

Cobaltates in the high-doping regime: Insights from first-principles calculations and extended dynamical mean-field theory

Abstract:

As many other layered transition-metal oxides, sodium-doped cobaltates, Na_xCoO_2 , present a rich phase diagram. They display numerous instabilities (magnetic, charge-order), originating most likely from electronic correlations. In this thesis, we focus on the case $x=2/3$, in the strong-doping limit (close to the band-insulating limit). An experimentally-observed charge disproportionation on the cobalt atoms makes this particular composition an interesting playground to study charge-correlation functions. The theoretical treatment of this system is difficult in several aspects. In order to capture electronic correlations, one needs to resort to advanced non-perturbative approaches. Also, the system is sensitive to its microscopic details, as encoded in the real electronic structure. This is why, in this thesis, we adopt model as well as *ab initio* approaches to address both these issues.

We first study the effect of correlations at the model level, on a triangular lattice, specifically designed for the cobaltates. The interplay between local and non-local Coulomb interactions gives rise to charge fluctuations, which we capture using the Extended Dynamical Mean-Field Theory. We establish the phase diagram of our model as a function of local and non-local interactions. It displays a second-order phase transition between a homogeneous metallic phase, and a charge-ordered phase. We compute one and two-particle observables in the homogeneous phase, and we analyse how they are influenced by correlations. We show that our findings can be understood as a consequence of the strong doping. We find a region of the phase diagram where the static screened Coulomb interaction becomes negative. Finally, we show how to incorporate a non-local Fock term in the calculation of the self-energy, and how it influences the phase diagram and the physical observables.

Next, in order to complement the model approach, we study the microscopic details of the real sodium-cobaltates by using Density-Functional Theory. We analyse the effect of oxygen hybridisation and electronic hopping processes on the band structure of cobalt-oxygen planes. We study the effects of sodium doping, crystal structure and magnetism, on the band structure of this material. Then, we compute the charge susceptibility from first principles in the independent-particle approximation and in the random-phase approximation. We use the insight gained from the model calculation to discuss these results.

The comparison between the model and the *ab-initio* calculations shows that these approaches are complementary. The model enables us to define the best approximations for the calculation of charge correlation functions. The *ab-initio* calculations, and the detailed understanding of microscopic electronic processes are the prerequisite for a model that is both realistic and predictive.