2J_H$), and LS-HS ($2J_\mathrm{H} < \Delta < 3J_H$) states do not depend on E_0 and E_1

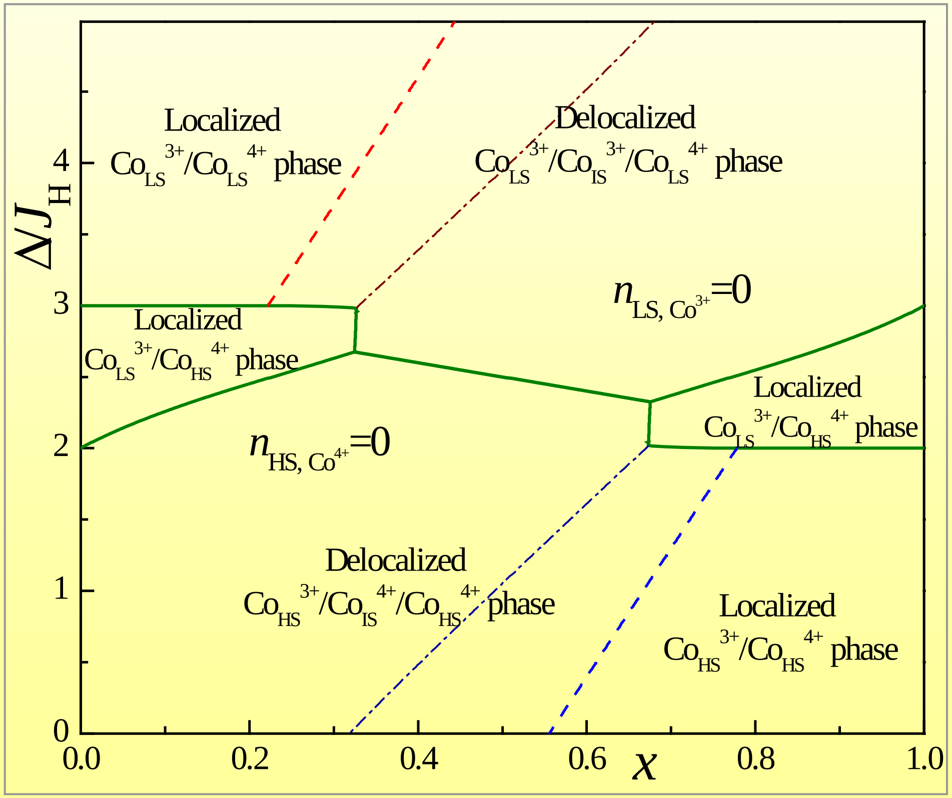
Phase diagram with homogeneous states.

The structure of the phase diagram depends on the value of hopping integral. At small *t*, there is an intermediate region, where the charge carries are localized at any doping level with LS Co^{3+} and HS Co^{4+} ions. This intermediate region gradually disappears with the growth of *t*. The phase diagram changes if we take into account inhomogeneous states.

$t/J_H = 1$



$t/J_H = 1.5$

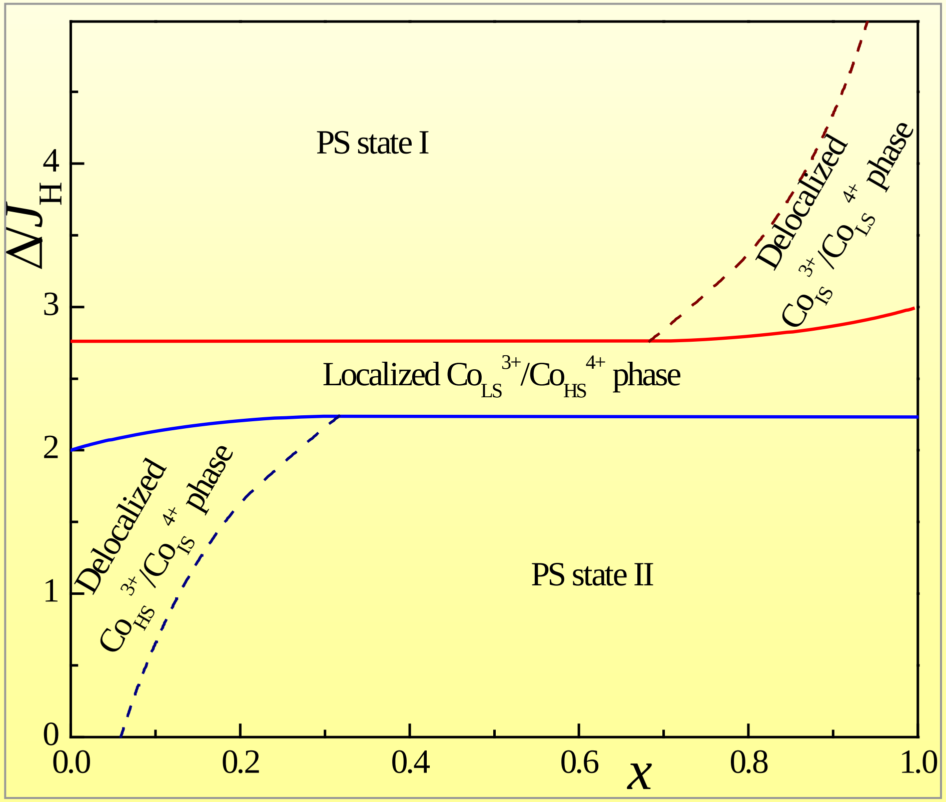


Phase diagram including phase-separated states

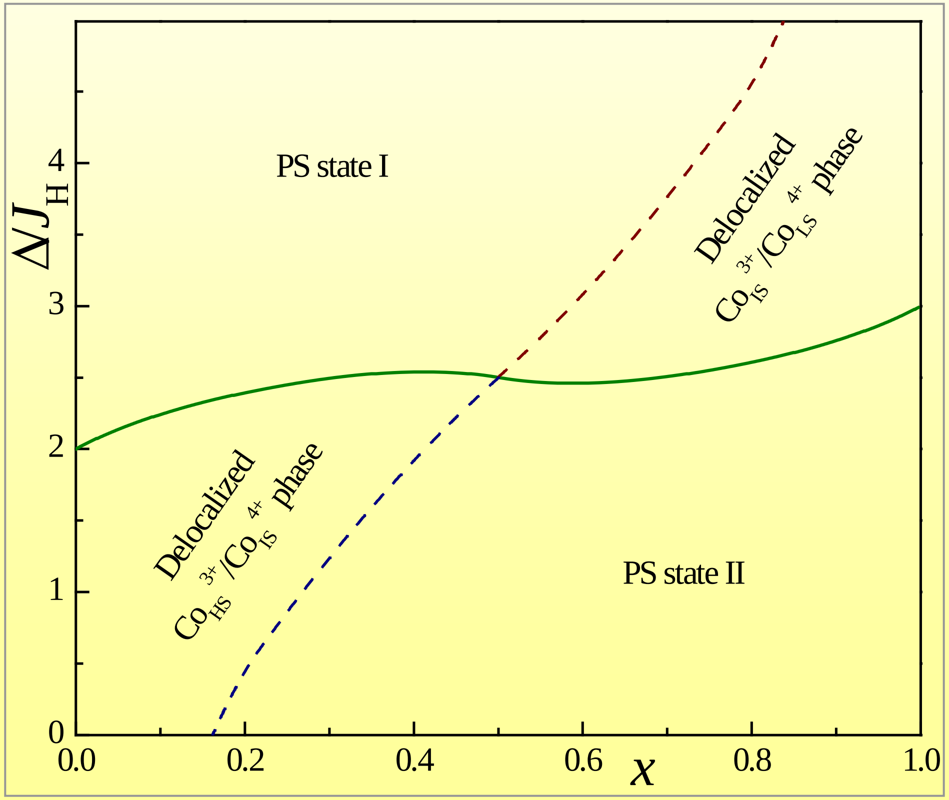
PS state I is the phase-separated state including the regions with localized charge carriers, corresponding to LS Co^{3+}, and delocalized charge carries promoted to IS Co^{3+}.

PS state II is the similar phase-separated state where the regions with and without itinerant charge carriers correspond to IS Co^{4+} and HS Co^{4+}, respectively.

$t/J_H = 1$



$t/J_H = 1.5$



Conclusions

- A simplified model of a strongly correlated electron system with spin-state transitions was formulated
- 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 Δ.
- The form of the phase diagram turns out to be strongly dependent on the value of the hopping integral t.

A.O. Sboychakov, K.I. Kugel, A.L. Rakhmanov, and D.I. Khomskii, Phys. Rev. B **80**, 024423 (2009); arXiv:0904.4760.