Localization in ruthenates: magnetic and electronic properties of Ca$_{2-x}$Sr$_x$RuO$_4$

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The electronic structures of the metallic and insulating phases of Ca$_{2-x}$Sr$_x$RuO$_4$ (0 ≤ x ≤ 2) are calculated using LDA, LDA+U and Dynamical Mean-Field Approximation methods. For x = 0 the ground state is an orbital non-degenerate antiferromagnetic insulator. For 0.2 < x < 0.5 we propose a state with partial orbital and spin ordering. For x > 0.5 the observed Curie-Weiss paramagnetic metallic state possessing a local moment with the unexpected spin S = 1/2 is explained by the localization of only two of the three Ru-4d-orbitals.

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The isoelectronic alloy series Ca$_{2-x}$Sr$_x$RuO$_4$ is a rare example of a metal-insulator transition with a multi-band electronic structure. Sr$_2$RuO$_4$ has been well studied of late because of its unconventional superconductivity and strongly correlated Fermi-liquid behavior in the normal phase. The other end member, Ca$_2$RuO$_4$ is a localized Mott insulator, antiferromagnetically (AF) ordered, and with a distorted crystal structure. It is very interesting to examine how this isoelectronic system evolves between these two contrasting end members.

Very recently Nakatsuji and Maeno (NM) reported transport, magnetic and crystallographic measurements on the intermediate phases. Especially noteworthy is the pronounced increase in paramagnetism in a metallic phase as x is decreased from pure Sr$_2$RuO$_4$ (x = 2) down to a critical value x$_c$ = 0.5. In this range 2 > x > 0.5 (called Region III by NM), the susceptibility evolves to show free Curie behavior (i.e. x ≈ C/T) at x = x$_c$ with a Curie constant C corresponding to a spin S = 1/2 per Ru$^{4+}$-ion. This result presents two puzzles: the apparent absence of exchange interactions in this concentrated spin system and the unexpected reduction in the value of the local moment from the usual S = 1, for localized Ru$^{4+}$-ions. Further reduction of x < x$_c$ leads to Region II characterized by a magnetic metallic phase in which both a tilting of the RuO$_6$ octahedra and AF correlations between the S = 1/2 moments appear in a metallic phase. Finally in Region I (0 < x < 0.2) a metal-insulator transition occurs as the temperature is lowered. The end member Ca$_2$RuO$_4$ is an AF Mott insulator with the expected S = 1 local moment and a more strongly distorted crystal structure. This complex evolution of the electronic structure from a well-formed Landau-Fermi liquid in Sr$_2$RuO$_4$ to the AF Mott insulator in Ca$_2$RuO$_4$ must be interpreted in terms of the multiband electronic structure of these materials.

In this Letter we report calculations of the electronic structure of Ca$_{2-x}$Sr$_x$RuO$_4$ using local density (LDA), local density with onsite correlations (LDA+U) and Dynamic Mean-Field (DMFT) approximation schemes, in each range for compositions for which crystal structures are determined. In this way we track the evolution in the electronic structure from the metal at x = 2 to the AF insulator at x = 0.

Sr$_2$RuO$_4$ has the single-layered K$_2$NiF$_4$-structure (space group I4/mmm) with layers of RuO$_6$-octahedra, slightly elongated along the c-axis and tetragonal local symmetry for a Ru$^{4+}$-ion. The band structure has completely filled O-2p-bands, 4 electrons in Ru $t_{2g}$ 4d-band and an empty $e_g$-band. Due to the tetragonal symmetry, the $xy$-orbitals of the $t_{2g}$-band are not equivalent to the $(xz, yz)$-orbitals. The crystal field splitting between them is small but the $xy$-orbitals $\pi$-hybridize with the 2p-orbitals of all 4 in-plane O-neighbors while $xz$ $(yz)$-orbitals $\pi$-hybridize only with the 2 O-neighbors on the x-axis (y-axis). As a result the $xy$-band has two-dimensional dispersion and a bandwidth nearly twice that of the $(xz, yz)$-orbitals (see Fig. 1). The measured effective masses, however, are typically enhanced by factors of 3 to 4, indicating strong correlations. Note the volumes contained within the Fermi surface sheets show an approximately equal occupation of all 3 orbitals — a state we denote as (8/3, 4/3) where $(n_{t_{2g}}, n_{e_g})$ are the occupation of the $(yz, xz)$- and $xy$-orbitals, respectively.

Turning to the other end member, we note that the ionic radius of Ca$^{2+}$ is smaller than Sr$^{2+}$, so that a stabilization of the metallic state might be expected. However with the substitution of Sr by Ca in Ca$_{2-x}$Sr$_x$RuO$_4$, the average (Sr,Ca)-ion size becomes too small for its space symmetry, the ionic radius of Ca$^{2+}$ decreases significantly and the compression of the RuO$_6$-octahedra. The lattice reacts by rotating and tilting the octahedra so as to decrease this space. Also the smaller size of the Ca$^{2+}$-ion decreases the interlayer distance (c-axis lattice constant) which results in a smaller elongation of the RuO$_6$-octahedra (for Ca$_2$RuO$_4$ the octahedra are even compressed). These structural changes lead to a smaller bandwidth due to the reduction of the Ru-O-Ru-bond angle from the ideal value of 180° and the compression of the octahedra changes the sign of the $xy$-$(xz, yz)$ energy splitting.

We consider the evolution of the electronic structure starting from the good metal, Sr$_2$RuO$_4$. Here the frac-
tional occupation of all 3 bands that cross the Fermi surface clearly inhibits Mott localization, since none of the Fermi sheets allows elastic umklapp electron-electron scattering at the Fermi energy. Yet the evolution from \( x = 2 \) to \( x = 0.5 \) clearly points to the partial localization of the 4d-electrons. Metallic strongly correlated electron systems have been successfully described by the recently developed DMFT [11,12]. We have used LDA to determine the band parameters of the non-interacting Hamiltonian and then treated the interactions within the DMFT. The effective Anderson impurity model in the DMFT scheme has been solved by the non-crossing approximation (NCA) [13]. This leads to the combined method called LDA+DMFT+NCA [14].

The most puzzling aspect is the effective \( S = 1/2 \) moment observed in the Curie-Weiss-like susceptibility, since the ionic value for the low-spin state of a Ru\(^{4+}\)-ion is \( S = 1 \). In the absence of full crystallographic data for this region, we applied the LDA+DMFT+NCA scheme to the Sr\(_{2}\)RuO\(_4\) structure, with \( U \) values varying from 1.0 eV to 2.5 eV. The partially filled Ru-4d-bands derived from the \( xy \) and \((yz, zx)\) orbitals do not hybridize with each other by symmetry. Since the effective bandwidth of the \( xy \)-band is considerably larger (Fig.1a), a larger value of \( U \) is needed to drive the metal-insulator transition for the \( xy \)-band than for the \((yz, zx)\)-band. The LDA+DMFT+NCA calculations showed that \( U_c = 1.5 \) eV is a critical value for localization of the \((yz, zx)\)-electrons while a larger value of \( U_c = 2.5 \) eV is needed for the \( xy \)-band. These results imply that for intermediate values of \( U \) (1.5 eV \( < U \) \(< 2.5 \) eV), there will be a regime of partial localization of the 4d-electrons. In practice the RuO\(_6\)-octahedra rotate when \( x \) \(< 1.5 \), reducing the n.n. hopping and narrowing the band. For constant \( U \), Mott localization will appear first in the \((xz, yz)\)-band. This leads us to propose that the region \( x \sim x_c \) has a novel electronic structure illustrated in Fig. 1b. Of the 4 electrons in the \( I_2g\)-bands, 3 electrons (or 1 hole) are in the Mott localized \((xz, yz)\)-bands and are the origin of the \( S = 1/2 \) local moments. The remaining 1 electron forms a half-filled but still metallic \( xy \)-band. Integer occupancy of the different sub-bands is the key to achieving Mott localization. Our LDA + DMFT + NCA calculations give a self-consistent solution with exactly \((3, 1)\) occupancy.

We now turn to the magnetic properties of the local \( S = 1/2 \) moments. While a Kondo-type of interaction between the two bands \((xz, yz)\) and \( xy \) can be excluded due to the absence of hybridization for symmetry reasons, an AF-type of RKKY interaction between the localized spins is still induced via Hund’s rule coupling. At the same time, however, Hund’s rule coupling causes the ferromagnetic correlation through the double exchange mechanism. Thus, the two types of spin interactions mediated by the itinerant electrons of the \( xy \)-band are likely to compensate each other, such that the exchange coupling between neighboring localized spins occurs mainly through superexchange processes in the \((yz, zx)\)-band.

The highly anisotropic hopping matrix elements between these orbitals, however, leads to an essential dependence of the superexchange interaction on the orbital configuration of the minority spin electron (or single hole) of each Ru\(^{4+}\)-ion in the degenerate \((xz, yz)\) bands. To gain insight into the possible form of orbital ordering we performed LDA+U calculations for the critical concentration \( x_c = 0.5 \) [13].

Ca\(_{1.5}\)Sr\(_{0.5}\)RuO\(_4\) has the space group \( I4_1/acd \) which has no tilting of RuO\(_6\)-octahedra, only rotations around the c-axis. The RuO\(_6\)-octahedra are also elongated causing the \( xy \)-orbital to be higher in energy than \((xz, yz)\)-orbitals leading to orbital degeneracy in a \((3, 1)\) state. The LDA+U calculation gave an orbital order of an antiferro-type. The minority-spin electrons occupy alternating \(xz\) and \(yz\)-orbitals \((|\tau^z\rangle = \pm 1)\) with a slight tilting of the orbital planes away from the c-axis. This orbital order favors ferromagnetic (FM) spin alignment and this could explain the experimentally observed enhancement of susceptibility with increasing of Sr concentration toward the \( x = 0.5 \) [14].

Specifically the localized orbital degrees of freedom are represented by the isospin \( \tau \) where the \( yz \)- and \( zz \)-orbitals on each site correspond to the states \(|+\rangle\) and \(|-\rangle\), respectively, with \( \tau^z|\pm\rangle = \pm \frac{1}{2} |\pm\rangle \). We parameterize the n.n. superexchange interaction as

\[
\mathcal{H}_s = \sum_{i,a} J_a(\tau_i, \tau_{i+a})\left\{ S_i \cdot S_{i+a} + b \right\}
\]  

with \( J_a(\tau_i, \tau_{i+a}) = J_{i} \mathbf{I}_{i,a} \cdot \mathbf{I}_{i+a,a} \). We define the orbital (2-component) vector operator \( \mathbf{I}_{i,a} = (\tau^x_i + g_1 \tau^0_i, \tau^z_i + g_2 \tau^0_i) \).
\( g a' \tau_i^y \) where \( a = (1, 0), (0, 1) \) is the vector connecting n.n. sites and \( g = a_x^2 - a_y^2 (\tau^0 = \frac{1}{2} \hat{1}_{2 \times 2}) \). This Hamiltonian is reduced to the essential parts from the most general possible form. The parameters \( \alpha, \alpha', b \) and \( J_1 \) are chosen to be consistent with the results of the LDA calculation. In particular, \( 0 < 1 - \alpha \ll 1 \) arising from the reduction of the overlap for orbitals with their planes \( \perp \hat{a} \). This leads to AF coupling, if the orbital states on a bond are the same (strongly reduced, if the bond is perpendicular to the plane), and to FM coupling for the configuration \( |+\rangle \otimes |-\rangle \). This competition between AF and F coupling suggests that there may be a strong cancellation due to fluctuations of the orbital occupation.

At lower values of \( x \) we enter Region II \( (0.5 > x > 0.2) \) characterized by a tilting plus rotation of RuO\(_6\)-octahedra. Ca\(_{1.8}\)Sr\(_{0.2}\)RuO\(_4\) has a low-symmetry crystal structure with the space group \( P2_1/c \) \([8]\), which can be obtained from the tetragonal \( I4/mmm \) structure by rotating and tilting of the RuO\(_6\)-octahedra similar to pure Ca\(_2\)RuO\(_4\) but with a smaller tilting angle \([8]\). There are now two types of in-plane oxygen ions and two types inequivalent of RuO\(_6\)-octahedra. The ratio of the Ru-O bond length for the apical and planar oxygen is larger than 1, so that the \( xy \)-level lies higher than the \( (xz, yz) \)-levels leading to an occupation \( (3, 1) \). The single minority-spin electron is orbitally degenerate in \( (yz, zx) \)-band. We performed LDA+U calculation for this tilted structure and obtained a rather complicated orbital order. The ground state is an AF insulator. The minority-spin electron (1 per Ru-atom) occupy the orbitals whose planes are in average directed along the \( a \)-axis (in tetragonal notation \([10]\) direction). However on every one of the 4 Ru-atoms in the unit cell those planes are rotated from the \( a \)-axis by +20° \((\langle \tau \rangle = (u, 0, v)) \) and +15° \((\langle \tau \rangle = (u', 0, v')) \) on one layer and by -20° \((\langle \tau \rangle = (-u, 0, v)) \) and -15° \((\langle \tau \rangle = (-u', 0, v')) \) on the next layer \((u = 0.643, v = 0.766, u' = \sqrt{3}/2 \) and \( v' = 1/2 \)). Also on one of the 2 Ru-atoms in every layer there is an additional tilting of the orbital plane from the long \( c \)-axis on 34° which is not represented within our model. The calculation of the easy axis using the second order perturbation theory for spin-orbit coupling gave the direction of magnetic moment as along the \( a \)-axis (tetragonal \([10]\) direction) with a 28° tilt from the layer plane. The measurements of the uniform magnetic susceptibility show a peak in the temperature dependence which is the most pronounced for the [110] direction of the magnetic field, in agreement with our LDA+U results \([5]\).

To include the aspect of spin anisotropy we extend the interaction adding the following terms,

\[
\sum_{i,a}[J_2 g(I_{i,a}^x I_{i-+a}^y - I_{i,a}^y I_{i-+a}^x)] (s_{i,a}^x s_{i-+a}^x - s_{i,a}^y s_{i-+a}^y)
+ J_3 g[(I_{i,a}^x I_{i-+a}^y + I_{i,a}^y I_{i-+a}^x)] (s_{i,a}^x s_{i-+a}^x + s_{i,a}^y s_{i-+a}^y)
+ J_4 (I_{i,a}^x I_{i-+a}^y - I_{i,a}^y I_{i-+a}^x)] (s_{i,a}^x s_{i-+a}^y - s_{i,a}^y s_{i-+a}^x)
+ J_5 s_{i,a}^x s_{i-+a}^x]
\]

where further phenomenological parameters appear. Our previous discussion based on LDA indicated that crystal field effects yield the dominant bias for the orbital orientation. This is taken into account by an additional term \( H_{cf} = -\sum_{i,\mu} Q_i^\mu \tau_i^\mu \) where \( Q_i \) is a local “Jahn-Teller” mean field which depends on the distortion introduced by Ca-doping and may show a complicated staggering as suggested by our LDA calculation.

We now can connect the experimental results for \( x = 0.2 \) with our model. Taking for simplicity \( Q_i \propto (1, 0, 0) \) uniformly of all orbitals is parallel to [110] and we obtain an effective AF anisotropic n.n. spin exchange of the form \( J_i s_i^\alpha s_i^\beta \). Here the coordinates \( \mu \) are the principal spin axis in the exchange (1) and (2). Two axis \((\mu = x', y') \) lie in the plane of the orbitals and the third axis \((\mu = y') \) lies orthogonal. Assuming \( J_3 > 0 \) and \( J_3 \approx J_3 \) leads to an “XXZ-type” Heisenberg model where the Ising part (spin quantization axis along [110]) is weaker. Consequently, the uniform susceptibility is larger along the [110]-direction. The temperature dependence of the susceptibility for all directions show peak features indicating the characteristic energy scale which is lower for [110] than the other two, consistent with the different AF exchange in our model. While the shape of the susceptibility for [110] and [001] are very similar the latter direction is enhanced by a constant. This can be attributed to the temperature-independent orbital Van Vleck contribution along the \( z \)-axis, related to the orbital operator \( \tau_i^\nu \).

Lastly we consider the end member Ca\(_2\)RuO\(_4\). The structure of Ca\(_2\)RuO\(_4\) is orthorhombic (space group \( Pbca \) \([8]\)) and is obtained from the high-symmetry tetragonal \( I4/mmm \) by rotating the RuO\(_6\)-octahedra around their long axis (001) and tilting around the diagonal in-plane axis (110), with the condition that all planar oxygen move the same distance from the plane. As a result there is only one type of in-plane oxygen in this structure and all RuO\(_6\)-octahedra are equivalent.

Ca\(_2\)RuO\(_4\) is an AF insulator and is relatively simple to describe with the LDA+U method \([10]\). This method is based on spin-orbital unrestricted Hartree-Fock equations (i.e. a static mean-field approximation) and generally gives good results for long range ordered Mott insulators \([10]\). The Coulomb direct and exchange interaction parameters values used in our calculation were \( U = 1.5 \) eV and \( J = 0.7 \) eV. The groundstate of Ca\(_2\)RuO\(_4\) was found to be an AF insulator with a sublattice moment of 1.51 \( \mu_B \) and a small energy gap, 0.30 eV, which compares well
with the experimental values $1.3\ \mu_B$ and $0.2\ \text{eV}$ respectively. The band $t_{2g}$ is now fully spin-polarized (the reduced moment relative to $S=1$ is due to hybridization with oxygen states). Of the 4 $t_{2g}$-electrons, 3 are in the majority-spin band and 1 is in the minority-spin band. In general, this implies an orbital degenerate state. However in Ca$_2$RuO$_4$, this degeneracy is lifted, since the $xy$-level lies considerably lower than the $(xz, yz)$-levels and is fully occupied in the insulating state. In the notation introduced above, we have integer $(2, 2)$ occupancy of the orbitals in contrast to the $(3, 1)$ occupancy found for Regions III and II with $x > 0.2$. Using second order perturbation theory for spin-orbit coupling, we find the magnetic moment along the $b$-axis in orthorhombic notations (or [110] direction in a tetragonal notation), in agreement with the experimental data. The AF insulating phase extends to $x = 0.2$ where by a first order structural change occurs to Region II $(0.2 < x < 0.5)$ which exhibits short-range AF correlation and is metallic. This first order boundary marks the transition from the $(2, 2)$ to $(3, 1)$ configurations with increasing $x$. In summary, we have presented a consistent picture for the unusual phases of the iso electronic alloy series Ca$_{2-x}$Sr$_2$RuO$_4$ based on the full multi-band electronic structure (see Table I). Starting from the good metal Sr$_2$RuO$_4$, we find the effect of Ca-substitution is to transfer electrons from the wider $(xy)$-band to the narrower $(xz, yz)$ bands until at a critical value of $x_c = 0.5$ there is integer occupancy of both subbands. The progressive rotation of the RuO$_6$ octahedra in this region leads to Mott localization of the 3 electrons in the narrower $(xz, yz)$ bands while the wider $xy$-band which is now half-filled, remains metallic. This partial localization of the 4$d$ electrons can explain the puzzling observation of the coexistence of free $S=1/2$ local moments and metallic behavior in Ca$_{1.5}$Sr$_{0.5}$RuO$_4$. The ordered phases appearing in the Ca-rich Regions I $(0 \leq x < 0.2)$ and II $(0.2 \leq x < 0.5)$, are based on localized $(yz, zx)$-orbitals, while the $xy$-orbital plays the role of a charge reservoir, yielding a completely filled (insulating) or half-filled (metallic) band in the two regions, respectively. In the former case the ordered local spin has $S = 1$, but in the latter case short-range correlations of a local $S=1/2$ spin combined with orbital order are realized, generating a pronounced anisotropy in the magnetic response.

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Table I. The three Regions of Ca$_{2-x}$Sr$_2$RuO$_4$ with their orbital occupancy, the localized orbital and spin degrees of freedom and the order or (dominant correlations) (AF = spin antiferromagnetic, FM = spin ferromagnetic, AFO = anti-ferro-orbital).

| Region | $(n_{yz,zx}, n_{xy})$ orbital | spin | order |
|--------|-----------------------------|------|-------|
| I $(0 \leq x < 0.2)$ | (2, 2) | - | $S=1$ | AF |
| II $(0.2 \leq x < 0.5)$ | (3, 1) | $(yz, zx)$ | $S = \frac{1}{2}$ | FO, (AF) |
| III $(x \rightarrow 0.5)$ | (3, 1) | $(yz, zx)$ | $S = \frac{1}{2}$ | (AFO), (FM) |
| III $(x = 2)$ | $(\frac{1}{2}, \frac{1}{2})$ | - | $S=0$ | - |