

# Orbital selective localization enhancement in $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$

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The discovery of unconventional superconductivity at  $T_c = 0.93$  K in  $\text{Sr}_2\text{RuO}_4$  which is isostructural to High- $T_c$  layered copper-based perovskites [1, 2] motivated the search for a new Ru-based superconductor and gave rise to interest in the investigation of the electronic and magnetic properties of ruthenates. Synthesis and study of a complete series of  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  alloys with isoelectronic substitution of  $\text{Sr}^{2+}$  by smaller  $\text{Ca}^{2+}$  ion was performed by Nakatsuji and Maeno [3, 4]. At concentration  $x = 0.5$  the susceptibility shows a Curie form with a  $S = 1/2$  moment (not  $S = 1$ ) per Ru ion and the alloy exhibits metallic transport properties. At higher concentrations of Sr,  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  has a paramagnetic metallic state. At a higher Ca concentration, the alloy remains metallic, but with AFM fluctuations at low temperatures. With a further increase in Ca concentration ( $x < 0.2$ ), the alloy becomes an insulator.

To describe the evolution of the electronic structure at intermediate concentration, the orbital selective Mott transition model was proposed [5]. In this model  $t_{2g}$  manifold is divided into two groups of orbitals: degenerate  $xz, yz$ -orbitals and in-plane  $xy$ -orbital strongly  $\pi$ -hybridized with oxygen  $2p$ -orbitals. Using LDA results as input parameters for the DMFT method within the NCA computation scheme [6] the authors obtained orbital-selective behavior: the appearance of Mott localization in ( $xz, yz$ ) subbands, while the broader half-filled  $xy$ -band remains itinerant.

In the present paper the DFT + DMFT method was applied to study the electronic structure of  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  [7, 8]. The non-interacting band structure was calculated using the GGA (generalized gradient approximation) [9] as implemented in the Quantum Espresso package [10]. An effective Hamiltonian was constructed using the basis of atomic-centered Wannier functions as described in [11]. The DMFT impurity problem was solved by hybridization expansion

of the continuous-time quantum Monte Carlo method (CT-QMC) [12] as implemented in the AMULET package [13]. QMC calculations were performed for the paramagnetic state at an electronic temperature  $\beta = 20$  eV<sup>-1</sup> (580 K).

Local spin-spin correlation function  $\langle \mathbf{S}_z(\tau)\mathbf{S}_z(0) \rangle$  on the imaginary time axis characterizes the lifetime of the local moment. If the magnetic moments are localized, this correlation function is constant:  $\langle \mathbf{S}_z(\tau)\mathbf{S}_z(0) \rangle \approx S^2$  and the imaginary time dependence of this correlation function indicates the delocalization of spin moments, which is the Fermi liquid regime. The real part of the local spin-spin correlation function on the real frequency axis can be used to characterize the degree of localization: the half-width of  $\langle \mathbf{S}_z(\omega)\mathbf{S}_z(0) \rangle$  peak at a half-height is in inverse proportion to the lifetime of the local moment [14].

The local spin-spin correlation functions  $\langle \mathbf{S}_z(\omega)\mathbf{S}_z(0) \rangle$  for different  $x$  are shown in Fig. 1 (upper panel). For  $x = 2$  the peaks of  $t_{2g}$   $d_{xy}$  and  $d_{xz, yz}$

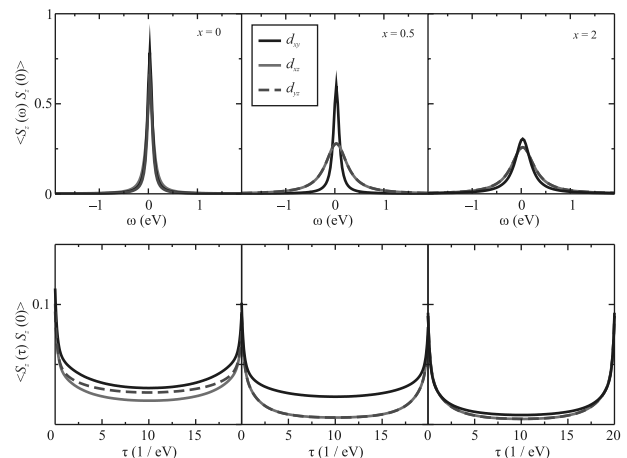


Fig. 1. (Color online) Local spin-spin correlation function  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  calculated within DFT + DMFT at  $\beta = 20$   $U = 1.5$  eV and  $J_H = 0.7$  eV for  $x = 0, 0.5$  and  $2.0$  on imaginary time axis (lower panels) and real frequencies (upper panels)

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orbitals have almost equal width and shape which is consistent with small distortion of oxygen octahedra in  $\text{Sr}_2\text{RuO}_4$ . The broad local spin-spin correlation functions correspond to a metallic phase with weakly localized electrons. On the other hand, in the case of  $\text{Ca}_2\text{RuO}_4$  ( $x = 0$ ) the peaks become sharp and the width reduces by a factor  $\approx 2$ . The  $\langle \mathbf{S}_z(\tau)\mathbf{S}_z(0) \rangle$  correlator has substantial value in the whole range  $[0, \beta]$  as well as lifting of degeneracy of  $d_{xz,yz}$  orbitals due to strong distortion of crystal structure. One can say, that  $d$ -electrons in  $\text{Ca}_2\text{RuO}_4$  are more localized, as expected for Mott insulator regime. The case of  $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{RuO}_4$  is much more indicative. Ru  $t_{2g}$  orbitals are separated into two subsystems with completely different behavior: while  $\langle \mathbf{S}_z(\omega)\mathbf{S}_z(0) \rangle$  curves for  $d_{xz,yz}$  orbitals are broad and these states can be treated as itinerant and reminiscent metallic  $\text{Sr}_2\text{RuO}_4$  the  $d_{xy}$  orbital has sharp peak and resembles  $\text{Ca}_2\text{RuO}_4$ . The half-widths of  $\langle \mathbf{S}_z(\omega)\mathbf{S}_z(0) \rangle$  peak at a half-height for  $d_{xy}$  and  $d_{xz,yz}$  orbitals as well as their lifetimes differs in  $\approx 6$  times. This agrees well with the model proposed in [5]. Variation of  $J_H$  does not change orbital-selective behavior. The width of  $\langle \mathbf{S}_z(\omega)\mathbf{S}_z(0) \rangle$  peaks and hence the lifetime on local moments decreases in  $\approx 3$  times with increasing  $J_H$  from 0.5 to 0.9 eV. Note also, that orbital-selective behavior exhibits more distinctly for smaller  $J_H$ . Most likely, this effect could be explained by the change in the value of mean Coulomb interaction term which is 1.1 eV for  $U = 1.5$  eV and  $J_H = 0.9$  eV and 1.28 eV for  $U = 1.5$  eV and  $J_H = 0.5$  eV.

Analysis of the local spin-spin correlation function reveals that the end members of series  $\text{Sr}_2\text{RuO}_4$  and  $\text{Ca}_2\text{RuO}_4$  are conventional itinerant metals and correlated insulators, respectively, without any distinct sign of orbital selectivity. In contrast,  $\text{Ca}_{0.5}\text{Sr}_{1.5}\text{RuO}_4$  demonstrates a clear picture of orbital selective behavior. The sharp dependence of magnetic properties and degree of localization on the Hund parameter  $J_H$  are an evident sign that intermediate members of the  $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$  series belong to the Hund's metals. Variation of Hund's parameter shows that the localization degree depends on  $J_H$  while the orbital-selectivity is regulated by average Coulomb interaction value.

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