Mott-insulator transition in Ca$_{2-x}$Sr$_x$RuO$_4$: A study of the electronic and magnetic properties

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Abstract. The electronic structures of the metallic and insulating phases of the alloy series Ca$_{2-x}$Sr$_x$RuO$_4$ ($0 \leq x \leq 2$) are calculated using LDA, LDA+U and Dynamical Mean-Field Approximation methods. In the end members the groundstate respectively is an orbitally non-degenerate antiferromagnetic insulator ($x = 0$) and a good metal ($x = 2$). For $x > 0.5$ the observed Curie-Weiss paramagnetic metallic state which possesses a local moment with the unexpected spin $S = 1/2$, is explained by the coexistence of localized and itinerant Ru-4d-orbitals. For $0.2 < x < 0.5$ we propose a state with partial orbital and spin ordering. An effective model for the localized orbital and spin degrees of freedom is discussed. The metal-insulator transition at $x = 0.2$ is attributed to a switch in the orbital occupation associated with a structural change of the crystal.

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1 Introduction

The discovery of unconventional superconductivity in Sr$_2$RuO$_4$ has evoked considerable interest in the electronic properties of ruthenates. Curiously the substitution of the smaller Ca$^{2+}$-ions for Sr$^{2+}$-ions does not lead to a more metallic state but to an antiferromagnetic (AF) Mott insulator with a staggered moment of $S = 1$ as expected for a localized Ru$^{4+}$-ion which has 4 electrons in the $t_{2g}$-subshell. As will be discussed below, this insulating behavior is driven by a crystallographic distortion and a subsequent narrowing of the Ru-4d bands. The complete series of isoelectronic alloys for intermediate concentrations has recently been synthesized and studied by Nakatsuji and Maeno. This gives a rare opportunity to examine the evolution of the electronic structure from a multi-band metal to a Mott-insulator transition in an iso-electronic system. The evolution is not at all monotonic and the metal-insulator transition does not take place as a simple Mott transition but proceeds through a series of intermediate regions with unexpected behavior.

The most dramatic example is the system at a concentration $x = x_c = 0.5$. At this critical concentration the susceptibility shows a free Curie form with a $S = 1/2$ moment (not $S = 1$) per Ru-ion coexisting with metallic transport properties. This critical concentration represents the boundary of the paramagnetic metallic region which evolves as Ca is substituted in the good metal, Sr$_2$RuO$_4$. At higher Ca concentrations ($x_c > x > 0.2$), the alloys enter a region with AF correlations at low temperature but still with metallic properties. Insulating behavior appears only at smaller values of $x < 0.2$. The challenge that we address in this paper, is to understand this unexpected and nonmonotonic evolution and in particular the exotic behavior in the vicinity of the critical concentration at $x \approx x_c$. We begin by discussing the end members. Sr$_2$RuO$_4$ is a good metal. Its Fermi surface has been determined by de Haas-van Alphen experiments and agrees very well with the predictions of the local density approximation (LDA) in the density functional theory. C$_{a}$Ru$_{4}$O$_{4}$ is an AF Mott insulator and it can be well described by augmenting the LDA by a mean field to include the onsite correlation — the so-called LDA+U method. The third section of this paper is devoted to the examination of the intermediate concentrations by performing calculations for a series of characteristic $x$-values. The most challenging is the region $x \approx x_c = 0.5$ where there are strong correlations but no symmetry breaking so that both LDA and LDA+U are inapplicable. At this concentration we employ the recently developed $ab$ initio computational scheme combining local density approximation and dynamical mean field theory (LDA+DMFT). We use LDA calculations to determine the input parameters in the effective Anderson impurity model which in turn is treated using a non-crossing approximation (NCA). These calculational schemes give us reliable information on the evolution of the electronic distribution among the 3 orbitals in the $t_{2g}$-subshell, which we shall show is the key to un-
standing the electronic properties. The paper concludes with a discussion and summary of our results. A brief account of this work has appeared elsewhere [16].

2 End Members: Sr$_2$RuO$_4$ and Ca$_2$RuO$_4$

We start with Sr$_2$RuO$_4$ (or $x = 2$). This is a good metal, forming a 3-dimensional but anisotropic Landau-Fermi liquid at low temperatures [14,15]. Sr$_2$RuO$_4$ crystallizes in the undistorted single-layered K$_2$NiF$_4$-structure [19,20] (see Fig. 1) with lattice parameters quoted in Table 1. The RuO$_6$-octahedra are slightly elongated along the $c$-axis. The Ru-ions have a formal valence Ru$^{4+}$ and have a tetragonal local symmetry. The 2$p$-$O$ levels are completely filled, leaving 4 electrons in $t_{2g}$-shell of the 4$d$-Ru levels. The crystal field level scheme that would apply for an isolated Ru$^{4+}$-ion is shown in Fig. 2. The upper $e_g$-shell (not included in this figure) is empty. The splitting between the $xy$-orbitals and the degenerate $\{xz, yz\}$-orbitals is small. But the $xy$-orbitals $\pi$-hybridize with 2$p$-orbitals of all 4 in-plane O-neighbors while the $xz(yz)$-orbitals $\pi$-hybridize only with the 2 O-neighbors along the $x(y)$-axis. As a result the $xy$-bandwidth is approximately twice the $\{xz, yz\}$ bandwidth (see Fig. 3). The LDA calculations [3] give 3 Fermi surface sheets, one with essentially $xy$-orbitals at low temperatures [17,18]. Sr$_2$RuO$_4$ spin-down electron occupies $xy$-orbital (left panel); In Sr$_2$RuO$_4$ spin-down electron occupies $xz/yz$-orbitals (right panel).

The volumes contained by the Fermi surface sheets give an almost equal occupancy of each of the 3 $t_{2g}$-orbitals. If we denote the occupancy of the $\{xz, yz\}$ and $(xy)$-orbitals by $(n_{(\alpha, \beta)}, n_y)$, then Sr$_2$RuO$_4$ has the fractional occupancy $(8/3, 4/3)$. Altho’ there are clear signs of strong correlations in the enhanced effective mass (enhancements $\sim 3-4$ [21,22]) and low effective Fermi temperature, the low-temperature behavior is clearly that of a well-defined Landau-Fermi liquid.

Turning to the other end member, Ca$_2$RuO$_4$ or $x = 0$, the substitution of the smaller Ca$^{2+}$-ion for Sr$^{2+}$ does not lead to a uniform shrinking of the lattice parameter. Instead the RuO$_6$-octahedra undergo a combined rotation and tilt (Pbca-structure) so that the Ru-O bond length is preserved but the Ru-Ru separation contracts. In Fig. 4 we illustrate the relevant distortion of the crystal structure. This distortion bends the Ru-O-Ru bond angle away from 180°, thereby reducing the bandwidth of the $t_{2g}$-orbitals. Also the smaller size of the Ca$^{2+}$-ion decreases the interlayer distance (i.e. the $c$-axis lattice constant) which results in a change from elongation to a compression of the RuO$_6$-octahedra. This in turn changes the sign of the energy splitting between the $(xy)$- and $(xz, yz)$-orbitals, so that now the $xy$-orbital lies lower in energy (see Fig. 3). The crystal structure is orthorhombic (see Table 2). All RuO$_6$-octahedra are equivalent with a rotation around their long axis (001) and a tilt around the diagonal in-plane axis (110) (Fig. 4). Note all inplane O-ions are equivalent in this structure.
Ca$_2$RuO$_4$ is an AF insulator. The LDA+U method [1] which is based upon spin-orbital unrestricted Hartree-Fock equation (i.e. a static mean field treatment), generally works well for magnetic long range ordered insulators [23]. We applied this method to Ca$_2$RuO$_4$ choosing parameter values $U = 1.5$ eV and $J = 0.7$ eV for the onsite Coulomb repulsion and the intra-atomic Hund’s Rule coupling. The method converged to an AF insulator. The experimental investigations of Nakatsuji and Maeno show a complex evolution of the electronic structure which they break down into 3 concentration regions, labelled Region I ($0 < x < 0.2$), Region II ($0.2 < x < 0.5$) and Region III ($0.5 < x < 2$), each with its own characteristic behavior. Their results are summarized in the phase diagram (Fig. 5). Below we discuss each of these regions, starting with the Sr-rich region.

3.1 Region III ($2 > x > 0.5$)

The experiments of Nakatsuji and Maeno show that superconductivity is rapidly suppressed when Ca is substituted for Sr in Sr$_2$RuO$_4$. This suppression is a natural consequence of disorder for an unconventional superconductor. More interesting is the evolution of the spin susceptibility which progressively increases with Ca substitution and evolves from an enhanced Pauli susceptibility into a Curie-Weiss form. The characteristic (Curie-Weiss) temperature, $\theta_{CW}(<0)$, approaches zero for $x \rightarrow 0.5$. At the same time the linear term in the low temperature specific heat is also enhanced but the Wilson ratio defined at low temperatures is strongly enhanced and approaches a value of 40 as $x \rightarrow x_c$.

This value of $x_c = 0.5$ is a critical value, separating a metallic and orbitally ordered phase with antiferromagnetic spin correlation ($x < x_c$) from the paramagnetic metal for $x > x_c$. As mentioned above, one observes
\( \theta_{cu} \approx 0 \) for \( x \approx x_c \). Even more remarkable is the evolution of the magnetic moment which takes a value of \( S = 1/2 \) as \( x \rightarrow x_c \). This value is quite distinct from the value of \( S = 1 \) in Ca₂RuO₄ — the expected value for a localized Ru⁴⁺-ion with 2 holes in the \( t_2g \)-subshell. Moreover, alloys with \( x \approx x_c \) are metallic, not insulating. The explanation of this unexpected behavior presents a clear challenge.

As discussed above Sr₂RuO₄ is a good metal with an electronic structure that divides into two distinct and fractionally filled bands, a \( d_{xy} \)-band with \( \approx 4/3 \) electrons per Ru and the hybridized \( d_{xz, yz} \)-band pair with \( 8/3 \) electrons per Ru. Now the evolution with Ca substitution towards a Mott insulating state occurs because the bands are narrowed by rotation of the RuO₆ octahedra. In general, the evolution from a metal to a Mott-insulator is driven by growing Umklapp scattering. This is very clear in one dimension where studies of chains and ladders show insulating behavior at half-filling already for arbitrarily small Coulomb repulsion driven by elastic Umklapp scattering processes across the Fermi surface. Here we are dealing with an approximately two-dimensional multi-band situation. In the single band case the Umklapp surface, across which elastic Umklapp processes are allowed, will in general be different from the Fermi surface, but at half-filling each encloses the same volume. In Sr₂RuO₄ the fractional occupancy of each subband clearly forbids elastic Umklapp scattering across the Fermi surface in low orders. Indeed this may well be the reason that Sr₂RuO₄ forms a good Landau-Fermi liquid, even though it is clearly close to a Mott insulator. One way to enhance Umklapp scattering is to transfer electrons between the subbands. This will allow low-order Umklapp scattering, when integer occupancy of the subbands is reached.

The theoretical investigation at these concentrations is inhibited by the lack of symmetry breaking at \( x \approx x_c \). Therefore we cannot use the LDA+U method to build in the onsite correlations that are totally neglected in standard LDA calculations. Recently considerable progress has been achieved on the theory of the Mott transition in the Hubbard model by the use of the dynamic mean field theory (DMFT) method [11,12]. This is essentially an expansion around an infinite coordination number and formsulates the problem in terms of an effective Anderson impurity model which is to be solved self-consistently. In this way the growth of onsite correlations can be treated as the Mott transition is approached in a paramagnetic metal. Recent advances use LDA calculations to determine the input parameters and a non-crossing approximation (NCA) to solve the effective Anderson model.

We performed a series of calculations using this LDA + DMFT (NCA) approximation scheme [26,27] for the Sr₂RuO₄ structure. We increased the value of Hubbard- 

\[ U \] 

to examine how the onsite correlations grow. In Fig. 3 is a series of results for the density of states (DOS) in the \( xy \)- and \( (xz, yz) \)-subbands. Since these subbands have quite different widths, the onset of Mott localization occurs at different critical values of \( U \). Thus we see that as \( U \) is increased through a value of \( U \approx 1.5 \text{ eV} \) there is a transfer of electrons between the subbands so that the integer occupancy of 3 electrons and Mott localization appears in \( (xz, yz) \)-subbands while the broader half-filled \( xy \)-band remains itinerant. This unusual behavior is driven by the combination of the crystal field splitting, as shown in Fig. 3 \( [xz, yz] \) lower] and the narrower bandwidth of the \( (xz, yz) \)-orbitals. A further increase in the value of \( U \) to \( U \approx 2.5 \text{ eV} \) is required to obtain Mott localization also in the \( xy \)-subband.

These results lead us naturally to the following proposal to explain the anomalous properties in the critical concentrations \( x = x_c \). The electronic configuration is now \( (3,1) \). The 3 electrons in the \( \{xz, yz\} \)-subbands are Mott localized and have a local moment of \( S = 1/2 \). The remaining valence electrons are in the itinerant \( xy \)-band and is responsible for the metallic character. Thus at this concentration we have the unusual situation of localization in only part of the 4d-orbitals and coexisting localized and itinerant 4d-orbitals. Note that in the orthorhombic crystal structure at \( x = x_c \) the 2 subbands have different parity under reflection around a RuO₂-plane, similar to tetragonal Sr₃RuO₄, which forbids direct hybridization between the subbands. This proposal explains in a natural way the unexpected moment of \( S = 1/2 \) of the Ru-ions and the coexistence of metallic behavior and local moments.

Note that the calculations are carried out more conveniently by increasing the value of the onsite repulsion, \( U \) which however should not change appreciably with the
Table 1. Crystallographic data, which is used for LDA calculations: symmetry group, parameters of lattice, atomic positions and distance between nearest atoms. Symbol "\^" denotes that for this structure corresponding parameter do not exist.

| Compound          | Sr$_2$RuO$_4$ | Ca$_{2+}$SrO$_{0.5}$RuO$_4$ | Ca$_{2+}$Sr$_{0.5}$RuO$_4$ | Ca$_{2+}$RuO$_4$ |
|-------------------|---------------|-----------------------------|---------------------------|-----------------|
| Symmetry group    | I4/mmm        | I4$_1$/amd                   | P2$_1$/c                   | Pbca            |
| a[A]              | 3.8603        | 5.3195(1)                   | 5.3338(4)                 | 5.6323(3)       |
| b[A]              | 3.8603        | 5.3195(1)                   | 5.3162(4)                 | 11.7463(5)      |
| c[A]              | 12.729        | 25.1734(5)                  | 12.4143(8)                | 5.3877(2)       |
| V [Å$^3$]         | 189.69        | 712.33(2)                   | 352.01(4)                 | 356.45          |
| $\beta^{c}$      | /             | /                           | 90.06(1)                  | /               |
| Ca(Sr) x          | 0.0           | 0.0                          | 0.0141(21)                | 0.0021(5)       |
| Ca(Sr) y          | 0.0           | 0.25                         | 0.0373(23)                | 0.3525(2)       |
| Ca(Sr) z          | 0.14684       | 0.5492(1)                   | 0.3483(2)                 | 0.6921(5)       |
| O1 x              | 0.0           | 0.1933(2)                   | 0.1939(6)                 | 0.3095(4)       |
| O1 y              | 0.0           | 0.4433(2)                   | 0.3079(6)                 | 0.0272(2)       |
| O1 z              | 0.3381        | 0.125                        | 0.0/0.0196(5)             | 0.1952(4)       |
| O2 x              | 0.5           | 0.0                          | -0.0344(5)                | -0.0212(4)      |
| O2 y              | 0.0           | 0.25                         | -0.0064(7)                | 0.1645(2)       |
| O2 z              | 0.0           | 0.4568(1)                   | 0.1649(2)                 | -0.0692(3)      |
| Ru – O1[A]        | 1.930         | 1.929(1)                     | 1.936(3)/1.926(3)         | 2.015(2)        |
| Ru – O2[A]        | 2.061         | 2.059(3)                     | 2.056(3)/2.056(3)         | 1.972(2)        |
| Ca – O1[A]        | 2.692         | 2.399(2)                     | 2.316(7)/2.286(10)        | 2.292(3)        |
| Ca – O2[A]        | 2.439         | 2.326(4)                     | 2.294(4)/2.296(4)         | 2.287(3)        |
|                   | 2.737         | 2.664(1)                     | 2.416(12)/2.488(13)       | 2.362(3)        |
|                   |               |                              | 2.559(13)/2.444(13)       | 2.399(3)        |
|                   |               |                              | 2.772(13)/2.845(13)       | 3.118(3)        |
|                   |               |                              | 2.932(12)/2.912(13)       | 3.296(3)        |

In reality it is the bandwidth which is changing with the decreasing $x$ as the RuO$_6$-octahedra progressively rotate when Ca is substituted for Sr. The key result however is the existence of a parameter range where this partial localization is stable. The fact that we calculated only for the highly symmetric Sr$_2$RuO$_4$ structure, rather than the distorted structure is, we believe, unimportant in establishing this (3,1) configuration as a stable electronic configuration.

### 3.2 Region II (0.5 > $x$ > 0.2)

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 $P2_1/c$ [28], 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 [28]. There are now two types of in-plane oxygen ions and two types inequivalent of RuO$_6$-octahedra. The RuO$_6$-octahedra continue to be elongated in this region so that the $xy$-orbital continues to lie higher in energy. The metallic character of the alloys in this region shows that the itinerant character of the $xy$-subband is preserved, although the bandwidth will be narrowed by the additional tilting distortion of the RuO$_6$-octahedra. Our conclusion is that the (3,1) orbital occupation continues to hold also in Region II with localization of the electrons only in the $\{xz, yz\}$-subband.

### 3.3 Region I (0.2 > $x$ > 0)

The Ca-rich region is characterized by a transition to an insulating groundstate and simultaneously a change in the crystal structure. The S-Pbca structure of the groundstate in this region evolves continuously out the groundstate of pure Ca$_2$RuO$_4$. As discussed above, the change from elongated to compressed RuO$_6$-octahedra causes a switch in LDA+U in the orbital occupation numbers to (2,2) i.e. to a filled $xy$-subband and a half-filled $\{xz, yz\}$-complex. Therefore we assign the insulating groundstate in all of Region I, to an orbital occupation (2,2). The first order transition between Regions II and I as $x$ is decreased below 0.2, is to be associated with a switch in the orbital occupation from (3,1) to (2,2).

### 4 Magnetic Properties of the different regions

#### 4.1 Region III

We now turn to the magnetic properties at $x \geq x_c = 0.5$. These are dominated by the local $S = 1/2$ moments. A Kondo-type of interaction between the two bands $\langle xz, yz \rangle$...
and $xy$ can be excluded due to the absence of hybridization. The $xy$-orbital cannot hybridize with the other two, since they have opposite parity with respect to reflection on the basal plane. Via Hund’s rule coupling, however an RKKY interaction between the localized spins is induced,

$$\mathcal{H}_{\text{RKKY}} = -\sum_{\mathbf{q}} J^2_R \chi(\mathbf{q}) \mathbf{S}_\mathbf{q} \cdot \mathbf{S}_{-\mathbf{q}}$$

where $\mathbf{S}_\mathbf{q} = S_{yz,\mathbf{q}} + S_{zx,\mathbf{q}}$ and $\chi(\mathbf{q})$ is the static spin susceptibility in the $d_{xy}$-band and $J_H$ is the onsite Hund’s rule coupling, and promotes antiferromagnetic correlations. At the same time, however, Hund’s rule coupling may cause the ferromagnetic correlations through the double exchange mechanism. Thus, the two types of spin interactions mediated by the itinerant electrons of the $xy$-band tend to compensate each other, such that the net 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.

In order to gain more insight into the possible form of the orbital ordering we performed LDA+U calculations for the critical concentration $x_c = 0.5$. Ca$_{1.5}$Sr$_{0.5}$RuO$_4$ has the space group $I4_1/acd$ [23], i.e. the RuO$_6$-octahedra are only rotated around the $c$-axis with no tilting (Fig. 4b). The RuO$_6$-octahedra remain elongated to the same degree as for pure Sr$_2$RuO$_4$ such that the $xy$-orbital is still higher in energy than $(xz, yz)$-orbitals (Fig. 3 right panel). Our calculation suggests that, under these conditions, correlation yields the orbital degeneracy in a $(3, 1)$ state. LDA+U calculations generally overestimate the stability of the Mott insulating state. In the present case we find for $U = 1.5$ eV an insulating groundstate with a charge gap also in the $(xy)$-subband.

Furthermore, the result of the the LDA+U calculation shows that an orbital ordering of the AFO-type is favored yielding a ferromagnetic spin exchange. The minority-spin electrons occupy alternating $xz$- and $yz$-orbitals with a slight tilting of the orbital planes away from the $c$-axis. This tilting indicates the partial admixture of $d_{xy}$-orbitals within the LDA+U approach.

### 4.2 Region II

Since magnetic properties are intimately connected to the orbital order in $(xz, yz)$-subband, it is necessary to first examine the effect of the crystalline distortion on the orbital order. To this end we performed LDA+U calculation for this tilted structure and obtained a rather complicated orbital order. The groundstate is an AF insulator. The minority-spin electrons (1 per Ru-atom) occupy the orbitals whose planes are in average directed along the $a$-axis (in tetragonal notation $(110)$ direction). However on every one of the 4 Ru-atoms in the unit cell those planes are rotated from the $a$-axis by $+20^\circ$ and $+15^\circ$ on one layer and by $-20^\circ$ and $-15^\circ$ on the next layer. On the average the orbital orientation corresponds to the state $d_{yz} + d_{zx}$ 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 $34^\circ$ (see Fig. ??) which corresponds to the admixture of the $xy$-orbital component. The calculation of the easy axis using the second order perturbation theory for spin-orbit coupling gave the direction of the magnetic moment as along the $a$-axis (tetragonal $(110)$ direction) with a $28^\circ$ tilt from the layer plane (see Appendix). Measurements of the uniform magnetic susceptibility show a peak in the temperature dependence which is most pronounced for the $(110)$ direction of the magnetic field, in agreement with our LDA+U results [3].

### 4.3 Region I

The orbital configuration $(2, 2)$ is non-degenerate as Hund’s Rule determines a fully spin polarized $S = 1$ ionic ground-state with a single minority-spin electron in the $xy$-orbitals. The LDA+U method works well here and gives an AF Mott insulating groundstate.

Throughout Region I, there is a first order insulator to metal transition as the temperature is raised accompanied by a switch from compressed to elongated RuO$_6$-octahedra. It is tempting to interpret this as a first order transition between the orbital occupancies from $(2, 2)$ to $(3, 1)$. However a detailed examination of this proposal has not been made. In this context it would be also interesting to study the effect of pressure. Since the low-temperature phase of Ca$_2$RuO$_4$ has larger volume than the high-temperature phase (see Tab. I), pressure tends to stabilize the latter. Assuming that indeed the $(3, 1)$ electronic distribution is realized in this structural state, then an orbitally ordered phase accompanied by magnetic order based on the localized spin-1/2 degree of freedom could be realized at low enough temperature. Since the crystal structure is close to the one at $x = 0.2$ (see Tab. I) one might conclude that AF order would prevail. However, as we will see in the next section, the final form of the exchange interactions between the spins is a subtle issue, in particular, if a staggered orbital component are included.

### 5 Effective Model for the $(3,1)$ electron distribution

#### 5.1 Derivation of spin-isospin Hamiltonian

In this Section we derive the effective Hamiltonian for the localized spin and orbital degrees of freedom in the electron configuration $(\eta_{(\alpha, \beta)}, n_{m}) = (3, 1)$ which covers the boundary of region II and III and all of region II. The
electrons in the $d_{yz}$- and $d_{zx}$-orbital are localized, while the $\gamma$-band remains metallic, although it is half-filled. We ignore here this metallic band and concentrate on the localized degrees of freedom. The single hole occupying the two localized orbitals has a spin-1/2 and orbital index. The nearest-neighbor hopping due to $\tau$-hybridization between the $d_{yz}$-(x) and $d_{zx}$-orbital. The isospin operator $I$ acts on these states by $I^z|\pm\rangle = \pm|\pm\rangle$ and is a generator of an SU(2) transformation in orbital space.

We will concentrate on the strongest interaction between the localized degrees of freedom. The nearest-neighbor hopping due to $\tau$-hybridization between the $d_{yz}$- and $d_{zx}$-orbital. Including the onsite interactions the Hamiltonian for these two orbitals has the form

$$
\mathcal{H} = -t \sum_{\mathbf{i},\mathbf{a},s}(c_{\mathbf{i}+\mathbf{a},z, -,s}^\dagger c_{\mathbf{i}, -,s} + c_{\mathbf{i}+\mathbf{a},z, +,s}^\dagger c_{\mathbf{i}, +,s} + h.c.) + U \sum_{\mathbf{i},\mathbf{a},\gamma} n_{\mathbf{i},\gamma,+,\gamma} n_{\mathbf{i},\gamma,+,\gamma} + U' \sum_{\mathbf{i}} n_{\mathbf{i},s,+,s} n_{\mathbf{i},s,+,s} - 2J_H \sum_{\mathbf{i}} (S_{\mathbf{i},+,s} S_{\mathbf{i},+,s} + \frac{1}{4} n_{\mathbf{i},+,s} n_{\mathbf{i},+,s})
$$

where $t$ denotes the hopping matrix element, $U$ and $U'$ are the onsite intra- and interorbital Coulomb repulsion and $J_H$ is the Hund’s rule coupling (the vector $\mathbf{a} = (1, 0)$ and $(0, 1)$ connects the nearest neighbor sites). We can reduce the number of parameters by the relation $U = U' + 2J_H$.

We now consider the case of a nearest-neighbor bond along the $x$-direction and calculation the effective spin-spin interaction for different orbital configurations. For illustration of the processes involved we introduce the following self-explanatory notation shown in the two examples,

$$
|+,\uparrow\rangle \otimes |+,\downarrow\rangle_{i+a_x} = \left| \begin{array}{c} \uparrow \downarrow \\ \downarrow \uparrow \end{array} \right>
$$

(3) The configuration $|+,\uparrow\rangle \otimes |-,\uparrow\rangle_{i+a_x}$ does not lead to any interaction. (2) The configuration $|-,\uparrow\rangle \otimes |-,\downarrow\rangle_{i+a_x}$ yields antiferromagnetic superexchange through the exchange path,

$$
\left| \begin{array}{c} \uparrow \downarrow \\ \uparrow \downarrow \end{array} \right> \rightarrow \left| \begin{array}{c} \uparrow \downarrow \\ \downarrow \uparrow \end{array} \right> \rightarrow \left| \begin{array}{c} \downarrow \uparrow \\ \downarrow \uparrow \end{array} \right>
$$

(5) This leads to an effective Hamiltonian

$$
\mathcal{H}' = J\langle\mathbf{i} | \cdot \mathbf{s}_{i+a_x} - \frac{1}{4}
$$

with an exchange coupling constant

$$
J = \frac{4t^2}{U'}.
$$

(7)

Finally the configuration $|+,\uparrow\rangle \otimes |-,\downarrow\rangle$ gives an ferromagnetic spin coupling by the following type of path,

$$
\left| \begin{array}{c} \uparrow \uparrow \\ \downarrow \downarrow \end{array} \right> \rightarrow \left| \begin{array}{c} \uparrow \uparrow \\ \uparrow \downarrow \end{array} \right> \rightarrow \left| \begin{array}{c} \uparrow \downarrow \\ \uparrow \downarrow \end{array} \right>
$$

(8) Here the intermediate state has lower energy, if the two spins are in a triplet configuration due to the Hund’s rule coupling. The interaction energies for the intermediate states corresponding to the spin singlet and triplet state are

$$
\Delta E_{\text{singlet}} = U' + J_H
$$

(9) \quad \Delta E_{\text{triplet}} = U' - J_H

(10) so that the effective Hamiltonian can be cast into the form

$$
\mathcal{H}' = J' \left(S_i \cdot S_{i+a_x} + \frac{1 + \alpha}{2(1 - \alpha)} \right)
$$

(11) with

$$
J' = -\frac{2t^2J_H}{U'^2 - J_H^2} = -J \left(\frac{1 - \alpha}{(3\alpha - 1)(\alpha + 1)} \right)
$$

(12)

where $\alpha = U'/U < 1$. Note that $\alpha$ should be sufficiently larger than 1/3 in order that the second-order perturbation approach is valid and the electron distribution (3,1) is unique. The orbital configurations in the basis of $|+\rangle$ and $|\rangle$ are not affected in this second order perturbation scheme. Therefore the effective isospin Hamiltonian is Ising-like.

Turning to the bond along the $y$-axis we need only to exchange the role of the two orbitals ($d_{yz}$ and $d_{zx}$) and obtain the same result. Therefore we can write the complete effective Hamiltonian for the localized degrees of freedom as,
where the coefficients are given by

\[ A = \frac{3\alpha^2 + 1}{(3\alpha - 1)(\alpha + 1)} \]
\[ B = \frac{-1 - \alpha^2}{(3\alpha^2 + 1)(3\alpha - 1)(\alpha + 1)} \]
\[ C = \frac{5 - 3\alpha}{4(3\alpha - 1)} \]
\[ D = -\frac{2}{(5 - 3\alpha)(3\alpha - 1)} \]
\[ \eta = -\frac{(3\alpha - 1)(\alpha + 1)}{2(3\alpha^2 + 1)} (a^2_x - a^2_y) \]
\[ \eta' = \frac{5 - 3\alpha}{3\alpha - 1} (a^2_x - a^2_y) \]

Note that the coefficients \( \eta \) and \( \eta' \) have opposite sign for the x- and y-axis bonds.

Lattice distortions breaking the tetragonal symmetry yield a bias for the local orbital configuration. For the two basic orthorhombic distortions, described by the lattice strain combinations \( \epsilon_1 = \epsilon_{xx} - \epsilon_{yy} \) and \( \epsilon_2 = \epsilon_{xy} \) (tetragonal notation), we can add the following coupling terms to the Hamiltonian,

\[ \mathcal{H}_{\text{dist}} = \sum_i [K_1 \epsilon_1 I_x^i + K_2 \epsilon_2 I_y^i] \]

where \( K_1 \) and \( K_2 \) are coupling constants. Note that the first term corresponds to a uniform field parallel to the z-axis of the isospin, while the second is a transverse field. Both drive a ferro-orbital correlation.

### 5.2 Mean field discussion

We analyze now the properties of our effective model by means of mean field theory ignoring fluctuations and the influence of the itinerant \( xy \)-band. This discussion shows that the main features of the different phases where the electron distribution (3,1) is applicable are indeed described well within our reduced effective model. A discussion beyond the mean field level will be given elsewhere.

#### 5.2.1 Tetragonal system

The analysis of the parameters of the effective Hamiltonian shows that a higher energy scale is associated with the isospins than with the spins. Their basic interaction is of Ising-AFO-type, because \( C > 0 \) for all \( \alpha \) in the proper range. As a consequence the spins correlate ferromagnetically at a lower energy scale. Hence, we will decouple the effective Hamiltonian for the spin and isospin with mean values,

\[ m_I = \langle I^z_i \rangle \quad \text{and} \quad s = \langle S^z_i \rangle \]

where \( m_I \) is staggered with opposite sign on the two sublattices and \( s \) is uniform. The coupled self-consistent equations are obtained readily,

\[ m_I = \sum_{r=\pm 1} e^{\beta C r m_I} \cosh \left( \beta \left( A \left( \eta_s^2 - \frac{r m_I^2}{2} \right) + B \right) s \right) \]
\[ s = \sum_{r=\pm 1} e^{\beta C r m_I} \sinh \left( \beta \left( A \left( \eta_s^2 - \frac{r m_I^2}{2} \right) + B \right) s \right) \]

where \( \beta = J/k_B T \) is the inverse temperature in units of the exchange energy \( J \). The isospin order has the higher transition temperature \( T_o \) determined by the equation

\[ k_B T_o = \frac{CJ}{4} \]

The onset of FM order occurs at much lower temperature so that it is justified to consider \( m_I \) as already saturated, \( m_I = 1/2 \). Then Curie-temperature for the spin is given by

\[ k_B T_C = -\frac{J}{4} \left[ a \left( \eta_s^2 - \frac{1}{4} \right) + B \right] \]

In Fig. 8 we show the phase diagram of temperature versus the parameter \( \alpha = U'/U \) which determines the coupling constants. The tendency towards FM order is in good agreement with the LDA+U result for \( x = 0.5 \), apart from the fact that the contributions of \( xy \)-orbital have been ignored. This analysis suggests that the orbital order is governed by the exchange processes included in our Hamiltonian.
5.2.2 Crystal distortion

Let us now consider the influence of a spontaneous crystal deformation which characterizes region II (0.2 < x < 0.5). We will not discuss the origin of the distortion, but take it as given with a strength which depends on x. The FO bias introduced by a uniform lattice distortion is in competition with the AFO exchange interaction. In particular, a finite strain \( \epsilon_2 \) would introduce a transverse field in the effective Ising Hamiltonian for orbital interactions. An Ising-model in a transverse field has a quantum critical point beyond which the AFO order would be suppressed for any temperature.

We consider here the general case where both \( \epsilon_1 \) and \( \epsilon_2 \) are finite, as realized in Region II. We distinguish now between the two sublattices \( A \) and \( B \) on the square lattice and assign different mean fields to them. Analogous to the case above we may separate the spin and the isospin problem. First we consider the isospin problem in the absence of spin correlation. The corresponding self-consistent equations have the form,

\[
m_{IA} = f(\beta, m_{IB}) \quad \text{and} \quad m_{IB} = f(\beta, m_{IA})
\]

(26)

with

\[
f(\beta, m) = -\frac{2Cm + K_1 \epsilon_1}{2\sqrt{(2Cm + K_1 \epsilon_1)^2 + K^2_2 \epsilon_2}}
\]

(27)

\[
\times \tanh \left( \beta \sqrt{(2Cm + K_1 \epsilon_1)^2 + K^2_2 \epsilon_2} \right).
\]

It is easy to verify from this set of equations that for finite crystal distortion there is a uniform component \( m = (m_{IA} + m_{IB})/2 \) at all temperatures and that the staggered moment \( m_I = (m_{IA} - m_{IB})/2 \) occurs only at low temperature or not at all, depending on which side of the quantum critical point the system lies. Hence the staggered moment may play a minor role on the background of the uniform FO orbital arrangement.

The numerical solution of Eq. (26,27) is shown in Fig. 9, assuming that both \( \epsilon_1 \) and \( \epsilon_2 \) are finite with a ratio \( K_1 \epsilon_1 / K_2 \epsilon_2 = 3/2 \). Turning \( \epsilon_1,2 \) gradually on we observe that the staggered AFO component is diminished in favor of the FO arrangement (Fig. 9a) with a critical point where the staggered component completely vanishes. Fig. 9b shows the orbital orientation on the two sublattices \( |d\rangle_{A,B} = \cos \phi_{A,B} |+\rangle + \sin \phi_{A,B} |\rangle \). Obviously, very close to the quantum critical point we find a dominant FO arrangement with a weak staggered component. This describes qualitatively the favored ordering pattern in the LDA+U calculation for \( x = 0.2 \), where in each layer the orbital plane has an alternating orientation of 20° and 15° with respect to the [110] (FO) direction. The comparison with our mean field data suggests that the system is then rather close to the quantum critical point.

Assuming again that at the energy scale where spin correlation sets in the orbital pattern is basically established, we draw the diagram of transition temperature versus the strain in Fig.9c. Then we analyze the spin correlation fixing the orbital order by the \( T = 0 \)-solution of Eq. (26,27). This is again justified by the observation that the isospin mean field has saturated at the temperature when spin order sets in. We find weak ferromagnetic coupling for small distortion and stronger antiferromagnetic coupling for larger distortion. The crossover in the spin interaction is still in the region of rather strong staggered orbital correlations. Note that the crossover point between FM and AF spin exchange depends on \( \alpha \) and moves towards larger \( K_\epsilon \) for smaller \( \alpha \).

Guided by this phase diagram we may interpret the region II in terms of increasing strain as we progress from \( x = 0.5 \) to 0.2. At \( x = 0.2 \) the quantum critical point has been approached but not passed. This interpretation is entirely based on the localized orbitals of the \( \alpha-\beta \)-bands. From the LDA+U calculation we conclude, however, that the \( \gamma \)-band is also involved in the spin correlations, as is seen in the tilting of the orbital plane away from the z-axis for the minority spins. As mentioned earlier the \( \gamma \)-band should introduce an RKKY-interaction via the Hund’s rule coupling, which is most likely antiferromagnetic, thus further diminishing the FM correlation.

An interesting feature occurs in our effective model in connection with the sign change of the spin exchange interaction as mentioned above. Ca\(_{2-x}\)Sr\(_x\)RuO\(_4\) as a random alloy does not provide a uniform crystal deformation, but the strain depends on the local Sr and Ca distribution around each Ru-ion. Thus, in the regime of switching between FM and AF coupling, this can lead to frustration effects at low temperature. Recent experimental data indicate indeed a glass-like behavior [30].
6 Discussion

We have presented a consistent picture for the unusual phases of the isoelectronic alloy series Ca$_{2-x}$Sr$_x$RuO$_4$ based on the full multi-band electronic structure (see Table). 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$_{1.2}$Sr$_{0.8}$RuO$_4$. The actual metal to insulator transition occurs between the Ca-rich Regions I ($0 \leq x < 0.2$) and II ($0.2 \leq x < 0.5$).

We interpret this transition as driven by a change in the orbital occupancy to a completely filled $xy$-band leaving 2 electrons in the localized ($xz$, $yz$) bands. In this case the ordered local spin has the conventional value, $S = 1$, whereas in the metallic Region II short-range correlations of a local $S = 1/2$ spin combined with orbital order are realized, generating a pronounced anisotropy in the magnetic response.

One of the curious aspects of Region II is the fact that the half-filled $xy$-orbital remains itinerant. It is not easy to test experimentally which among the bands is really responsible for the metallic behavior. The basic feature of the state we propose is the presence of a single Fermi surface of electron-like character in the $xy$- or $\gamma$-sheet. One method which might be able to probe this proposal is angle-resolved photo emission spectroscopy (ARPES).

Recently the electronic structure and magnetic properties of Ca$_{2-x}$Sr$_x$RuO$_4$ have also been investigated by LSDA calculations [29]. The authors have concluded that the crystal structure distortions (rotation, tilt and compression of the O-octahedra) when Ca is substituted for Sr lead to a narrowing and shifting of the bands and hence to the enhancement of ferro- and antiferromagnetic instabilities. However these calculations do not include the effects of onsite Coulomb interactions between d-electrons which are responsible for the suppression of charge fluctuations and for the Mott metal-insulator transition as Ca$_2$RuO$_4$ is approached.

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A Effect of spin-orbit coupling

For the Ru 4$d$-t$_{2g}$-orbitals spin-orbit coupling plays an important role. If we restrict to the three $t_{2g}$-orbitals, the onsite spin-orbit coupling Hamiltonian can be given by

$$H_{s-o} = \lambda \sum_{i} \sum_{\alpha, \beta, \gamma} \sum_{s,s'} c_{i\alpha s}^\dagger \sigma_{s's'}^\alpha c_{i\beta s'}$$

where $\lambda$ is the coupling constant and $\epsilon_{abc}$ the completely antisymmetric tensor ($a, b, c = \{x, y, z\}$). We identify the indices $x, y$ and $z$ with the orbitals $d_{xy}, d_{xz}$ and $d_{yz}$, respectively.

In the framework of LDA+$U$ calculation the easy axis direction was calculated via minimizing the energy of spin-orbit coupling in the second order perturbation theory as a function of Euler angles ($\alpha, \beta, \gamma$) defining the direction of magnetization:

$$E(\alpha, \beta, \gamma) = \sum_{\mathbf{k}} \sum_{n\sigma, n'\sigma'} \frac{E_{n\sigma\mathbf{k}} - E_{n'\sigma'\mathbf{k}}}{E_{n\sigma\mathbf{k}}(\mathbf{k}) - E_{n'\sigma'\mathbf{k}}(\mathbf{k})} |\langle \Psi_{n\sigma\mathbf{k}}^\dagger | \hat{s}_z | \Psi_{n'\sigma'\mathbf{k}} \rangle|^2,$$

$$\hat{s}_z = \sum_{\mu} \hat{I}_z \cdot \hat{s}_z = \sum_{\mu} \hat{I}_z \cdot \hat{U}_{\mu\nu}(\alpha, \beta, \gamma) s_\nu$$

where $E_{n\sigma\mathbf{k}}(\mathbf{k})$ is the energy of $n$-th band for spin projection $\sigma$ at point $\mathbf{k}$ in the Brillouin zone, $f_{n\sigma\mathbf{k}}$ is equal 1 if the corresponding band is occupied (its energy is below the Fermi level) and is equal 0 in the opposite case. $\Psi_{n\sigma\mathbf{k}}$ is the Bloch wave function, $\hat{I}_z$ and $\hat{s}_z$ are components of vector operators of orbital and spin moments, $\hat{U}_{\mu\nu}(\alpha, \beta, \gamma)$ is transformation matrix for rotation of a vector for Euler angles ($\alpha, \beta, \gamma$).

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