Interplay of charge, spin, orbital and lattice correlations in colossal magnetoresistance manganites

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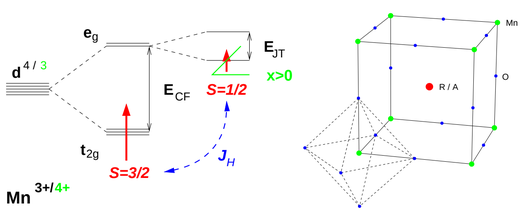
Abstract

Based on a recently derived microscopic model [1], which includes the dynamics of Jahn-Teller and Holstein-type lattice vibrations, we study the complex interplay of charge, spin, orbital and lattice degrees of freedom in doped colossal magnetoresistance manganites (e.g. $La_{1-x}Ca_xMnO_3$). Using exact diagonalisation techniques for a four site cluster we demonstrate how the coupling to the lattice affects spin and orbital order as well as charge mobility. In addition we analyse the role of superexchange for the optimally doped compounds.

Schematic phase diagram of $La_{1-x}Ca_xMnO_3$ (see [2, 3]).

Basic properties

- Due to the crystal field in cubic symmetry the Mn-d-levels split into e_g and t_{2g}.
- Strong Coulomb interaction U and Hund's rule coupling J_h prefer high-spin electronic configurations and affect charge mobility via double-exchange.
- e_g electrons interact with phonon modes of the same symmetry, which leads to a uniform Jahn-Teller distortion or polaronic effects.



Electron-electron interaction

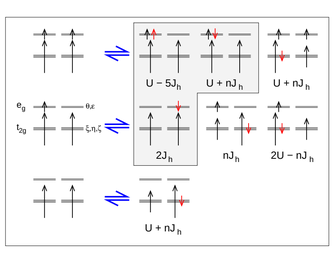
- We restrict the local electronic Hilbert space to the large Hund's rule ionic ground-states:
  Mn^{3+} (d^4) $\Rightarrow$ S=2 orbital doublet ${}^5E$: $t_2^3({}^4A_2)e$
  Mn^{4+} (d^3) $\Rightarrow$ S=$\frac{3}{2}$ orbital singlet ${}^4A_2$: t_2^3
- The effective electronic Hamiltonian is derived by second order perturbation theory with respect to the intersite hopping of Mn e_g and t_{2g} electrons, $t, t_\pi \ll U, J_h$. [1, 4]

$$H_{\text{el}} = H_{\text{double-exchange}} + H_{\text{superexchange-orbital}}$$
$$= -\sum_{\substack{\langle ij\rangle,\sigma \\ \alpha\beta}} t_{ij}^{\alpha\beta}\; a_{i,\sigma}a_{j,\sigma}^\dagger\; d_{i,\alpha}^\dagger n_{i,\bar\alpha} d_{j,\beta} n_{j,\bar\beta}$$
$$+ \sum_{\substack{\langle ij\rangle \\ \xi\eta}} (J_{ij}^{\xi\eta}\mathbf{S}_i\mathbf{S}_j + \Delta_{ij}^{\xi\eta}) P_i^\xi P_j^\eta$$

- Orbital degrees of freedom are represented by Fermi operators d_α and projectors P^α:

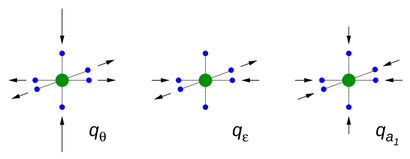
$$|\theta\rangle = d_\theta^\dagger|0\rangle, \quad |\varepsilon\rangle = d_\varepsilon^\dagger|0\rangle, \quad |a_2\rangle = d_\theta^\dagger d_\varepsilon^\dagger|0\rangle,$$
$$P_i^\theta = n_{i,\theta}(1-n_{i,\varepsilon}), \quad P_i^\varepsilon = n_{i,\varepsilon}(1-n_{i,\theta}), \quad P_i^{a_2} = n_{i,\varepsilon}n_{i,\theta}\,.$$

- On-site spin is described by Schwinger bosons: $2\mathbf{S} = a_\nu^\dagger \sigma_{\nu\mu} a_\mu$
- Note that the hopping $t_{ij}^{\alpha\beta}$ is anisotropic with respect to the orbitals $\alpha, \beta \in \{\theta, \varepsilon\}$. The exchange coupling $J_{ij}^{\xi\eta}$ and the offset $\Delta_{ij}^{\xi\eta}$ are of the order $t_{(\pi)}^2/J_h$ or $t_{(\pi)}^2/U$ and depend on the orbital orientation $\xi, \eta \in \{\theta_x,\ \theta_y,\ \theta_z,\ \varepsilon_x,\ \varepsilon_y,\ \varepsilon_z,\ a_2\}$.



- Spin part of the 2nd order processes

Electron-phonon interaction



At every site two Jahn-Teller modes of E_g symmetry, q_θ and q_ε, interact with the orbital degrees of freedom of the e_g electrons. In addition the breathing-mode q_{a_1} couples to the electron density. To a good approximation the three modes are optical, dispersion-less phonons.

$$H_{\text{JT}} = g\sum_i \Big[(n_{i,\varepsilon} - n_{i,\theta})(b_{i,\theta}^\dagger + b_{i,\theta}) + (d_{i,\theta}^\dagger d_{i,\varepsilon} + d_{i,\varepsilon}^\dagger d_{i,\theta})(b_{i,\varepsilon}^\dagger + b_{i,\varepsilon})\Big]\,,$$
$$H_{\text{br}} = \tilde g \sum_i (n_{i,\theta} + n_{i,\varepsilon} - 2n_{i,\theta}n_{i,\varepsilon})(b_{i,a_1}^\dagger + b_{i,a_1})\,,$$
$$H_{\text{ph}} = \omega\sum_i \Big[b_{i,\theta}^\dagger b_{i,\theta} + b_{i,\varepsilon}^\dagger b_{i,\varepsilon}\Big] + \tilde\omega \sum_i b_{i,a_1}^\dagger b_{i,a_1}\,.$$

Numerics

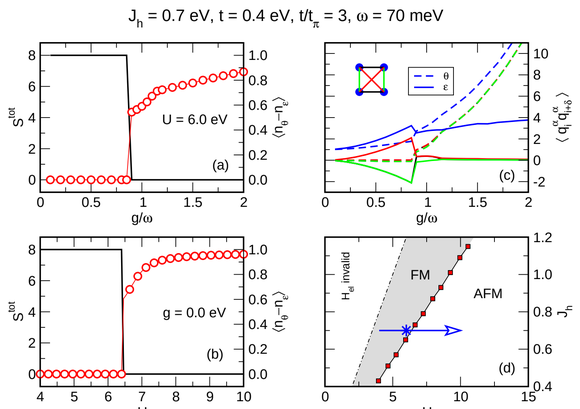
- The Hilbert space of the complete model,

$$H = H_{\text{el}} + H_{\text{JT}} + H_{\text{br}} + H_{\text{ph}}\,,$$

  is large and grows rapidly with system size.
- Solution: Density matrix based optimisation of the phonon space [5] and consideration of discrete symmetries (S^z spin, particle number, mirror symmetries).
- But: Method requires repeated solution of an eigenvalue problem of dimension $\approx 10^6$, which is not very sparse $\Longrightarrow$ large scale computers
- Parallel Lanczos diagonalisation using MPI

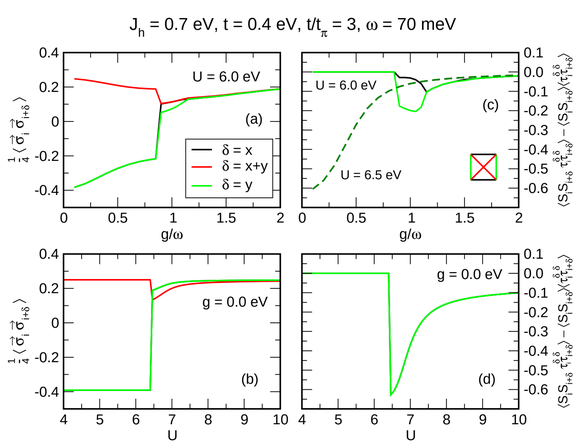
Undoped manganites

- Experimentally: A-type antiferromagnetic order and long-range Jahn-Teller distortion.
- Band structure calculations [6–9]: Lattice distortions are important for the observed magnetic order.
- Mean-field studies [4]: Antiferromagnetism of purely electronic origin.
- Our calculation: Both mechanisms, U/J_h and g, can drive a FM to AFM transition.



- Electronic model [$g = 0$, see panel (d)]:
  FM for $5J_h < U \lesssim 9.2J_h$
- Increasing g or U [panels (a) and (b)]:
  Spin: FM $\rightarrow$ AFM (cf. S^{tot})
  Orbitals: AF $\rightarrow$ F (cf. $\langle n_\theta - n_\varepsilon\rangle$)

However, depending on the driving interaction (U or g), spin and orbital correlations may differ substantially:

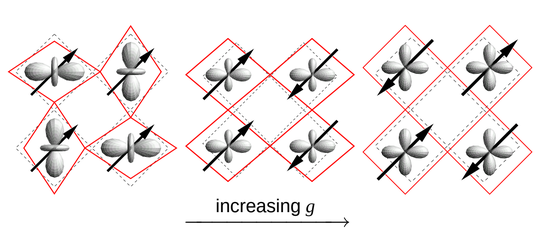


- Orbital Heisenberg correlation $\langle\sigma_i\sigma_{i+\delta}\rangle$ is comparable for both transitions [(a) and (b)].
- But: Electron-phonon interaction suppresses the coupling of the spin and orbital degrees of freedom measured by

$$\langle \mathbf{S}_i\mathbf{S}_{i+\delta}\,\tau_i^\delta\tau_{i+\delta}^\delta\rangle - \langle\mathbf{S}_i\mathbf{S}_{i+\delta}\rangle\langle\tau_i^\delta\tau_{i+\delta}^\delta\rangle\,.$$

- Can be crucial for effective theories [10, 11].

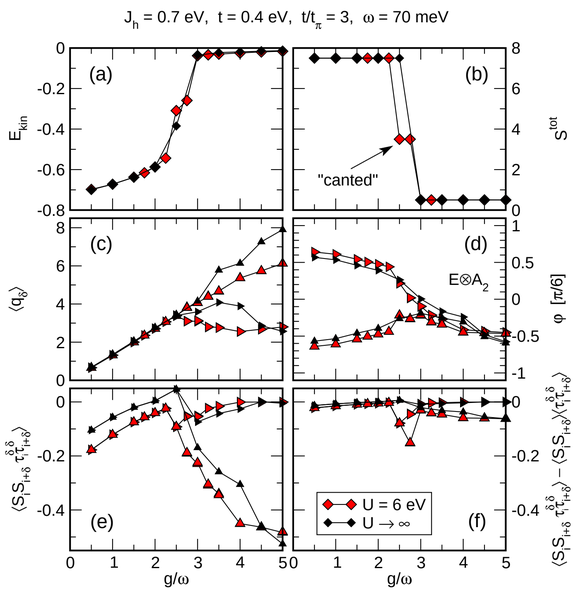
The evolution of spin, orbital, and lattice correlations can be summarised graphically:



Finite doping

In the doped compounds ferromagnetism is stabilised by the double exchange interaction. Only if strong electron-phonon coupling causes localisation of the carriers the spin order switches to AF. However, at doping $x = \frac{1}{2}$ a tendency towards charge ordering promotes antiferromagnetism.

Doping $x = 0.25$:

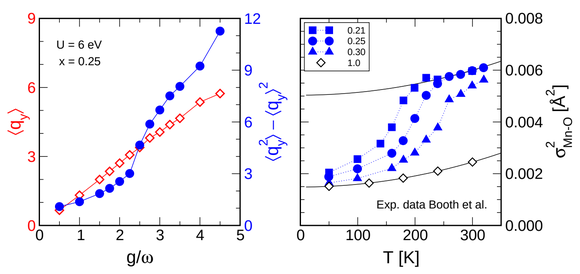


- FM→AFM transition coincides with trapping of charge carriers.
- AFM phase is accompanied by a finite lattice distortion
- Comparison of $U = 6$ eV and $U \rightarrow \infty$ reveals secondary role of superexchange interactions for orbital correlations.
- Orbital polaron [12] requires mobile carriers.
- Orbital correlations can be obtained from the reduced density matrix for two sites, whose eigenstates can be classified as:

$$|a(\varphi,\psi)\rangle_{ij} = \tfrac{1}{\|.\|}(|\varphi\rangle_i\otimes|\psi\rangle_j + |\psi\rangle_i\otimes|\varphi\rangle_j)$$
$$|s\rangle_{ij} = \tfrac{1}{\sqrt2}(|\theta\rangle_i\otimes|\varepsilon\rangle_j - |\varepsilon\rangle_i\otimes|\theta\rangle_j)$$
$$|o(\varphi)\rangle_{ij} = \tfrac{1}{\sqrt2}(|\varphi\rangle_i\otimes|a_2\rangle_j + |a_2\rangle_i\otimes|\varphi\rangle_j)$$

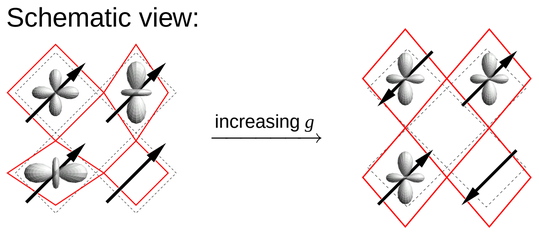
with

$$|\varphi\rangle_i = \cos(\varphi)|\theta\rangle_i + \sin(\varphi)|\varepsilon\rangle_i$$



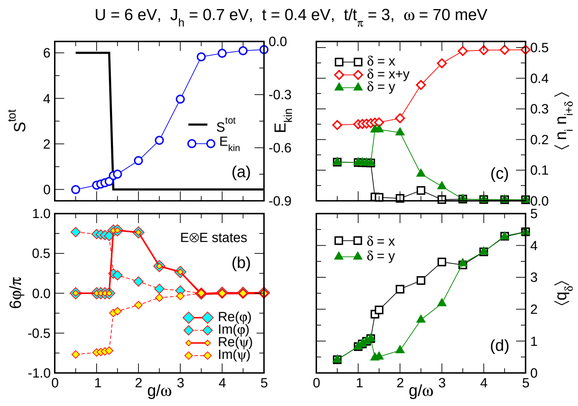
- Although the lattice distortion $\langle q_y\rangle$ may grow linearly in g, close to the FM-AFM transition the variance $\langle q_y^2\rangle - \langle q_y\rangle^2$ shows a kink
  $\rightarrow$ Reminds experimental (XAFS) data [13].

Schematic view:



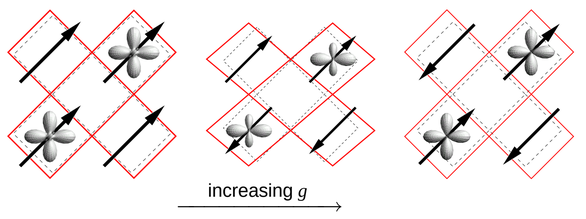
Doping $x = 0.5$:

With increasing electron-phonon coupling the system switches from an itinerant FM phase via an itinerant, q_ε-distorted AFM phase to an insulating charge ordered AFM phase.



- CDW $\rightarrow$ charge order transition with increasing g, cf. $\langle n_i n_j\rangle$, panel (c).
- Spin correlations affect kinetic energy only marginally.
- Correlation of complex orbitals in the itinerant phase.

Schematic view:



Conclusions

- By affecting charge mobility and orbital degrees of freedom the electron-phonon interaction effectively controls spin and orbital order of doped CMR manganites.
- Electron-phonon interaction can cause suppression of the spin-orbital coupling.
- Changes in the short-range spin correlations are reflected in dynamic lattice correlations.
- Calculation shows that complex orbital states are a suitable approximation.
- Exact diagonalisation of even a small system provides detailed insight into correlations and driving interactions behind the rich phase diagram of the manganites. It facilitates the development of approximate theories.
- Optimised phonon approach [5] proves to be applicable to a nontrivial Jahn-Teller problem.

References

[1] A. Weiße and H. Fehske, Eur. Phys. J. B **30**, 487 (2002).

[2] P. Schiffer, A. P. Ramirez, W. Bao, and S.-W. Cheong, Phys. Rev. Lett. **75**, 3336 (1995).

[3] A. Moreo, S. Yunoki, and E. Dagotto, Science **283**, 2034 (1999).

[4] L. F. Feiner and A. M. Oleś, Phys. Rev. B **59**, 3295 (1999).

[5] A. Weiße, H. Fehske, G. Wellein, and A. R. Bishop, Phys. Rev. B **62**, R747 (2000).

[6] D. D. Sarma, *et al.*, Phys. Rev. Lett. **75**, 1126 (1995).

[7] W. E. Pickett and D. J. Singh, Phys. Rev. B **53**, 1146 (1996).

[8] S. Satpathy, Z. S. Popović, and F. R. Vukajlović, Phys. Rev. Lett. **76**, 960 (1996).

[9] I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev. Lett. **76**, 4825 (1996).

[10] G. Khaliullin and V. Oudovenko, Phys. Rev. B **56**, R14243 (1997).

[11] L. F. Feiner, A. M. Oleś, and J. Zaanen, J. Phys. Condens. Matter **10**, L555 (1998).

[12] R. Kilian and G. Khaliullin, Phys. Rev. B **60**, 13458 (1999).

[13] C. H. Booth, *et al.*, Phys. Rev. Lett. **80**, 853 (1998).