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Frustrated polarons and percolation in chemically and electrostatically doped cobaltite $LaCoO_3$

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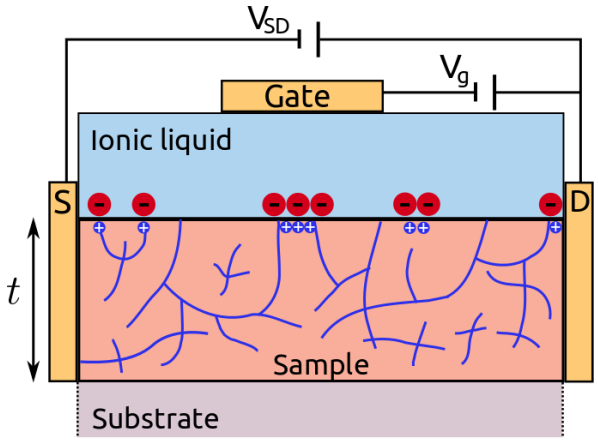
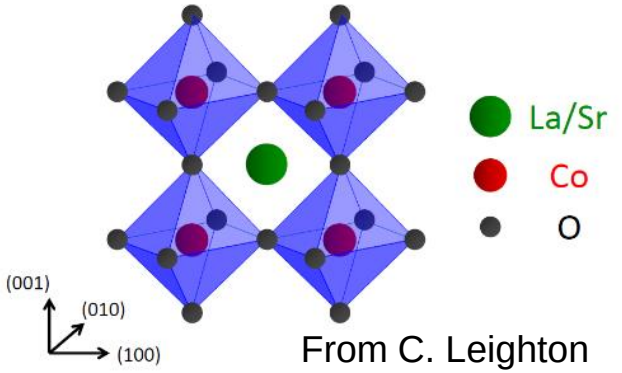
University of Minnesota

In collaboration with Jeff Walter, Chris Leighton (Minnesota), Daniel Phelan (Argonne), Rafael Fernandes, Boris Shklovskii (Minnesota).

Superstripes 2016, Ischia, 27 June 2016



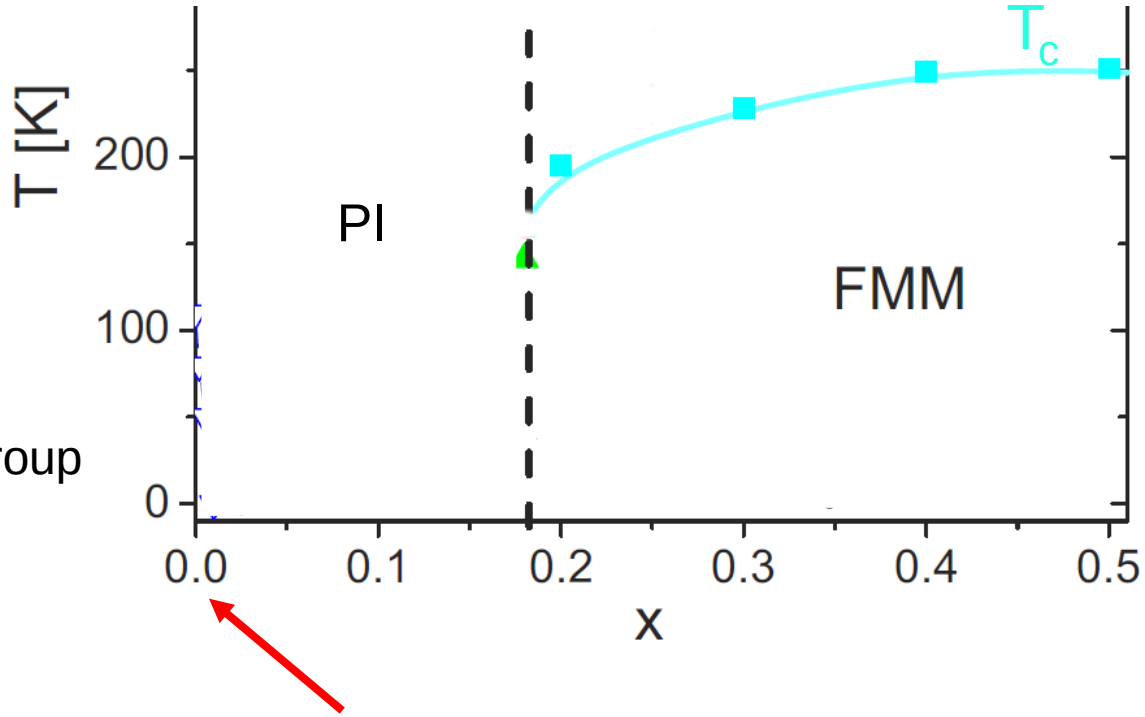
Bulk phase diagram of $La_{1-x}Sr_xCoO_3$



From C. Leighton

x = 0: trigonal $R\bar{3}c$ space group

From [2]



- Parent compound $LaCoO_3$ is a diamagnetic insulator (PI)

[1] J. Wu and C. Leighton, PRB **67**, 174408 (2003); [2] C. He *et al.*, PRB **76**, 014401 (2007); Raccah and Goodenough, JAP (1968); Senaris-Rodriguez *et al* JSSC (1995); Caciuffo *et al* PRB (1999)

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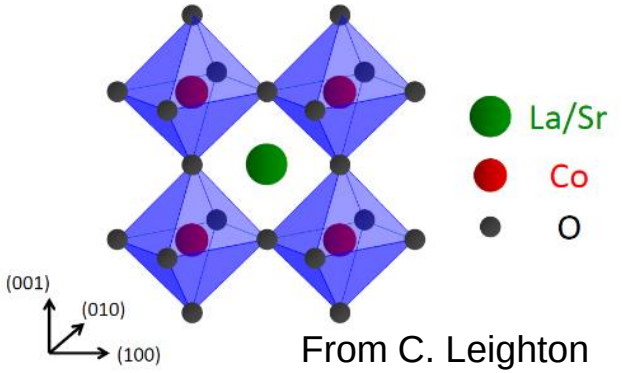
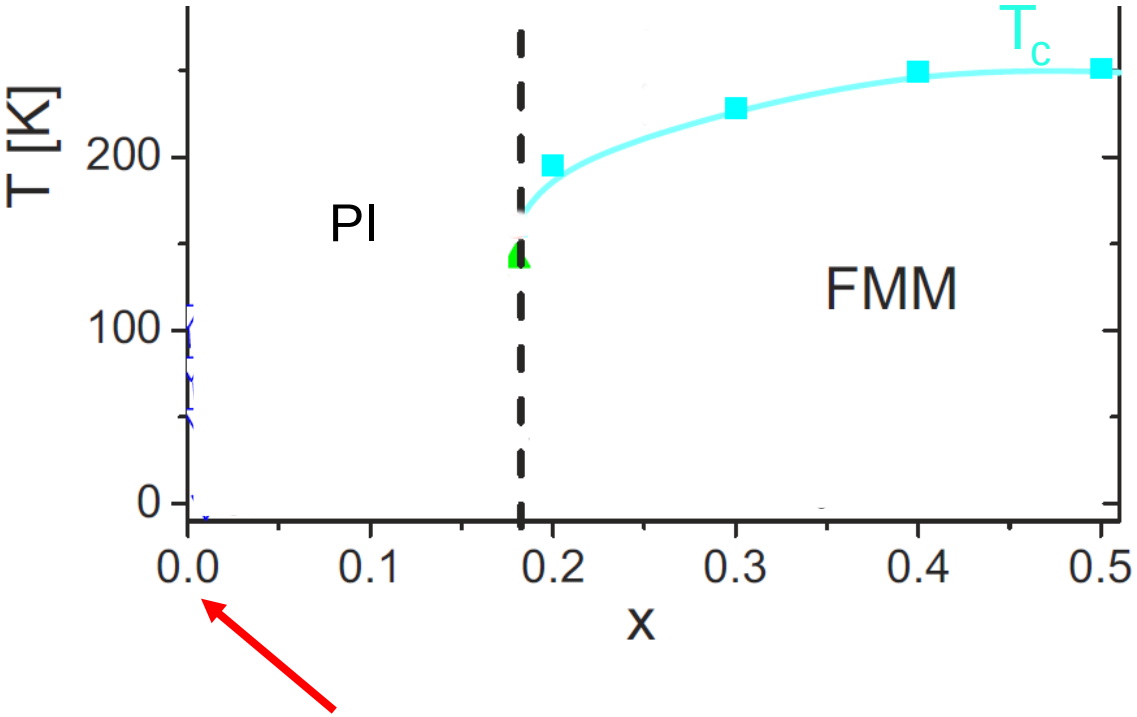
Bulk phase diagram of $La_{1-x}Sr_xCoO_3$



From C. Leighton

From [2]



- Spin state of Co^{3+}

e_g ——

t_{2g} ↑↓ ↑↓ ↑↓

Co^{3+} is $3d^6$

Co^{3+} LS (Low Spin)
S = 0

$\Delta_{CF} > J_H$

- Parent compound $LaCoO_3$ is a diamagnetic insulator (PI)

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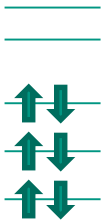
Bulk phase diagram of $La_{1-x}Sr_xCoO_3$

From [2]

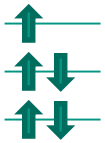
- Spin state of Co^{3+}



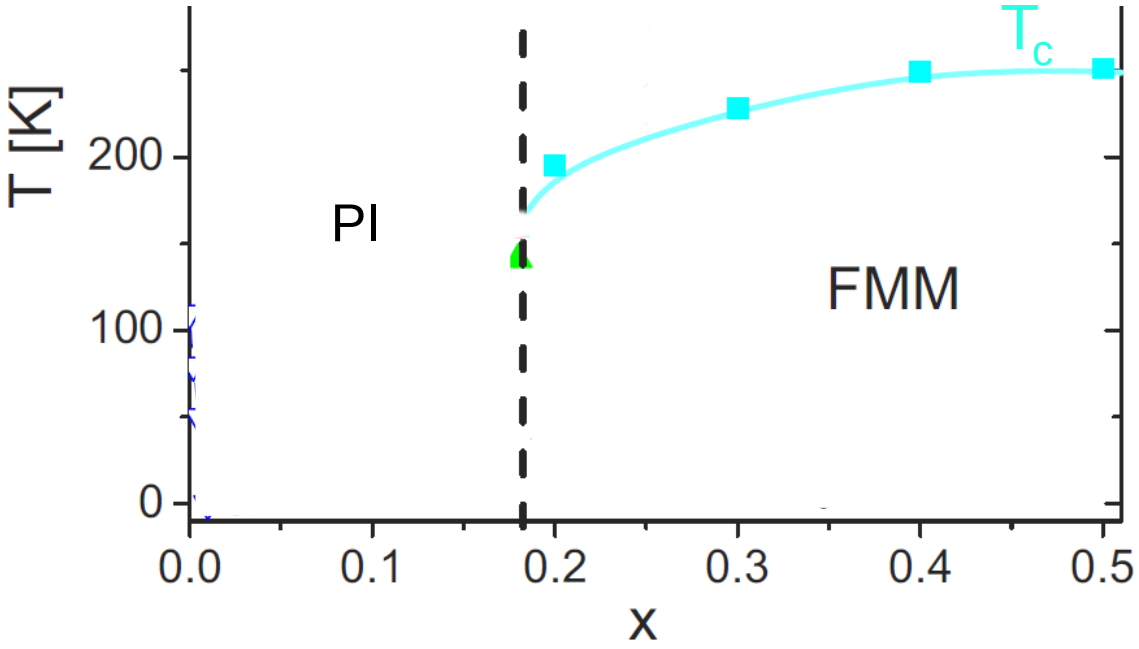
Co^{3+} is $3d^6$

Co^{3+} LS (Low Spin)
S = 0

- Spin state of Co^{4+}



Co^{4+} LS
S=1/2

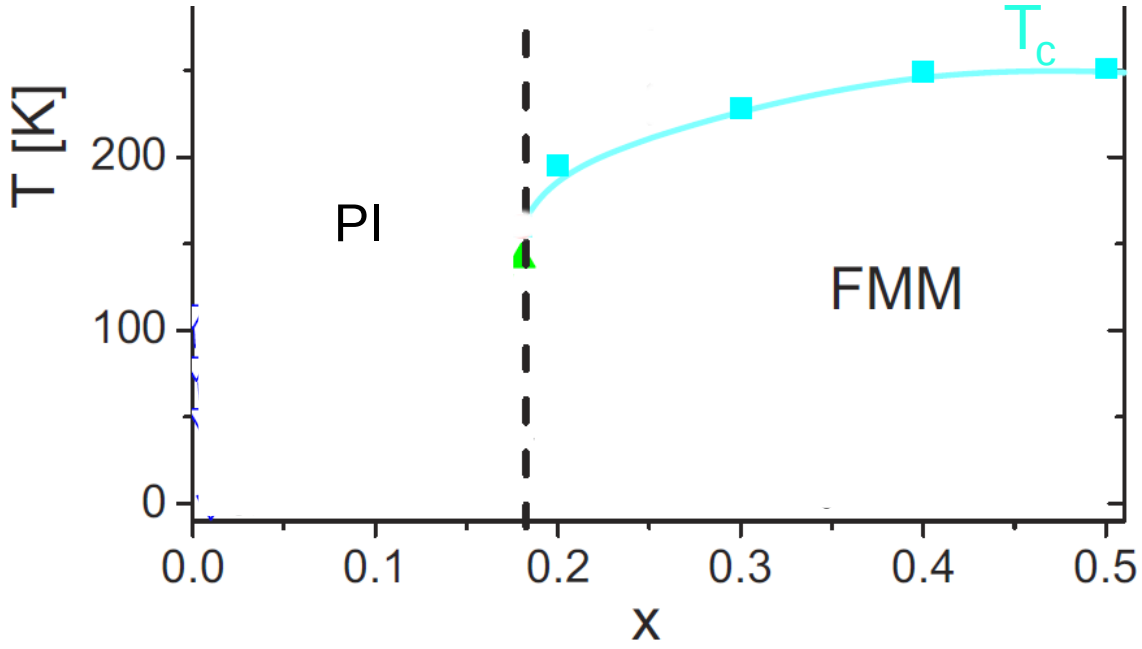


- Replace La^{3+} by Sr^{2+} ➡ changes Co^{3+} to Co^{4+}
- Hole doping and induces spin
- Fully doped compound $SrCoO_3$ is a ferromagnetic metal (FMM)

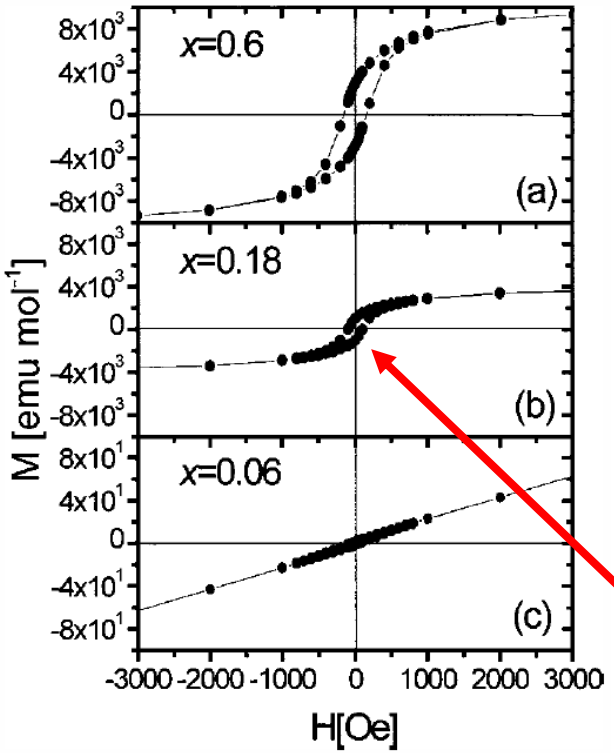
[1] J. Wu and C. Leighton, PRB **67**, 174408 (2003); [2] C. He *et al.*, PRB **76**, 014401 (2007).

Bulk phase diagram of $La_{1-x}Sr_xCoO_3$

From [2]



At T = 100 K



From [1]

- System becomes ferromagnetic at x_c=0.18

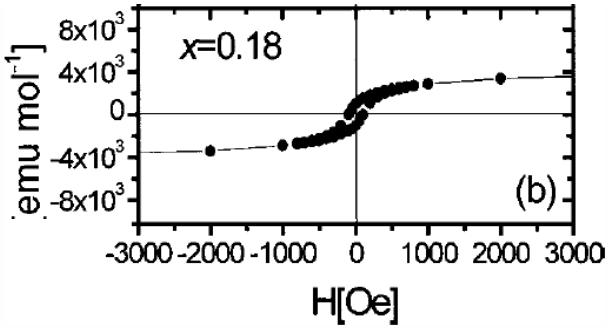
Hysteresis

[1] J. Wu and C. Leighton, PRB **67**, 174408 (2003); [2] C. He *et al.*, PRB **76**, 014401 (2007).

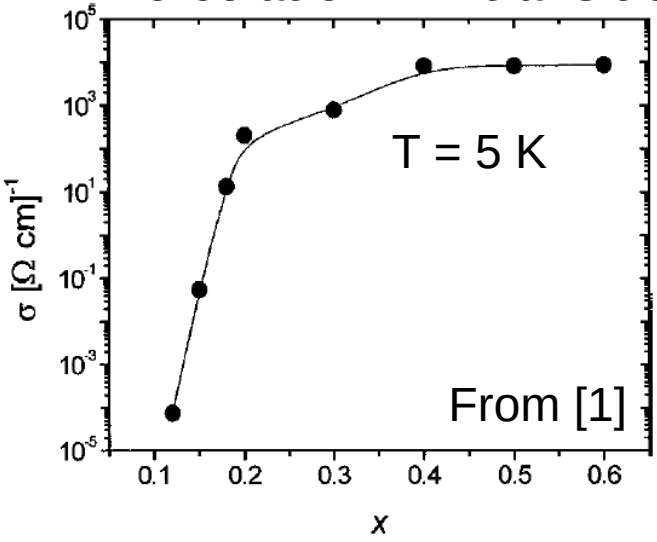
Bulk phase diagram of $La_{1-x}Sr_xCoO_3$

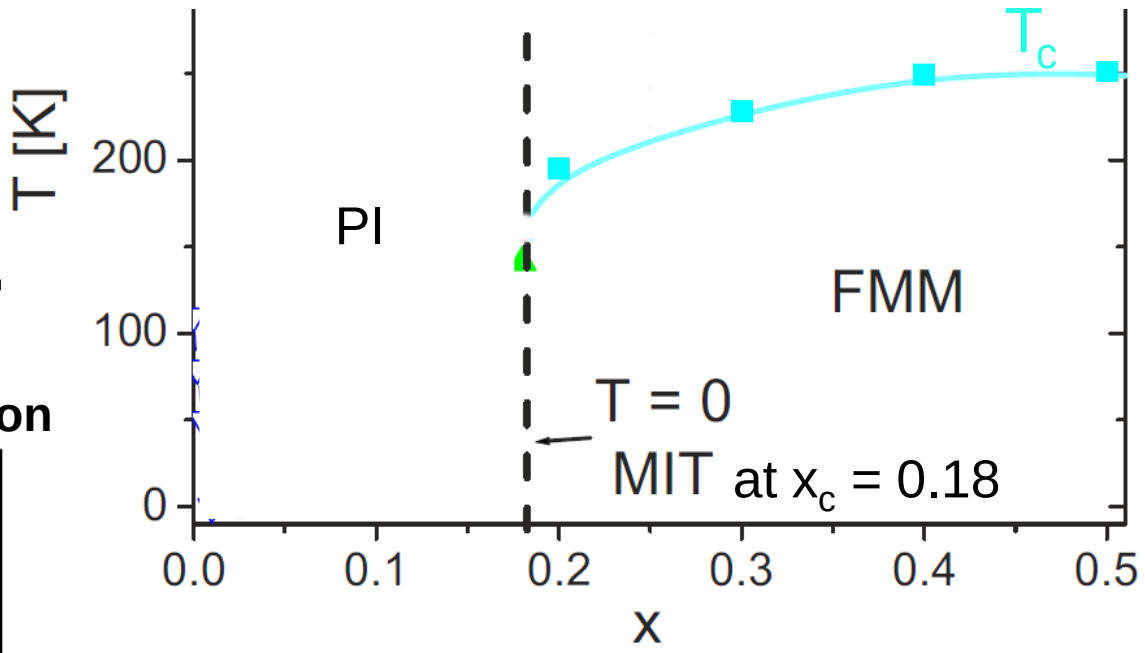
From [2]

FM phase transition



Percolation MIT transition





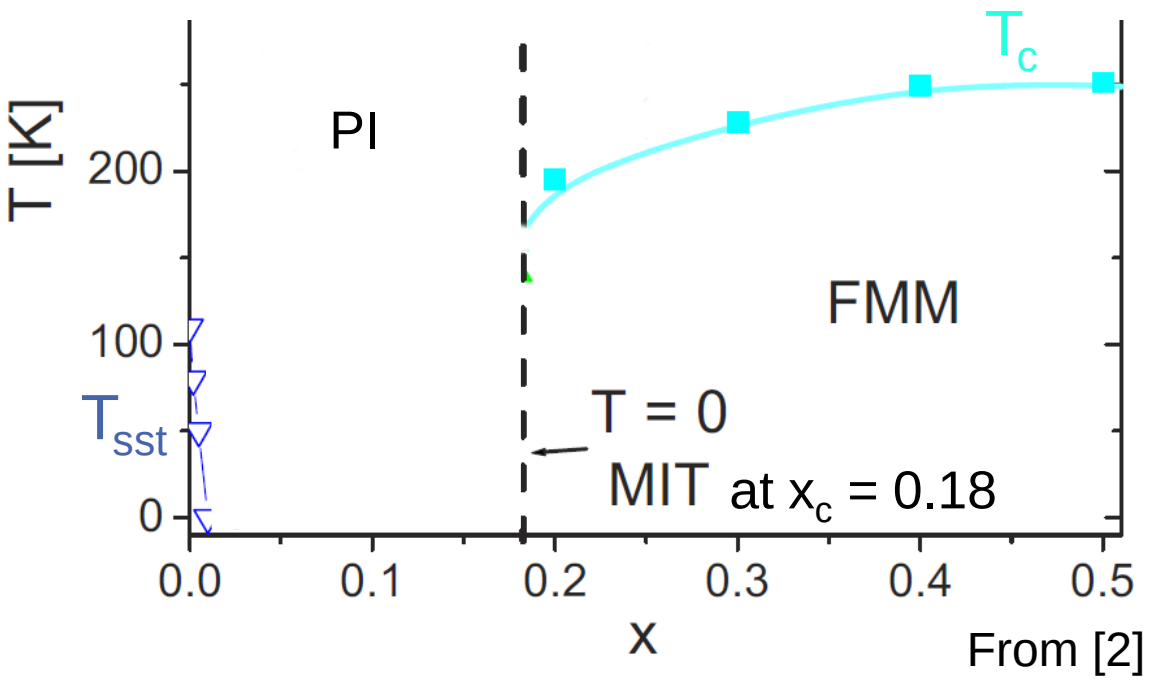
- System becomes ferromagnetic at x_c=0.18
- Metal-insulator transition at x_c = 0.18 via percolation

Ferromagnetic and MIT transition coincide

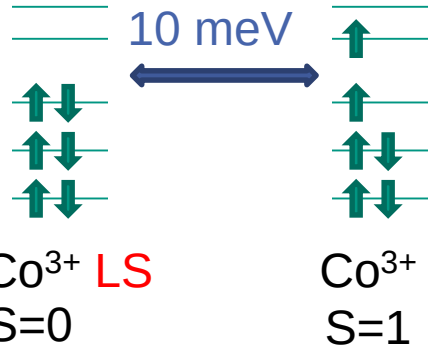
➡ Percolation mechanism? Role of spins?

[1] J. Wu and C. Leighton, PRB **67**, 174408 (2003); [2] C. He *et al.*, PRB **76**, 014401 (2007).

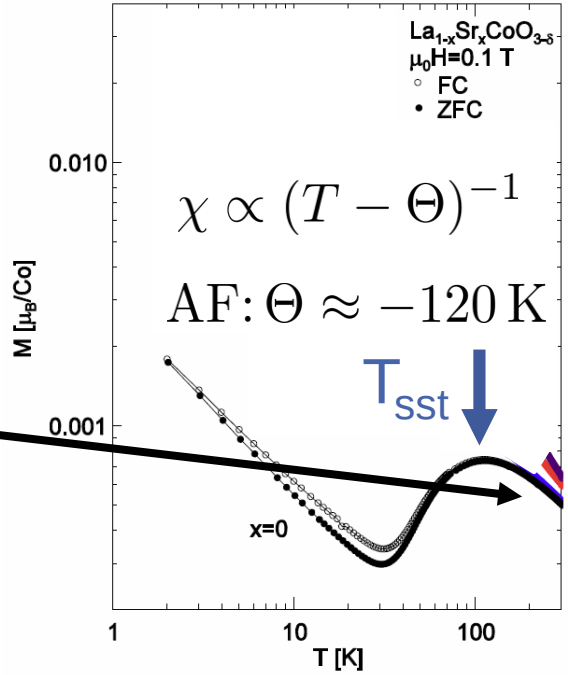
Spin state transitions of Co



- Spin states of Co^{3+}



- Crystal field splitting and Hund's coupling are comparable ➡ **Spin state transitions**



[1] J. Wu and C. Leighton, PRB **67**, 174408 (2003); [2] C. He *et al.*, PRB **76**, 014401 (2007).

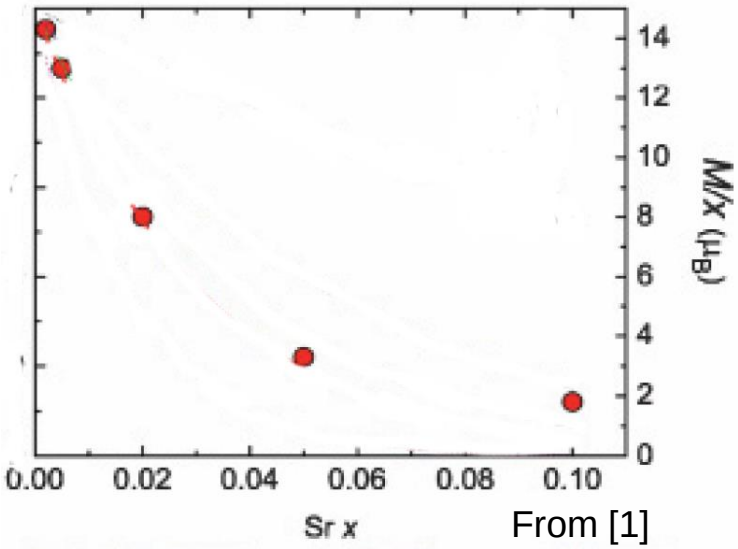
Spin polaron formation

- Small Sr doping results in large increase of susceptibility
- **Large magnetic moment per Sr^{2+}:**

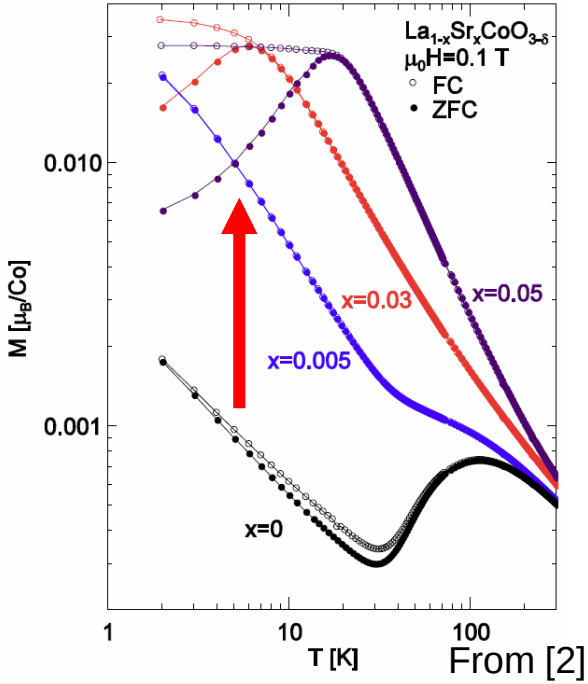
$M/x = 13\mu_B$ ➡ Spin polarons

Low spin states Co^{3+}/Co^{4+}

Co^{3+} LS S=0 Co^{4+} LS S=1/2



From [1]

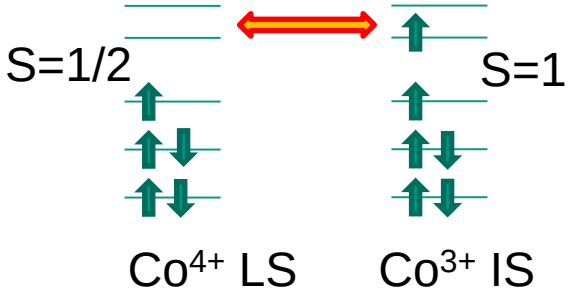


From [2]

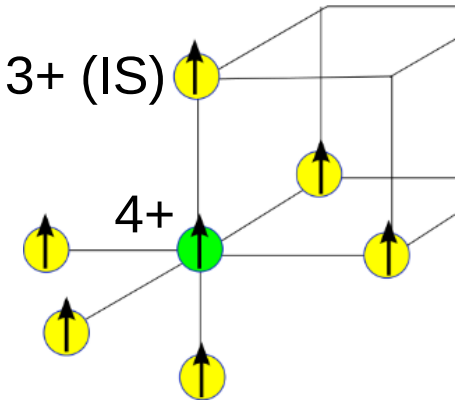
[1] A. Podlesnyak *et al.*, PRB **83**, 134430 (2011); [2] D. Phelan, PPO *et al.* (to be submitted).

Evidence for seven-site spin polarons

- **FM** double exchange between Co^{3+}/Co^{4+}

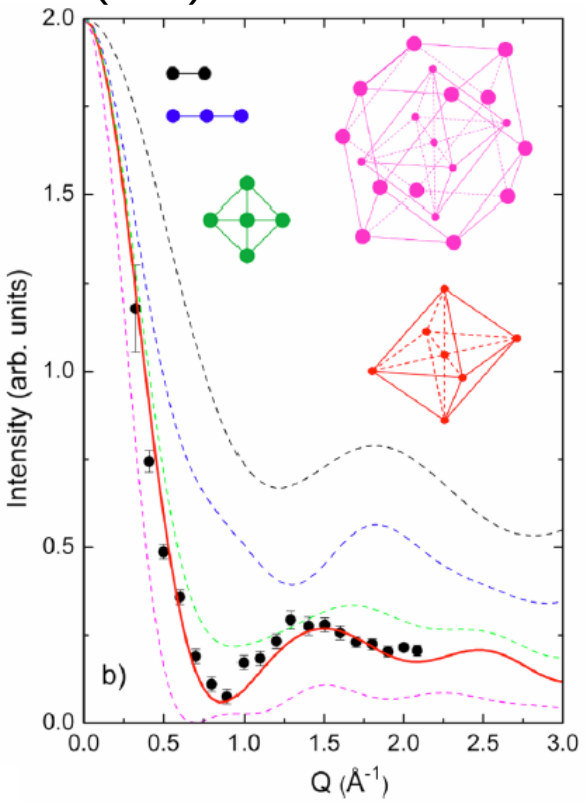


Leads to formation of **7-site spin polarons** at small doping x [1, 2, 3]



Total spin
S=13/2

Inelasatic neutron scattering (INS) form factor



From [2]

[1] A. Podlesnyak *at al.*, PRL **101**, 247603 (2008); [2] A. Podlesnyak *et al.*, PRB **83**, 134430 (2011); [3] D. Phelan, PPO *et al.* (to be submitted).

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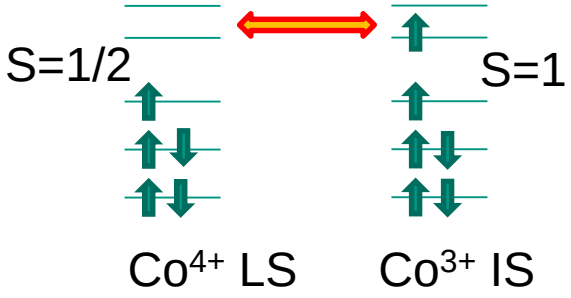
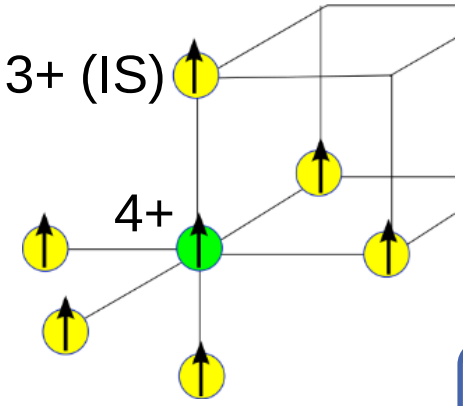
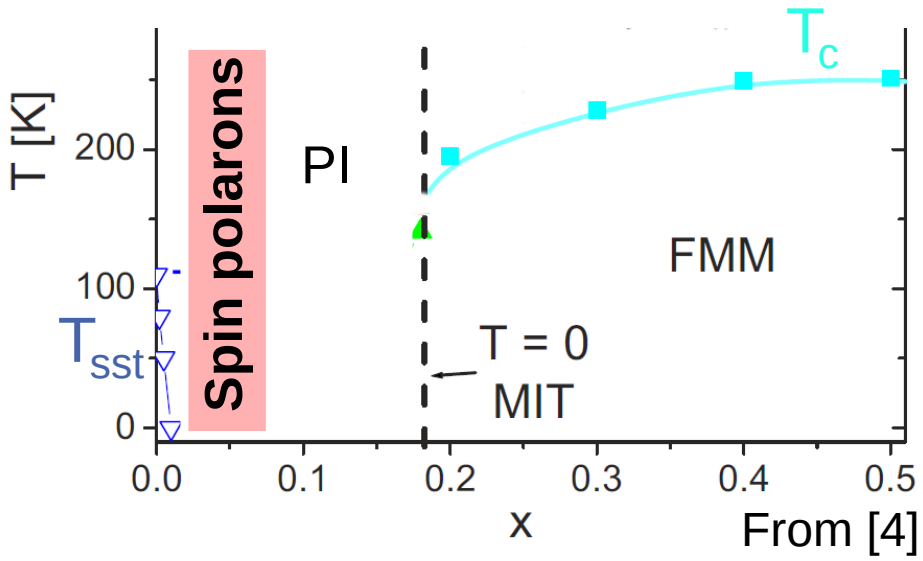
Spin polarons in the phase diagram of LSCO

- **FM** double exchange between Co^{3+}/Co^{4+}





Total spin
S=13/2



Do the polarons percolate at the FM transition?

[1] A. Podlesnyak *at al*., PRL **101**, 247603 (2008); [2] A. Podlesnyak *et al.*, PRB **83**, 134430 (2011); [3] D. Phelan, PPO *et al.* (to be submitted); [4] C. He *et al.*, PRB **76**, 014401 (2007).

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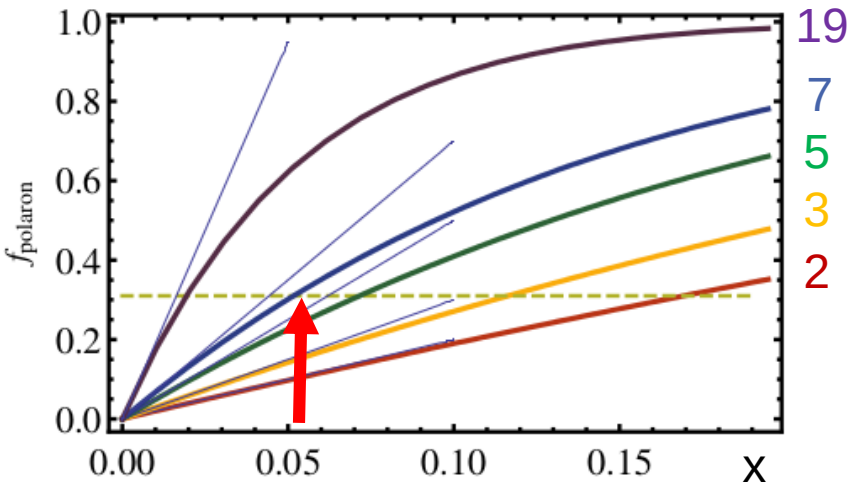
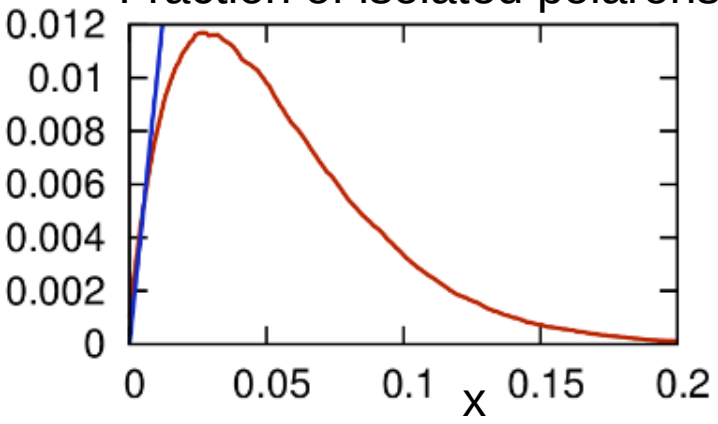
Seven-site spin polarons interactions

- 7-site polarons connect at x = 0.05
- FM percolation of polarons expected. Is it observed?

Fraction of polaronic sites



Fraction of isolated polarons



Interaction/percolation of polarons important for x > 0.05

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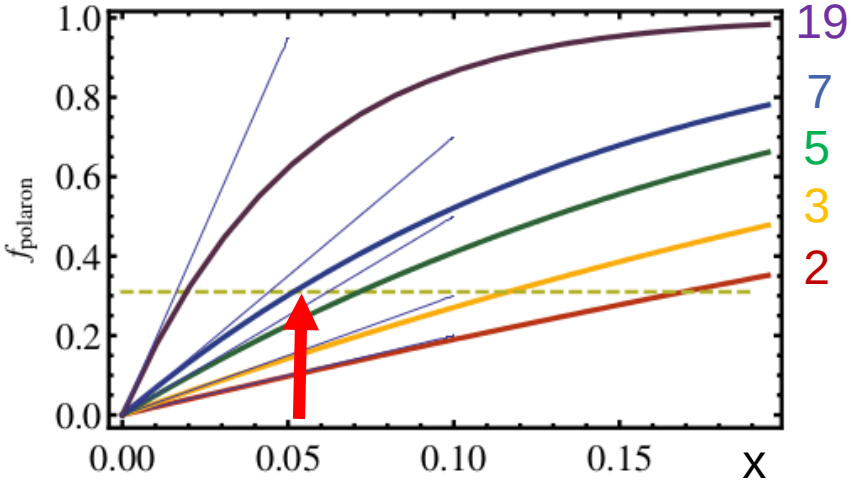
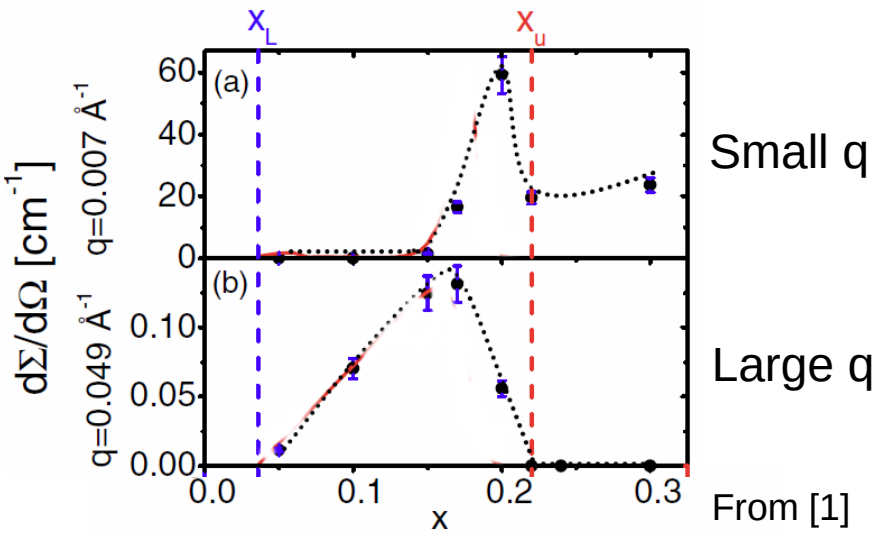
Spin-glass formation instead of percolation of polarons

- 7-site polarons connect at x = 0.05
- FM percolation of polarons expected, but not observed? NO!
- Instead: only short-range ferromagnetic correlations observed and spin-cluster glass forms

Fraction of polaronic sites



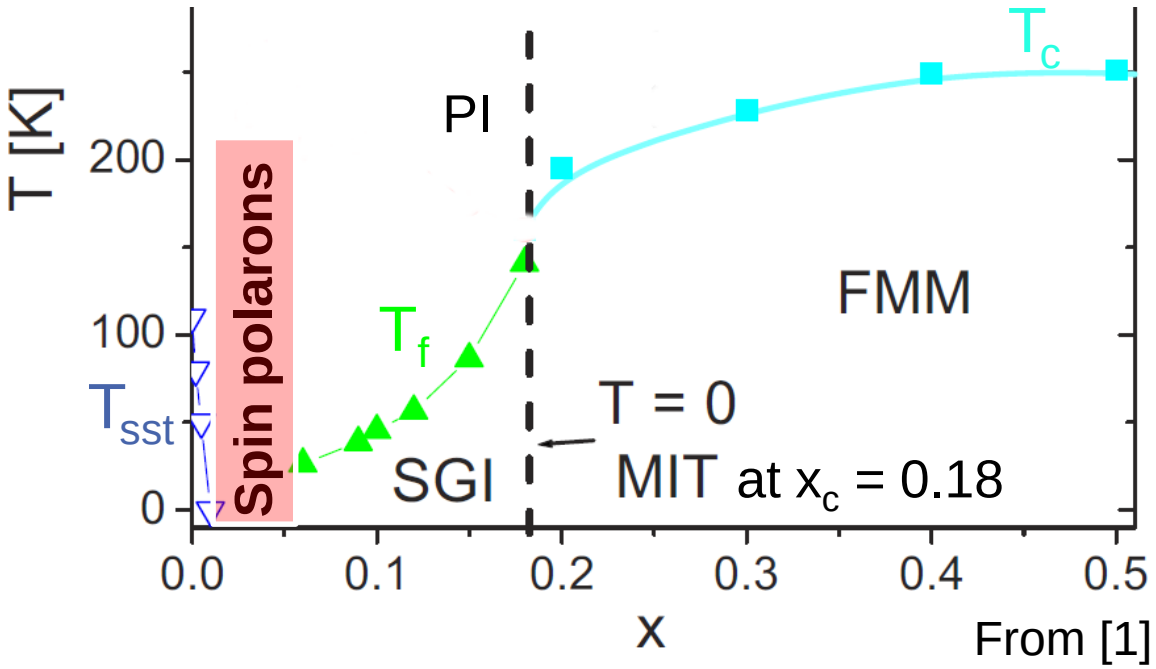
FM only develops at much larger x = 0.18



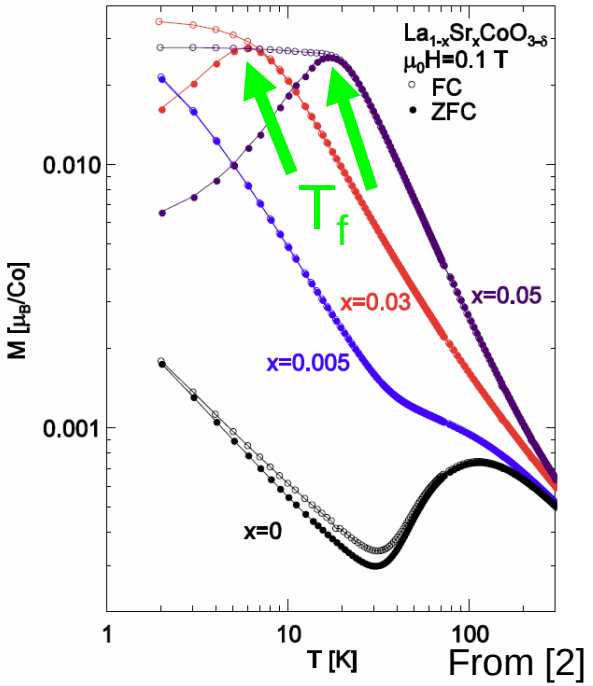
Small angle neutron scattering

[1] C. He *et al.*, EPL **87**, 27006 (2009).

Transition from isolated polarons to frustrated clusters



- Spin freezing appears at x=0.05
- Spin cluster glass insulating (SGI) behavior



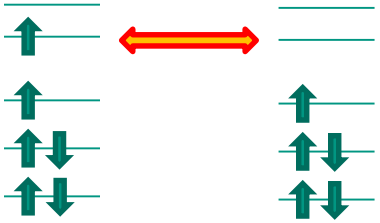
[1] C. He *et al.*, PRB **76**, 014401 (2007); [2] D. Phelan, PPO *et al.* (to be submitted).

Mechanism of polaronic frustration

We propose that this follows from competition of

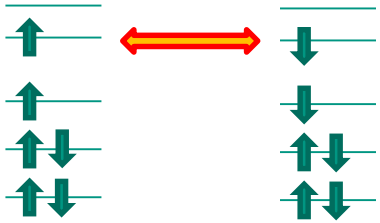
- **FM** double exchange between Co^{4+} /Co^{3+}
- **AFM** super-exchange between Co^{3+}/Co^{3+}

- Double exchange Co^{3+}/Co^{4+}

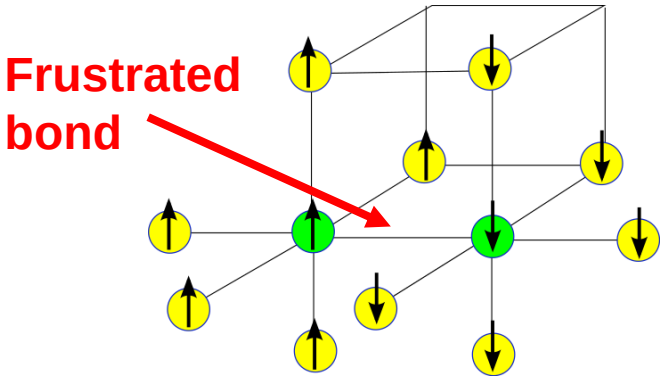


Co^{3+} IS Co^{4+} LS

- Super-exchange Co^{3+}/Co^{3+}



Co^{3+} IS Co^{3+} IS



→ **Frustration of polarons**

[1] C. He *et al.*, PRB **76**, 014401 (2007).

Theory of polaron frustration:
Modeling and numerical Monte-Carlo calculation

Disordered Ising spin model

- Place Co^{4+} Ising spins $\boldsymbol{S}^{(4)}$ on fraction x of random sites in 3D cubic lattice
- Add Co^{3+} Ising spins $\boldsymbol{S}^{(3)}$ on free polaronic nearest-neighbor sites
- Nearest-neighbor spin-spin interactions described by the Hamiltonian

$$H = -|J_{44}| \sum_{\langle i,j \rangle_{44}} \boldsymbol{S}_i^{(4)} \cdot \boldsymbol{S}_j^{(4)} - |J_{34}| \sum_{\langle i,j \rangle_{34}} \boldsymbol{S}_i^{(3)} \cdot \boldsymbol{S}_j^{(4)} + J_{33} \sum_{\langle i,j \rangle_{33}} \boldsymbol{S}_i^{(3)} \cdot \boldsymbol{S}_j^{(3)}$$

- FM $J_{44} < 0$: $SrCoO_3$ is ferromagnetic

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Disordered Ising spin model

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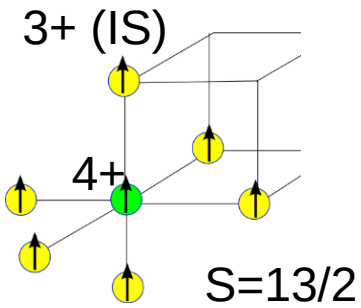
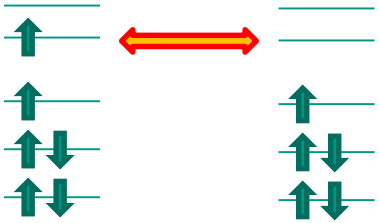
- FM $J_{44} < 0$: $SrCoO_3$ is ferromagnetic
- FM $J_{34} < 0$: ferromagnetic spin polaron due to double-exchange



- Double exchange Co^{3+}/Co^{4+}



Co^{3+} LS
S=0

Co^{4+} LS
S=1/2

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Disordered Ising spin model

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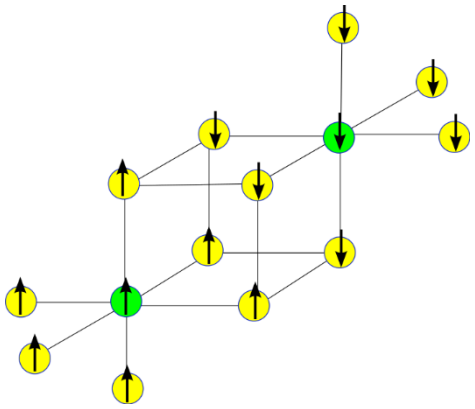
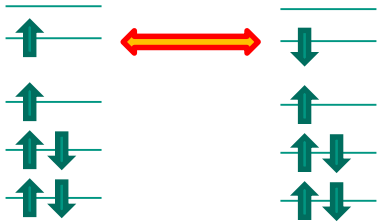
- FM $J_{44} < 0$: $SrCoO_3$ is ferromagnetic
- FM $J_{34} < 0$: ferromagnetic spin polaron due to double exchange
- AF $J_{33} > 0$: negative Curie temperature $\theta < 0$ in $LaCoO_3$



- Super-exchange Co^{3+}/Co^{3+}



Co^{3+} IS S=1

Co^{4+} IS S=1

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Disordered spin model

$$H = -|J_{44}| \sum_{\langle i,j \rangle_{44}} \boldsymbol{S}_i^{(4)} \cdot \boldsymbol{S}_j^{(4)} - |J_{34}| \sum_{\langle i,j \rangle_{34}} \boldsymbol{S}_i^{(3)} \cdot \boldsymbol{S}_j^{(4)} + J_{33} \sum_{\langle i,j \rangle_{33}} \boldsymbol{S}_i^{(3)} \cdot \boldsymbol{S}_j^{(3)}$$

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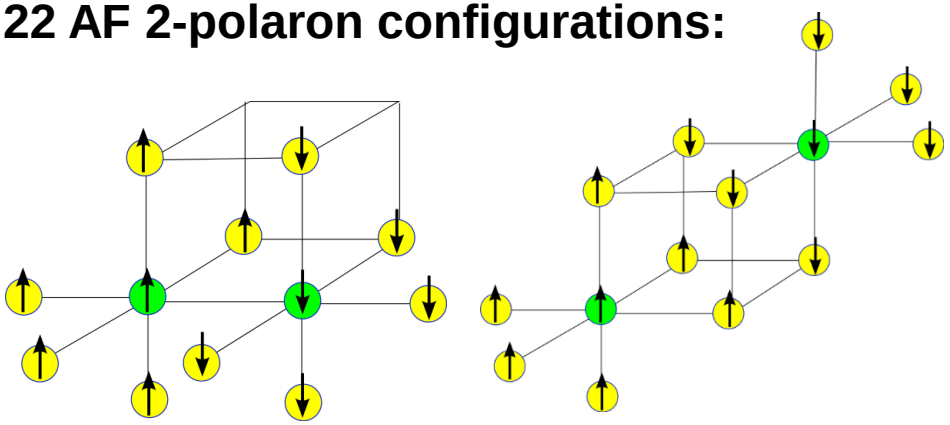
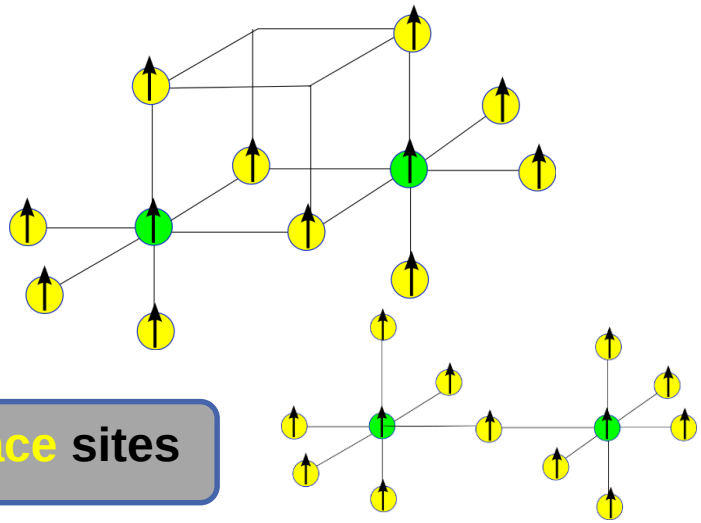
- AF $J_{33} > 0$: negative Curie temperature $\theta < 0$ in $LaCoO_3$

22 AF 2-polaron configurations:



18 FM 2-polaron configurations:

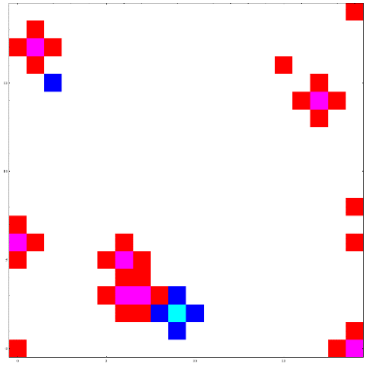


Competition of interaction b/w core and surface sites

Snapshots of spin configurations in Monte-Carlo simulation

- Classical Monte-Carlo simulation of spins at low temperatures
- Experimentally realistic spin exchange $J_{44} = -1, J_{34} = -1, J_{33} = 0.32$
- Blue: $S = -1$, Red: $S = +1$. Light colors (bottom row) are core sites.

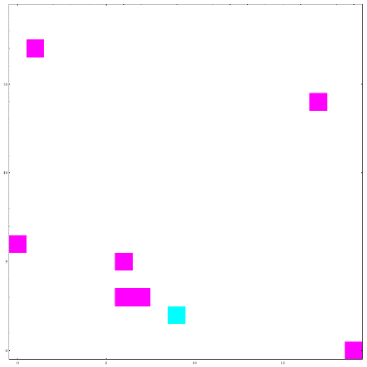
x = 0.005



2D cuts through 3D system with L=20, temperature $T = |J_{44}|/4$

Isolated FM polarons

AF interaction between surface Co^{3+}/Co^{3+} sites



Only core sites shown for comparison

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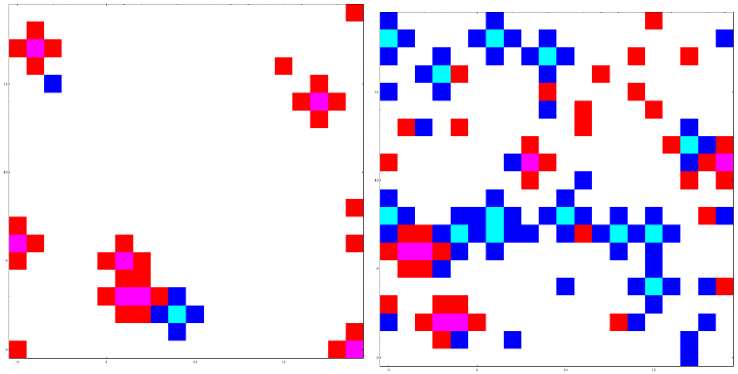
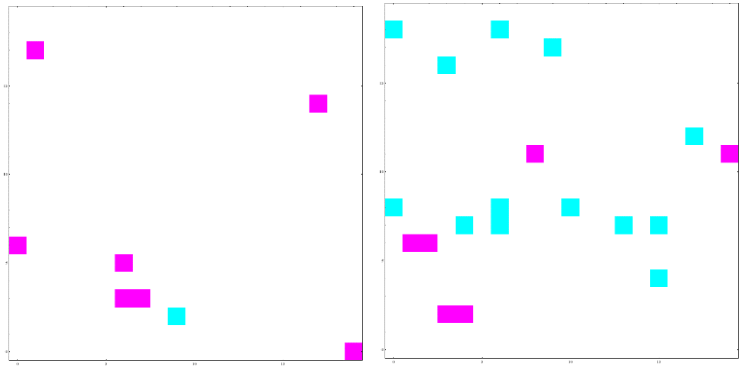
Snapshots of spin configurations

- Classical Monte-Carlo simulation of spins at low temperatures
- Blue: $S = -1$, Red: $S = +1$. Light colors (bottom row) are core sites. .

x = 0.005 x = 0.05





Percolation of polarons would occur if only FM interactions were present.

Distribution of clusters with spin S

➡ Freezing into cluster glass state.

Core sites still very diluted.

$$J_{44} = -1, J_{34} = -1, J_{33} = 0.32$$

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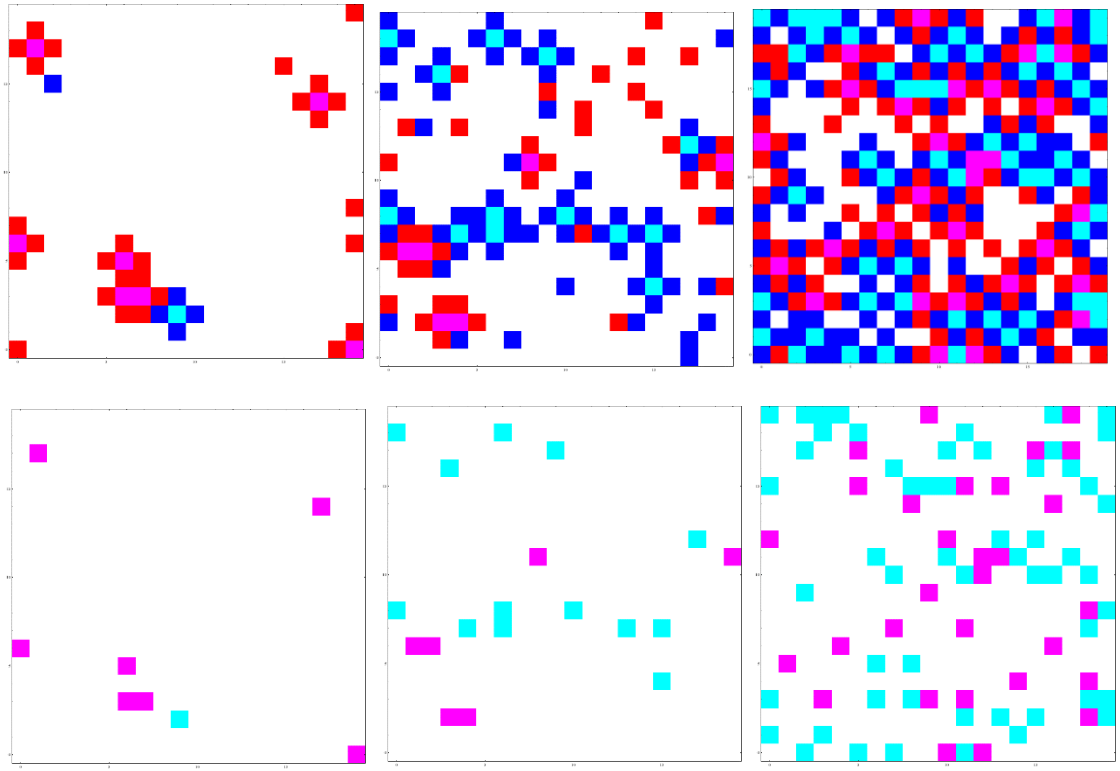
Snapshots of spin configurations

- 2D cuts through 3D system with L=10
- Blue: $S = -1$, Red: $S = +1$. Light colors (bottom row) are core sites.

x = 0.005 x = 0.05 x = 0.2



FM phase transition via percolation of macroscopic FM cluster

$$J_{44} = -1, J_{34} = -1, J_{33} = 0.32$$

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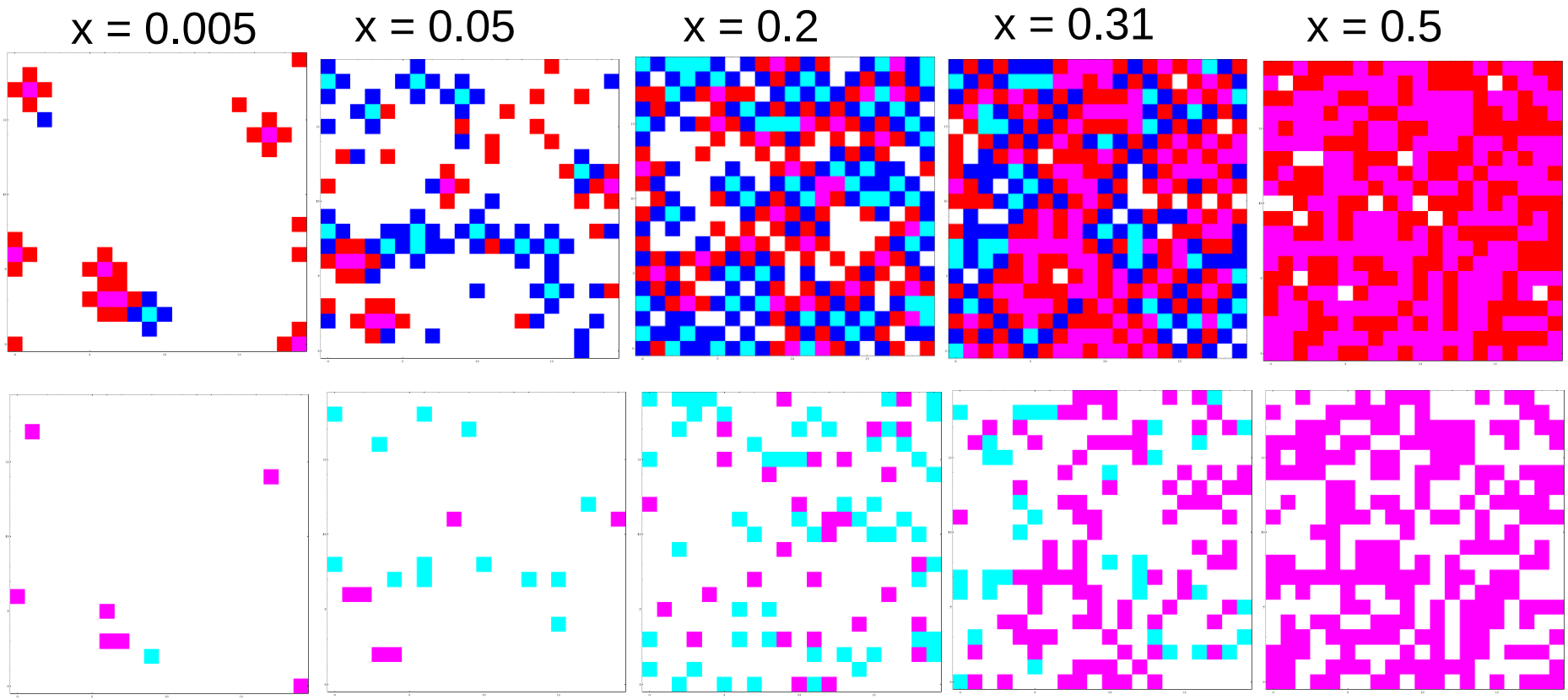
Snapshots of spin configurations

- 2D cuts through 3D system with L=10
- Blue: $S = -1$, Red: $S = +1$. Light colors (bottom row) are core sites.



$$J_{44} = -1, J_{34} = -1, J_{33} = 0.32$$

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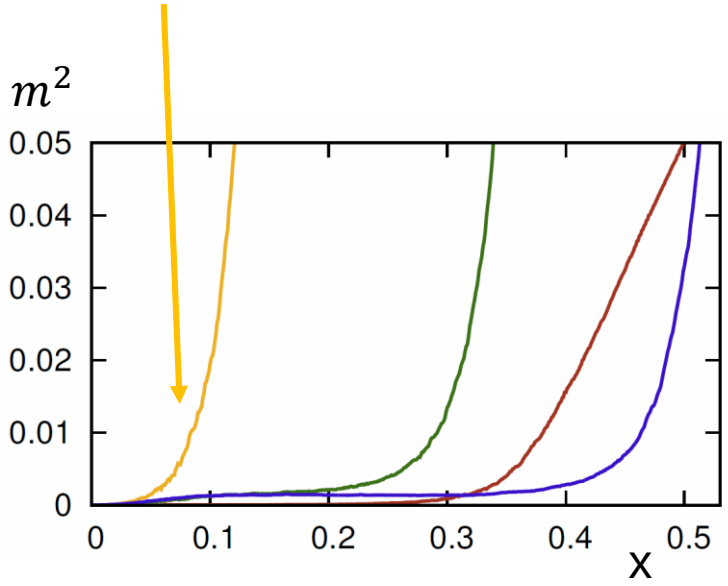
Percolation threshold depends on frustration

- Purely FM interactions: polarons percolate at $x_c = 0.05$

$$J_{44} = J_{34} = -1, J_{33} = 0$$



MC simulations: performed at different finite T to be representative of T=0 ground state.

System size N = 10x10x10; 500 disorder realizations.

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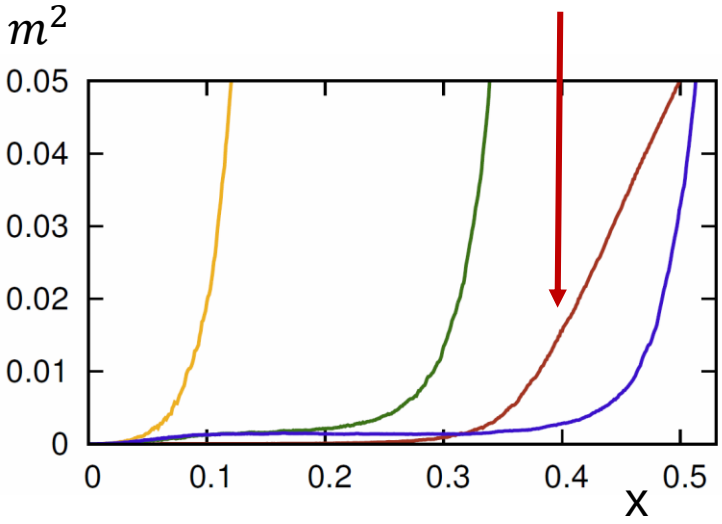
Percolation without polarons

- In absence of polarons: site percolation of spins at $x_c = 0.31$

$$J_{44} = -1, J_{34} = J_{33} = 0$$



MC simulations: performed at different finite T to be representative of T=0 ground state.

System size N = 10x10x10; 500 disorder realizations.

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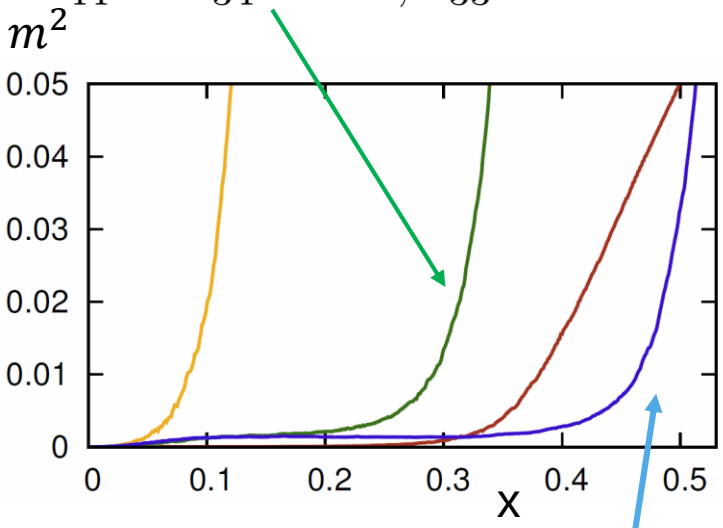
Percolation of frustrated polarons

- Percolation delayed due to AF interactions of surface Co^{3+}/Co^{3+} sites
- FM interaction of core Co^{4+}/Co^{4+} pairs wins at large x
- Percolation of frustrated polarons as $x_c = 0.18$ for $J_{33}/J_{34} = 0.3$

Experimentally realistic frustration

$J_{44} = J_{34} = -1, J_{33} = 0.32$



Strong frustration

$J_{44} = J_{34} = J_{33} = -1$

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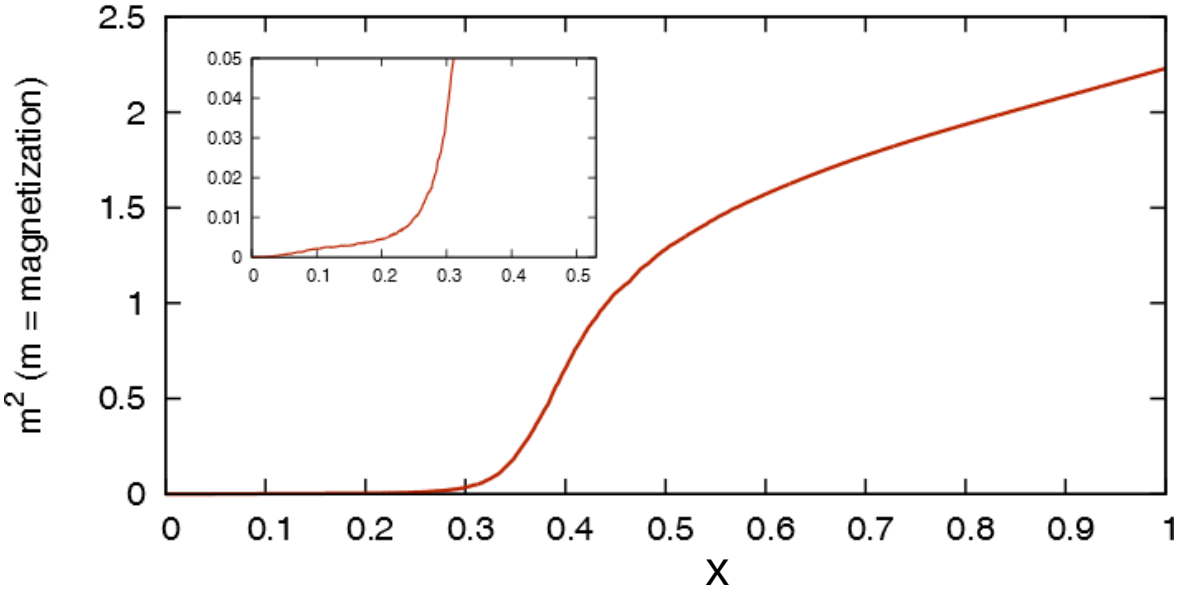
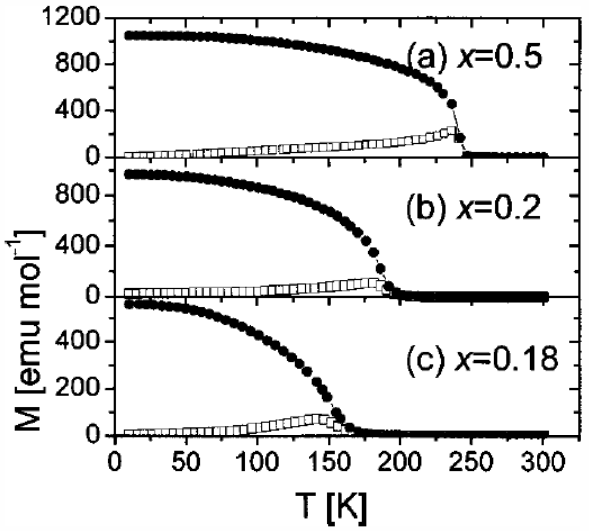
Magnetization

- Saturation magnetization as a function of doping for $|J_{33}/J_{44}| \approx 0.32$

Simulation for experimentally realistic frustration



Experiment (Wu, Leighton)

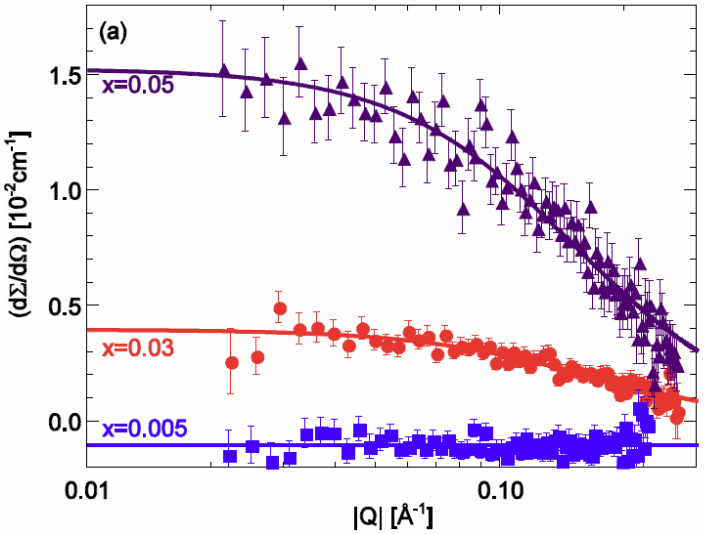


Qualitative agreement with experiment for realistic values of spin exchange constants.

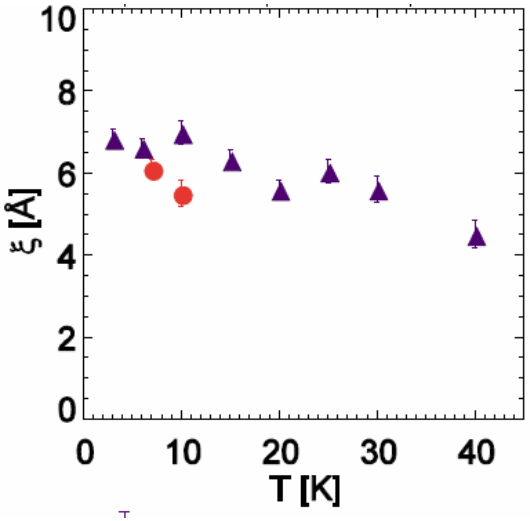
[1] J. Wu and C. Leighton, PRB **67**, 174408 (2003).

Small angle neutron scattering (SANS)

- Neutron scattering cross section integrated over energies $\approx 1\ meV$



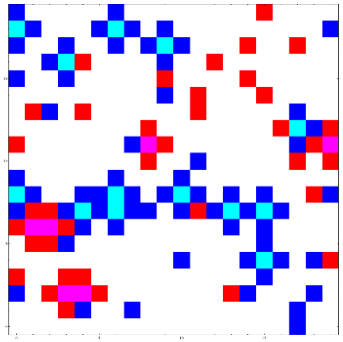
From [1]



From [1]

- Correlation length about two unit cells even for x=0.05 !
- 7-site polarons seed state of frozen FM clusters [1]

x=0.05



Compares well with our picture of frustrated polarons!

[1] D. Phelan, PPO, R. Fernandes, …, C. Leighton (to be submitted).

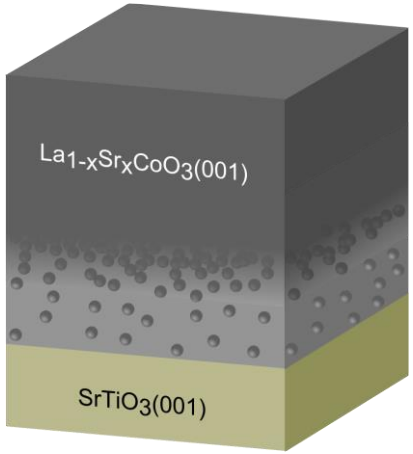
Thin films of LSCO: percolation via combined chemical and electrostatic doping

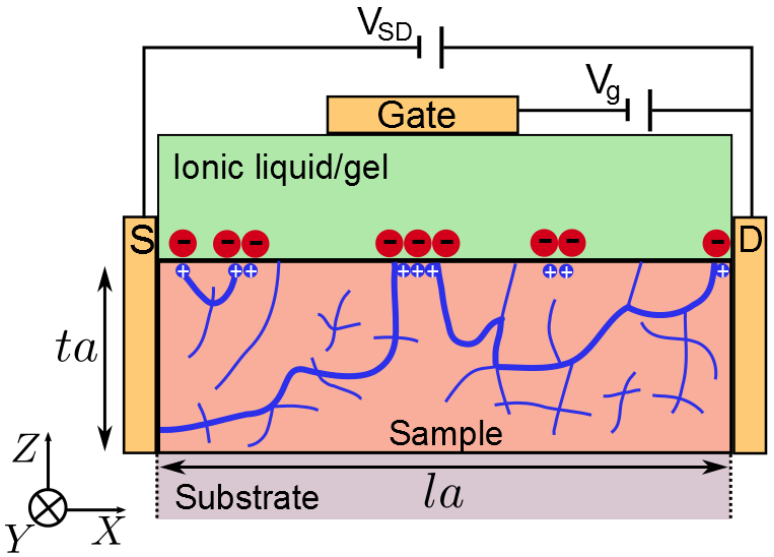
PPO, R. M. Fernandes, J. Walter, C. Leighton, B. I. Shklovskii, arXiv:1605.03463 (2016).

Thin films of $La_{1-x}Sr_xCoO_3$

- Goal: Control magnetic and electric properties electrostatically
- In LSCO/STO: carrier densities of $n > 10^{15}\ cm^{-2}$ must be tuned

➡ To reach percolation transition requires combined chemical and electrostatic doping

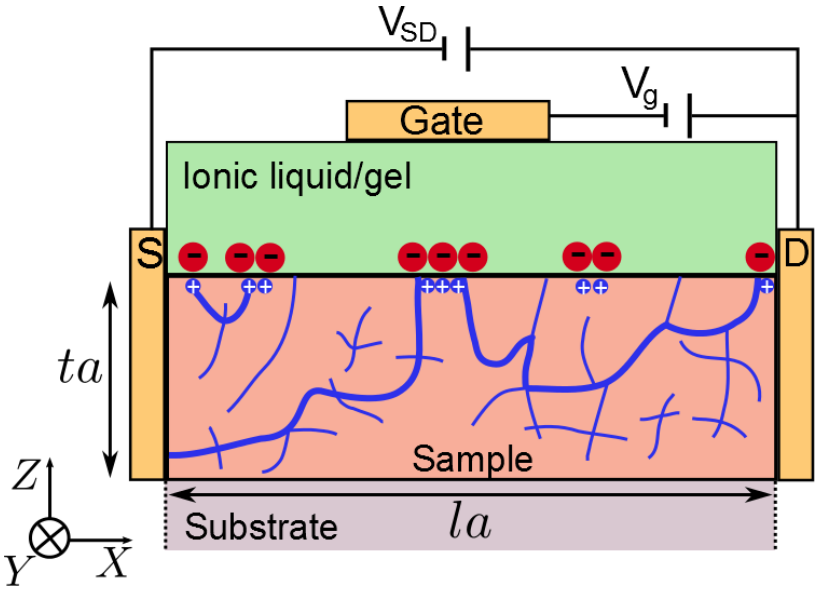




Predict amount of surface charge required for given chemical doping level x to reach ferromagnetic state.

[1] K. H. Lee *et al.*, Adv. Mater. **24**, 4457 (2012); [2] A. M. Goldman Annu. Rev. Mater. Res. **44**, 45 (2014); M. A. Torija *et al.*, Adv. Mat. **23**, 2711 (2011).

Setup and model for electrostatic gating



- Chemical doping level x in the bulk
- Electrostatic doping only affects top surface layer

Total (top) surface charge density

$$s = x + \Delta s$$

- Sample thickness $2 \leq t/a \leq L/a$
- Geometry $L \times L \times ta$

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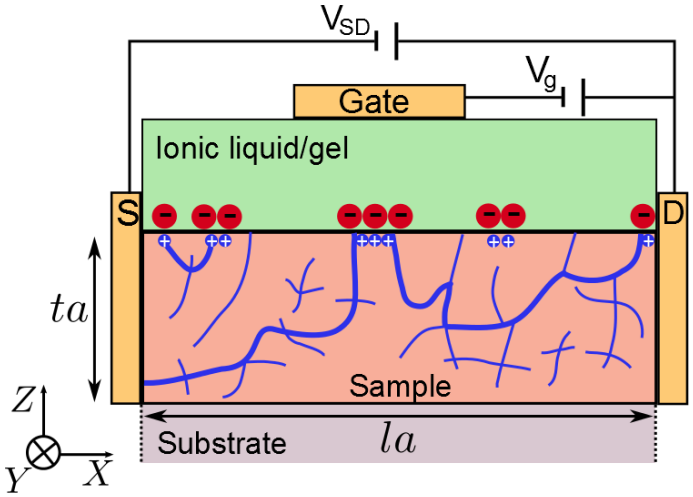
Added surface charge at percolation



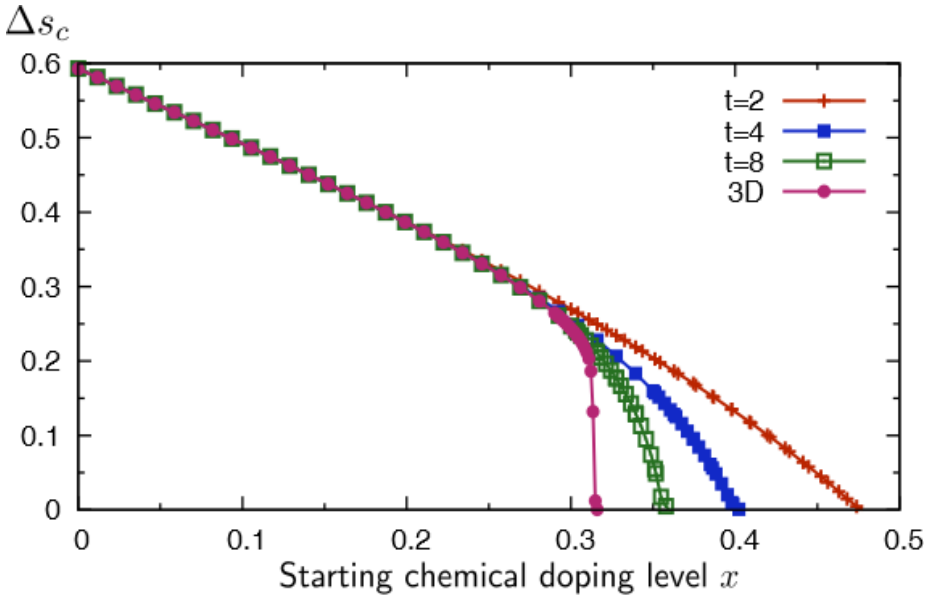
- Chemical doping level x in the bulk
- Electrostatic doping only affects top surface layer

Total (top) surface charge density

$$s = x + \Delta s$$

Added surface charge at percolation threshold Δs_c:

- 2D ($x = 0$): $s_c = \Delta s_c = 0.59$
- Only chemical ($x \geq x_c(t)$): $\Delta s_c = 0$



We employed numerical method by Newman and Ziff, PRL (2001).

[1] PPO, R. Fernandes, J. Walter, C. Leighton, B. Shklovskii, arXiv:1605.03463 (2016).

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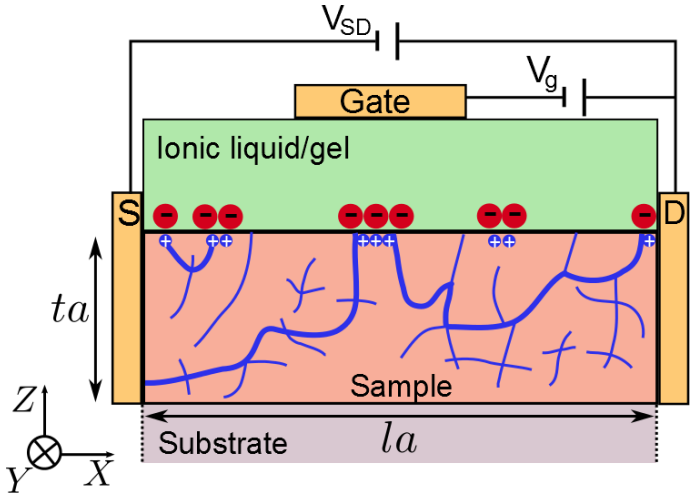
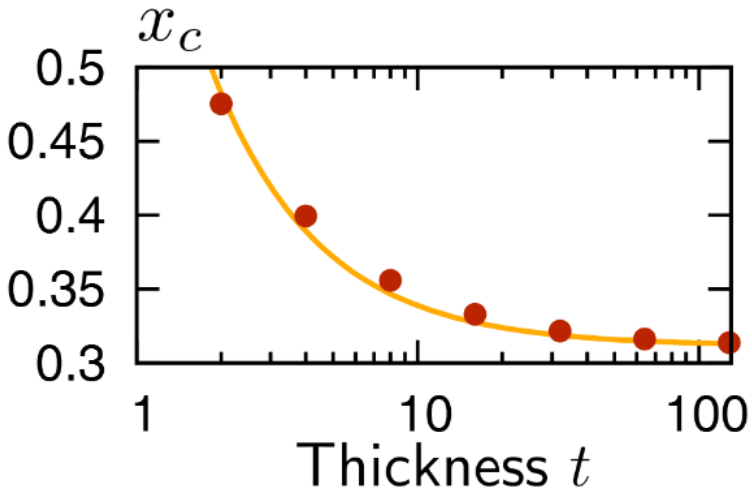
Added surface charge at percolation

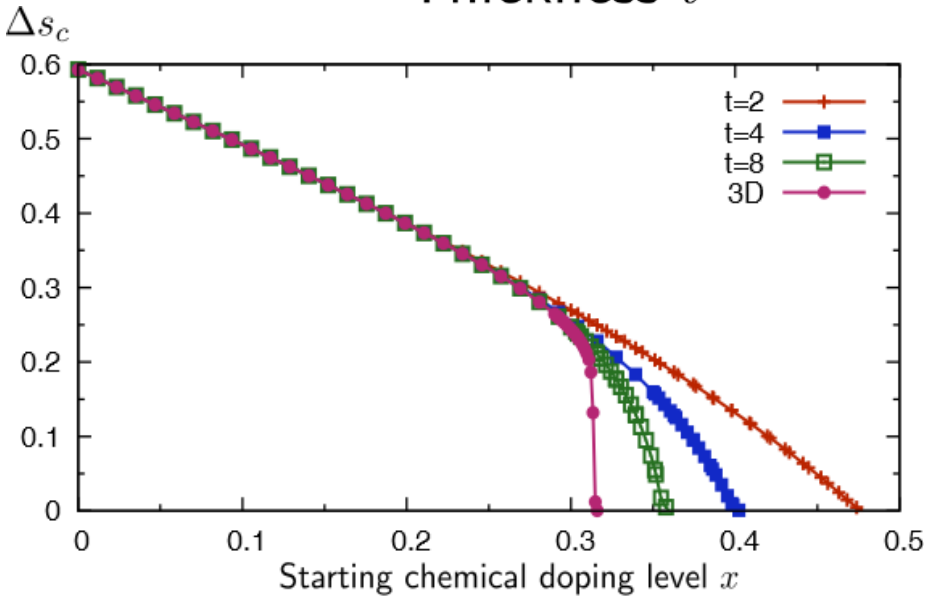




Added surface charge at percolation threshold Δs_c:

- 2D ($x = 0$): $s_c = \Delta s_c = 0.59$
- Only chemical ($x \geq x_c(t)$): $\Delta s_c = 0$

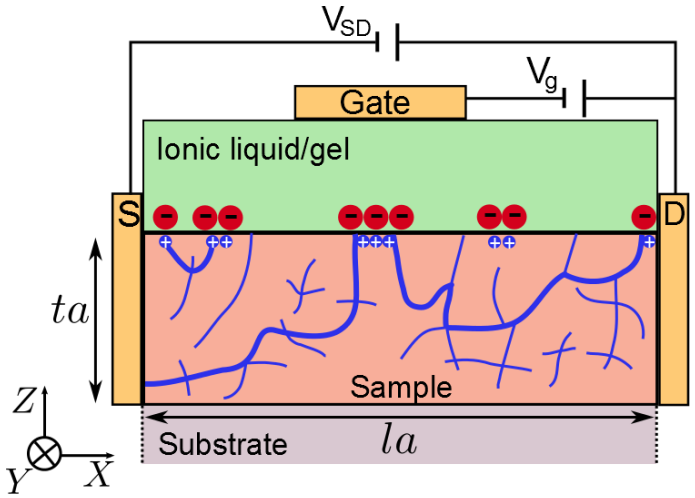
$$x_c(t) = x_c^{3D} + c_3 t^{-1/\nu}$$



We employed numerical method by Newman and Ziff, PRL (2001).

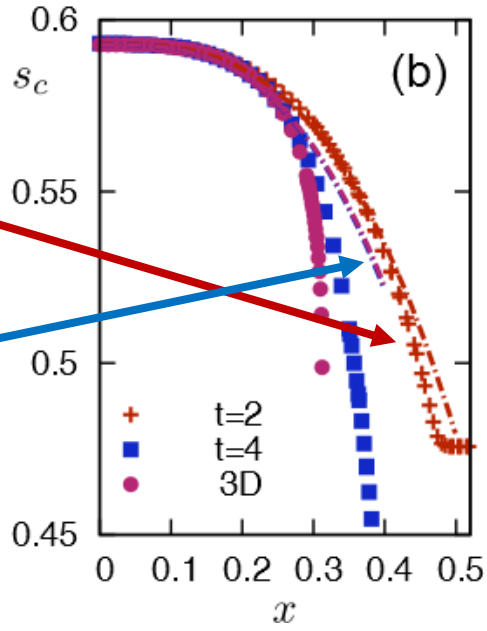
[1] PPO, R. Fernandes, J. Walter, C. Leighton, B. Shklovskii, arXiv:1605.03463 (2016).

(i): Bulk assisted surface percolation



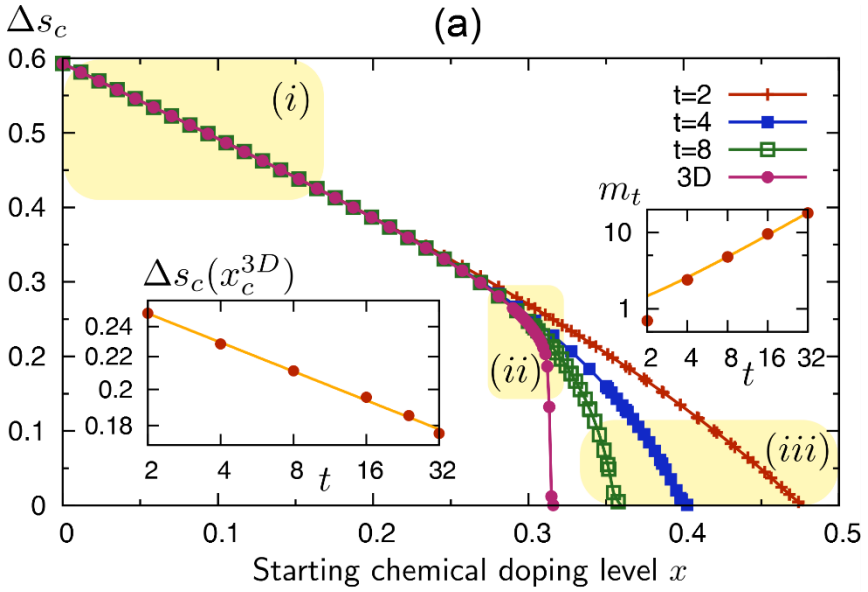
- Fit works all the way to x_c for $t = 2$
- Deviates for $t > 2$ at $x < x_c$

$$s = x + \Delta s$$



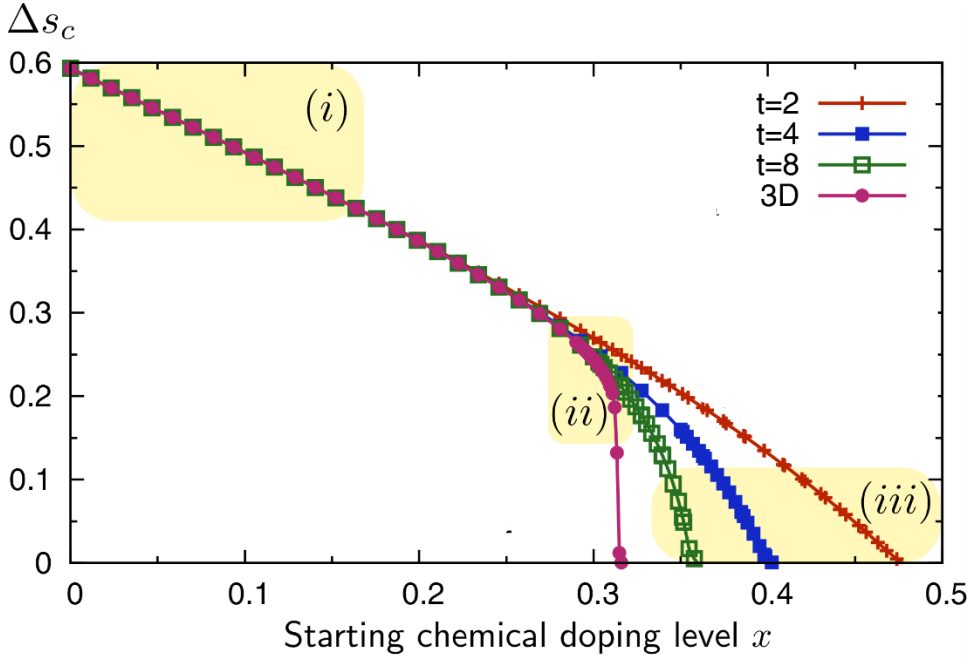
Added surface charge at percolation threshold Δs_c:

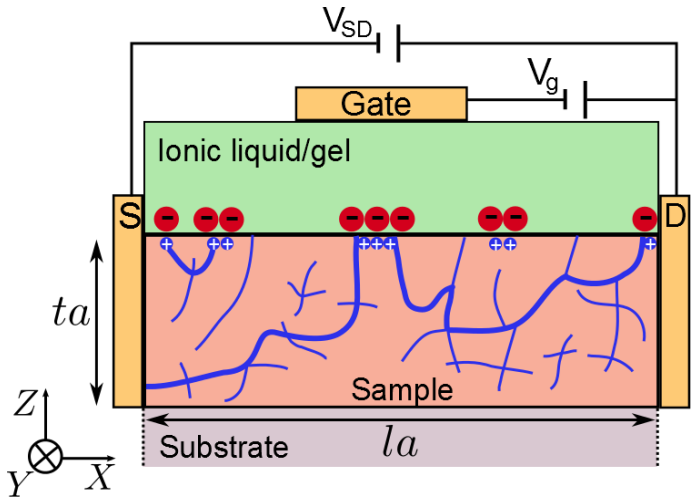
- 2D ($x = 0$): $s_c = \Delta s_c = 0.59$
- Pure chemical ($x \geq x_c(t)$): $\Delta s_c = 0$
- (i) Small x: $\Delta s_c = 0.59 - x - bx^3$
- Bulk bridges made of three sites



[1] PPO, R. Fernandes, J. Walter, C. Leighton, B. Shklovskii arXiv:1605.03463 (2016).

(ii) & (iii): Surface assisted bulk percolation

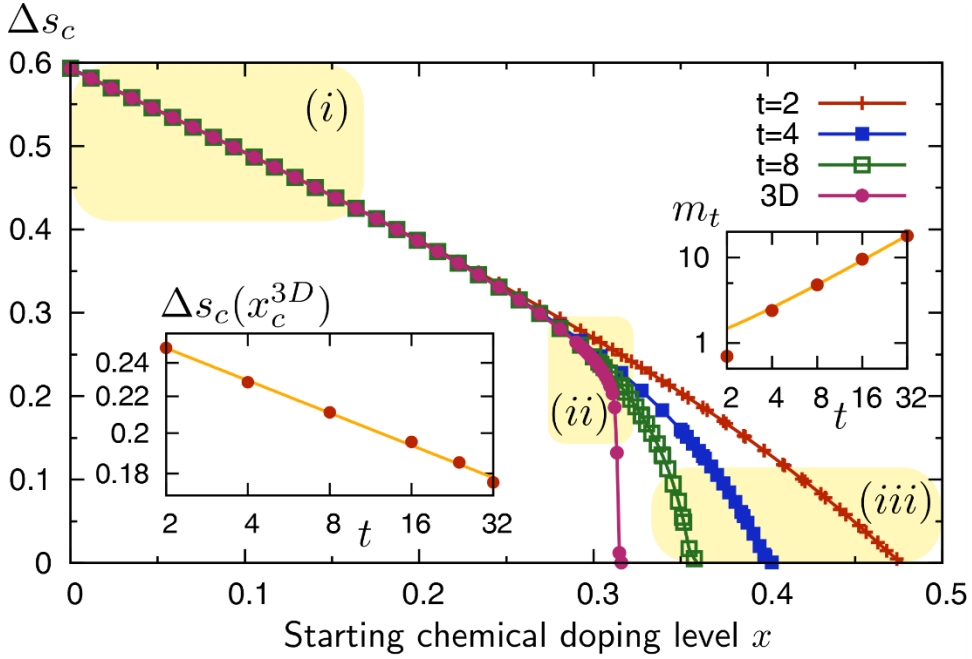




- Connecting large finite bulk clusters on the surface.
- Significant reduction for $x_c^{3D} < x < x_c(t)$
- Width $x_c(t) - x_c^{3D} \propto t^{-1/\nu}$
  - Crossover occurs more abruptly for thicker films

[1] PPO, R. Fernandes, J. Walter, C. Leighton, B. Shklovskii arXiv:1605.03463 (2016).

(ii) & (iii): Surface assisted bulk percolation



- (ii): Scaling prediction

$$s_c(x) = x_c^{3D} + c_2 t^{1-1/\nu}$$

- (iii): Scaling prediction

$$s_c(x) = x_c(t) + c_5 t(x_c(t) - x)$$

$$\Rightarrow \quad m_t = c_5 t$$

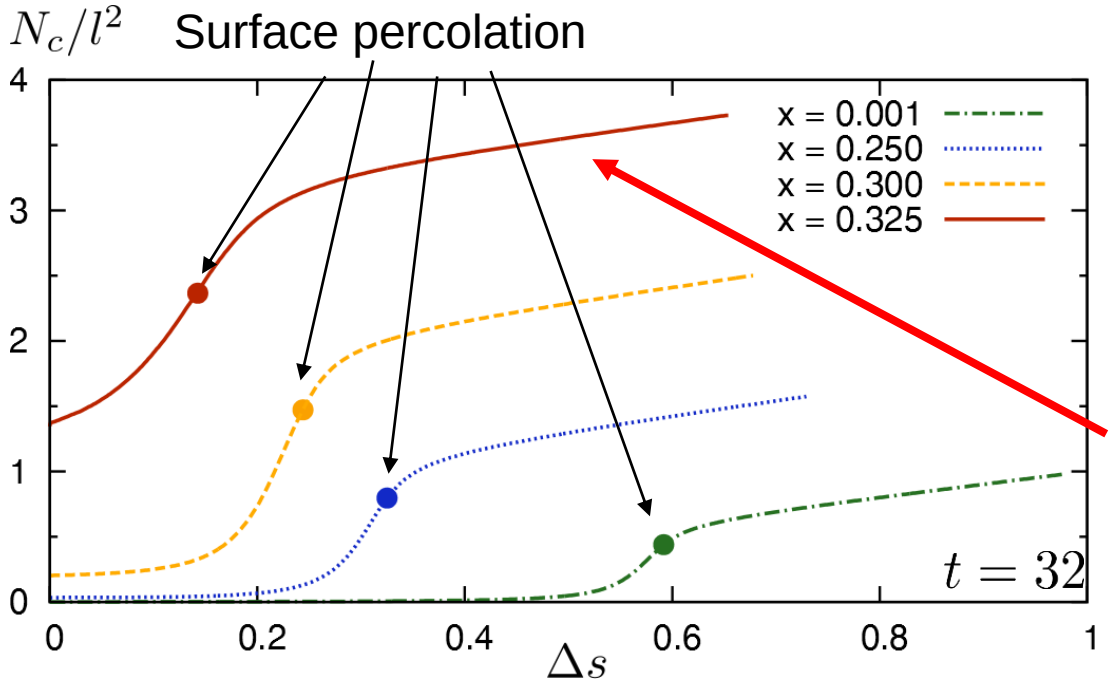
- Steep rise of Δs_c close to x_c
- Crossover occurs more abruptly for thicker films
- Significant reduction only for $x_c^{3D} < x < x_c(t)$

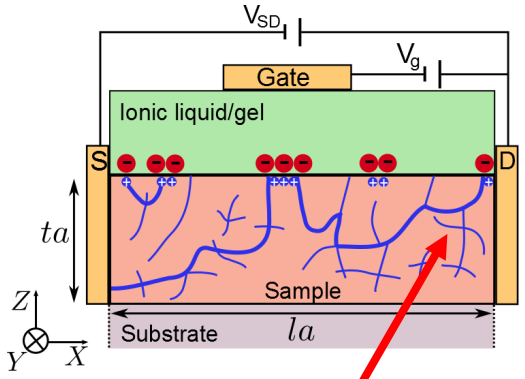
$\Rightarrow$ **Chemical doping only effective in assisting percolation in region of width $x_c(t) - x_c^{3D} \propto t^{-1/\nu}$**

[1] PPO, R. Fernandes, J. Walter, C. Leighton, B. Shklovskii arXiv:1605.03463 (2016).

Enhanced surface magnetization

- Saturation magnetization dramatically enhanced
- Ferromagnetic percolating cluster extends from surface into bulk
- Fractal cluster dimension between 2 < d < 3
- Predict unusual magnetization depth profile
  - can be measured using polarized neutron reflectometry.



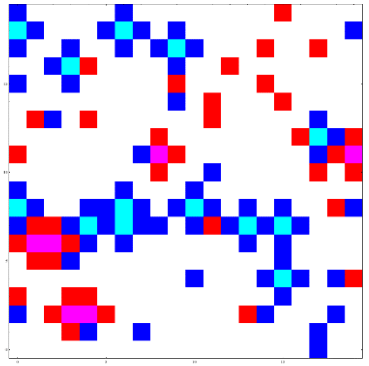


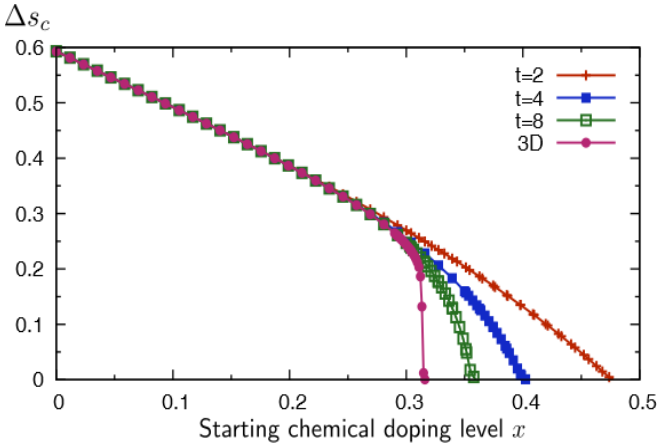
Magnetization enhanced by factor of 4 via magnetic backbone

[1] PPO, R. Fernandes, J. Walter, C. Leighton, B. Shklovskii arXiv:1605.03463 (2016).

Summary and Outlook

- Frustration of polarons due to competition of FM and AF interactions compares well with experimental results of magnetization for $0 < x < x_c$.
- Magnetization and correlations from simulations compare well with experiment.





- Chemical and surface doping assisted percolation in thin films
- New universal scaling properties predicted
- Chemical doping assists percolation in region of width $t^{-1/\nu}$
- Enhanced saturation magnetization

- PPO, R. M. Fernandes, J. Walter, C. Leighton, B. I. Shklovskii, arXiv:1605.03463 (2016).
- D. Phelan, J. Zhao, H. Zheng, S. El-Khatib, S. Wang, B. Skinner, J. Barker, J. F. Mitchell, PPO, R. Fernandes, C. Leighton (to be submitted).

Thank you for your attention!

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Backup slides