Nature of the Mott transition in Ca$_2$RuO$_4$

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(Dated: May 26, 2010)

We study the origin of the temperature-induced Mott transition in Ca$_2$RuO$_4$. As a method we use the local-density approximation+dynamical mean-field theory. We show the following. (i) The Mott transition is driven by the change in structure from long to short c-axis layered perovskite (L-Pbca $\rightarrow$ S-Pbca); it occurs together with orbital order, which follows, rather than produces, the structural transition. (ii) In the metallic L-Pbca phase the orbital polarization is $\sim 0$. (iii) In the insulating S-Pbca phase the lower energy orbital, $\sim xy$, is full. (iv) The spin-flip and pair-hopping Coulomb terms reduce the effective masses in the metallic phase. Our results indicate that a similar scenario applies to Ca$_{2-x}$Sr$_x$RuO$_4$ ($x \leq 0.2$). In the metallic $x \leq 0.5$ structures electrons are progressively transferred to the $xz/yz$ bands with increasing $x$, however we find no orbital-selective Mott transition down to $\sim 300$ K.

PACS numbers: 71.27.+a, 71.30.+h, 75.25.Dk, 71.15-m

The layered perovskite Ca$_2$RuO$_4$ (Ru 4$d^4$, $t_{2g}^4e_g^0$) undergoes a paramagnetic metal-paramagnetic insulator transition (MIT) at $T_{\text{MIT}} \sim 360$ K $^1$. A similar insulator-to-metal transition happens also by application of a modest ($\sim 0.5$ GPa) pressure $^2$ and finally when Ca is partially substituted by Sr (Ca$_{2-x}$Sr$_x$RuO$_4$, $x \leq 0.2$) $^3$$^4$. The nature of these transitions, in particular across $x = 0.2$, has been debated for a decade $^3$$^5$$^6$. While it is clear that a Mott-type mechanism makes the 2/3-filled $t_{2g}$ bands insulating, two opposite scenarios, with different orbital occupations $n = (n_{xy}, n_{xz} + n_{yz})$ and polarizations $p = n_{xy} - (n_{xz} + n_{yz})/2$, have been suggested. In the first, only the $xy$ band becomes metallic, i.e. the transition is orbital-selective (OSMT) $^5$; $n$ and $p$ jump from (2, 2) and 1 in the insulator to (1, 3) and $\sim 1/2$ in the metal. In the second, there is a single Mott transition, assisted by the crystal-field splitting $\Delta = \epsilon_{xy} - \epsilon_{yz} > 0$ $^5$$^6$$^7$, similar to the case of 3$d^4$ perovskites $^1$$^3$: $p > 0$ in all phases. To date the issue remains open. Recently, for $x = 0.2$ a novel ($xy$ insulating, $n_{xy} = 1.5$ and $p = 1/4$) OSMT was inferred from angle-resolved photoemission (ARPES) experiments $^8$, but other ARPES data show three metallic bands and no OSMT $^8$.

Ca$_2$RuO$_4$ is made of RuO$_2$ layers built up of corner-sharing RuO$_6$ octahedra (space group Pbca $^8$$^9$$^{13}$). This structure (Fig. 1) combines a rotation of the octahedra around the c axis with a tilt around the b axis. It is similar to that of the tetragonal unconventional superconductor Sr$_2$RuO$_4$; the corresponding pseudo-tetragonal axes $x$, $y$ and $z$ are shown in Fig. 1. The structure of Ca$_2$RuO$_4$ is characterized by a long c axis (L-Pbca) above $T_S \sim 356$ K and by a short one (S-Pbca) below $T_S$. The L- and S-Pbca phases are also observed in Ca$_{2-x}$Sr$_x$RuO$_4$ for all $x \leq 0.2$, but $T_S$ decreases with increasing $x$; for $x > 0.2$ the system becomes tetragonal (for $x < 1.5$: $I4_1/acd$, c-axis rotations only).

Because of the layered structure, the $\sim xz, yz$ band-width, $W_{xz/yz}$, is about one half of the $\sim xy$ bandwidth, $W_{xy}$. Due to the structural distortions, the $t_{2g}$ manifold splits into non-degenerate crystal-field states. Many-body studies of 3-band Hubbard models show that a large difference in bands widths, a crystal-field splitting $\Delta$ and a finite Coulomb exchange interaction can affect the nature of the Mott transition $^8$$^{13}$$^{16}$. Simple models neglect, however, the actual effects of distortions on the electronic structure; such effects could be crucial $^{13}$ to the mechanism of the MIT. On the other hand, approximate treatments of the many-body effects $^6$, or the neglect of the spin-flip and pair-hopping contribution to the Coulomb exchange interaction, could also lead to wrong conclusions on the origin of the transition.

FIG. 1: (Color online) Ca$_2$RuO$_4$ L-Pbca $^8$$^9$$^{13}$. The primitive cell is orthorhombic with 4 formula units; $x \sim (a + b)/2$, $y \sim (b - a)/2$, $z = c$ are the pseudotetragonal axes. Ru sites $i$ at $T_i$ ($i = 2, 3, 4$) are equivalent to site 1 at $T_1$, with operations $a \rightarrow -a$ ($i = 2$), $c \rightarrow -c$ ($i = 3$), $b \rightarrow -b$ ($i = 4$) and $T_i \rightarrow T_1$. In the S-Pbca structure the tilting angle is about twice as large, while the rotation angle is slightly smaller.
In this Letter we address the problem by means of the LDA+DMFT (local-density approximation + dynamical mean-field theory) approach [17] with a continuous-time quantum Monte Carlo (QMC) solver [18]. This method allows us to treat realistically both the material-dependence and the many-body effects. We show that the Mott transition occurs because of the L-→S-Pbca structural phase transition, which is also responsible for \( \sim xy \) orbital order (OO). In the metallic phases we find, with increasing \( x \), a progressive transfer of electrons from \( xy \) to \( xz/yz \) (\( p \leq 0 \)); down to \( \sim 300 \) K, we find, however, no orbital-selective Mott transition.

We use the \textit{ab-initio} downfolding approach based on the \( N \)-th Order Muffin-Tin Orbital (NOMTO) method to construct from first-principles material-specific Wannier functions [14] which span the \( t_{2g} \) bands, and the corresponding, material-specific, three-band Hubbard models, with full local Coulomb interaction [19]

\[
H = - \sum_{nm'i'i'} \frac{\tilde{t}_{nn'}^{i'i'}}{c_m^{i\sigma}c_{m'}^{i'\sigma}} + U \sum_{im} n_{im\uparrow} n_{im\downarrow} + \sum_{im \neq im'} \left( (U - 2J - J\delta_{\sigma,\sigma'}) n_{im\sigma} n_{im'\sigma'} \right) - J \sum_{im \neq im'} \left[ c_{i\uparrow}^{\dagger} \left( c_{im\uparrow}^{\dagger} c_{im'\downarrow}^{\dagger} + c_{im\downarrow}^{\dagger} c_{im'\uparrow}^{\dagger} \right) c_{i'm'\downarrow} \right].
\]

Here \( c_{i\sigma}^{\dagger} \) creates an electron with spin \( \sigma \) in the Wannier state \( m \) at site \( i \), and \( n_{im\sigma} = c_{i\sigma}^{\dagger} c_{im\sigma} \). The \textit{ab-initio} parameters \( t_{nn'}^{i'i'} \) (Table I) are the crystal-field splittings (\( i = i' \)) and hopping integrals (\( i \neq i' \)). \( U \) and \( J \) are the direct and exchange screened Coulomb interaction. We use \( U = 3.1 \) eV and \( J = 0.7 \) eV, in line with experimental [11, 20, 21] and theoretical [22] estimates. The last row in [1] describes the spin-flip and pair-hopping Coulomb terms. We solve [11] by DMFT [23] with a weak-coupling continuous-time QMC [18] solver. We retain the full self-energy matrix in orbital space, \( \Sigma_{m,m'} [14] \). Our calculations yield the Green function matrix on the imaginary axis; we obtain the spectral matrix on the real axis by using a stochastic approach [24]. For limit cases (no spin-flip and pair-hopping terms) we perform comparative calculations with an alternative LDA+DMFT scheme, based on the projection of LDA Bloch states (obtained via the projector-augmented wave method [25], Vienna Ab-Initio Simulation Package [26]) to local orbitals [27] and a Hirsch-Fye QMC solver [28]. The parameters obtained with the two methods are very similar.

The nearest-neighbor hopping integrals \( t_{xx}^{i,i+x}, t_{yy}^{i,i+y}, t_{yz}^{i,i+x} \), progressively decrease going from the ideal tetragonal Sr$_2$RuO$_4$ (see Ref. [29]) to the L-Pbca and then the S-Pbca structure of Ca$_2$RuO$_4$; correspondingly, the band-width decreases from 2.8 eV (L-Pbca) to 2.5 eV (S-Pbca). The cause is the increase in tilting of the RuO$_6$ octahedra and deformation of the Ca cage, via Ru-O but also Ca-Ru and Ca-O covalency [14]; for similar reasons the crystal-field splitting increases from \( \sim 100 \) meV (L-Pbca) to \( \sim 300 \) meV (S-Pbca). The crystal-field orbitals are displayed in Fig. 2. For the L-Pbca phase our LDA calculations yield \( p_{LDA} \sim 0 \). This may appear surprising, since at 2/3 filling due to the difference in bandwidth \( (W_{xz/yz} \sim 1.5 \text{ eV} \text{ and } W_{xy} \sim 2.8 \text{ eV}) \) one might expect \( p < 0 \). Such effect, however, is cancelled by the crystal-field splitting of about 100 meV; since the lowest energy state is \( \left| 1 \right> = 0.932 \left| xy \right> + 0.259 \left| yz \right> + 0.255 \left| xz \right> \) (see Fig. 2 and Table I), i.e. close to \( |xy\rangle \), neglecting the difference in bandwidth, the crystal-field splitting favours \( p > 0 \). For the S-Pbca structure we find \( W_{xz/yz} \sim 1.3 \text{ eV} \) and \( W_{xy} \sim 2.5 \text{ eV} \), i.e. the band-widths decrease by about 0.2 eV. The crystal-field splitting is 300 meV, and the lowest energy crystal-field orbital, \( |1\rangle \), is basically identical to \( |xy\rangle \). The effect of the crystal-field is stronger than in the L-Pbca structure leading to \( p_{LDA} \sim 0.37 \).

The LDA+DMFT solution of Hamiltonian [11] yields the following results: For the L-Pbca structure we find a metallic solution down to very low temperatures; the orbital polarization is \( p = 0 \) at 390 K, i.e. close to the LDA value. The self-energy (Fig. 3) exhibits a narrow Fermi-liquid regime with kinks [24]; a (lower) estimate of the effective masses of the quasi-particles, obtained from the slope of Im\( \Sigma_{m,m}(i\omega_n) \) at the first Matsubara frequency, is \( m^*/m \sim 5.0 \) (xy) and \( m^*/m \sim 4.2 \) (xz, yz). We find

| \( \text{L-Pbca Ca}_2\text{RuO}_4 \) |
|---|
| 100 | 10 | -88 | -6 | 75 | 242 | -50 | 230 |
| 010 | 242 | -88 | -35 | 75 | 10 | 26 | 230 |

| \( \Delta \mathcal{E}_{n=1} \) |
|---|
| 103 | (2) | \begin{pmatrix} 0.259 & 0.255 & 0.932 \\ 0.785 & -0.618 & -0.050 \\ 0.550 & 0.744 & -0.360 \end{pmatrix} |

| \( \text{S-Pbca Ca}_2\text{RuO}_4 \) |
|---|
| 100 | 11 | -61 | -25 | 38 | 123 | -47 | 205 |
| 010 | 123 | -61 | -34 | 38 | 11 | 45 | 205 |

TABLE I: Ca$_{2-x}$Sr$_x$RuO$_4$ \( (x = 0, 0.2) \): Hopping integrals \( t_{nn'}^{i,i'} \) between sites \( i \neq i' \), and \( (x = 0) \) crystal-field splitting \( \Delta \mathcal{E}_{n=1}/m\text{eV} = \alpha - \varepsilon_1 (\alpha = 1, 2, 3) \) and orbitals at site 1. Orbitals and hopping integrals for sites 2, 3 and 4 can be obtained using symmetries (Fig. 1).
similar behavior in Sr$_2$RuO$_4$; in Ca$_2$RuO$_4$ the mass enhancement is larger, because of the narrower band-width. Lowering the temperature down to 290 K turns the system into a ferromagnet with (almost) half-metallic behavior and $p \sim -0.05$ (the occupation of $|xy\rangle$ slightly decreases). The correlated bands for Ca$_2$RuO$_4$ are shown in Fig. 2. Along ΓX we find dispersive bands, while along XS the bands become almost flat.

For the S-Pbca structure the situation is completely different. We find a MIT between 390 K and 290 K, in very good agreement with the experimental 360 K [1]. At 580 K the spectral function exhibits a pseudo-gap; $n_{xy} \sim 1.9$ and $n_{xz/yz} \sim 1.1$, and the polarization is already as large as $p \sim 0.8$. At 290 K the gap is open and about 0.2 eV wide (see Fig.3), while $p \sim 1$. The most occupied state is basically identical to the LDA lowest energy crystal-field orbital (Table I); the orbital order is close to $xy$ ferro-order, with a small antiferro component. LDA+$U$ calculations for the anti-ferromagnetic phase yield an OO consistent with our results for the paramagnetic phase [5, 6]. Such orbital order in the S-Pbca phase and none in the L-Pbca phase is in line with transport and optical conductivity data [5].

Can this scenario be extended to Ca$_{2-x}$Sr$_x$RuO$_4$ ($x \leq 0.2$)? Let us examine the limit system $x = 0.2$, for which the L-Pbca phase persists down to 10 K. Neglecting the chemical effects of the Ca → Sr substitution and disorder effects, for the 10 K structure we find crystal-field splittings of 81 and 110 meV, slightly ($\sim 0.1$ eV) broader $t_{2g}$ bands than for $x = 0$, and $p_{\text{LDA}} \sim -0.03$. The main difference with the L-Pbca structure of Ca$_2$RuO$_4$ is in the crystal-field orbitals (e.g. $\langle xy|1\rangle \sim \langle xy|2\rangle \sim 0.66$), and can be ascribed to the differences in octahedra tilting and rotation, and corresponding distortions of the cation cage. All these effects stabilize the metallic solution. With LDA+DMFT (390-290 K) we find three metallic bands, in line with ARPES results from Ref. [6], with $m^*/m \sim 3.7$ ($xz$), 4.4 ($yz$), 5.6 ($xy$); $p \sim -0.14$. While the details slightly differ, depending on $x$, we conclude that for $x \leq 0.2$ the temperature-induced Mott transition is mostly driven by the change in structure, not by Cdoping. We find no OSMT down to 290 K.

What happens for $x > 0.2$? For the $x = 0.5$ structure [33] the crystal-field states are $|1\rangle = |xy\rangle$, and $|xz\rangle$, $|yz\rangle$, the crystal-field splitting is small, $p_{\text{LDA}} = -0.02$, $W_{xy} \sim 2.7$ eV, $W_{xz/yz} \sim 1.6$ eV. LDA+DMFT at 390 K yields again a metallic solution with $m^*/m \sim 4.0$ ($xz$/$yz$) and 5.6 ($xy$), and three metallic bands, in agreement with ARPES [33]; $p \sim -0.15$ at 390-290 K.

Thus, outside the S-Pbca phase we always find a metal, in line with transport and optical conductivity data [5].
Dashed lines: $A_{1.1}$ Dashed lines: $A_{2.2}$ and $A_{3.3}$. Left: density-density terms only. Right: rotationally invariant Coulomb vertex. First row: L-Pbca, $T=390$ K. Second row: S-Pbca, $T=290$ K. Inset: Real (thick lines) and imaginary (thin lines) self-energies.

With increasing $x$, $n_{xz} + n_{yz}$ increases, in line with XAS [37]; $p \sim 0$ or slightly negative, approaching the $p = -1/2$ of the OSMT scenario [8]; we find, however, no OSMT down to 290 K.

In conclusion, we have studied the origin of the metal-insulator transition in Ca$_2$RuO$_4$. We find that it is driven by the structural L→S-Pbca transition. Two mechanisms compete: while a small $W_{xz/yz}$ band width ratio enhances the occupation of the $xz/yz$ orbitals ($p < 0$) and could lead to an orbital-selective Mott transition with $p = -1/2$ [8], a large crystal-field splitting $\Delta_{3.1}$, with $|1⟩ \sim |xy⟩$ as the lowest energy state, favors $xy$ orbital order and $p > 0$, as in Ref. 13. In the $x = 0$ L-Pbca structure the two effects compensate: $\Delta_{3.1}/W_{xy} \sim 0.04$, $⟨1|xy⟩ \sim 0.93$ and $W_{xz/yz}/W_{xy} \sim 0.54$. We find a metallic solution above and well below $T_{\text{MIT}} \sim 360$ K, with orbital polarization $p \sim 0$ (no orbital order) at $T \sim 390$ K. At low temperatures the system becomes a ferromagnetic metal, in line with (moderate) pressure studies [4].

In the $x = 0$ S-Pbca structure $\Delta_{3.1}/W_{xy} \sim 0.13$, sizeably larger than for the L-Pbca structure, $⟨1|xy⟩ \sim 0.97$, and $W_{xz/yz}/W_{xy} \sim 0.52$; the system becomes insulating around $T_{\text{MIT}}$ and $p \sim 1$ ($xy$ ferro orbital order), in excellent agreement with experiments; orbital order follows, rather than drives, the transition. Our results indicate that this scenario can be extended to Ca$_{2-n}$Sr$_n$RuO$_4$ for all $x \leq 0.2$. Finally, for the metallic $x \leq 0.5$ phases we find that, differently than in the crystal-field scenario [13], $p \sim 0$ or negative, slowly approaching the $-1/2$ of Ref. [8]; with increasing $x$, but, down to $\sim 300$ K, we find no orbital-selective Mott transition.

Calculations were performed on the Jülich BlueGene/P. We thank A. Hendricks, T. Koethe, and H. Tjeng for sharing with us their data before publication.

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[33] The effect of the full substitution Ca → Sr is the following: for $x = 0$ both crystal-field splitting (76 and 147 meV) and $t_{2g}$ band-width increase slightly, $⟨1|xy⟩ \sim 0.89$, $p_{\text{LDA}} \sim 0.16$. For $x = 0.5$ the crystal-field splitting increases to $\sim 80$ meV, with $|1⟩ = |xy⟩$, and $p_{\text{LDA}} = 0.25$.
[34] For $x = 0.1$ LDA+DMFT (projection scheme) yields a metal for L-Pbca ($p \sim 0.03$ at 580 K) and a deep pseudogap for S-Pbca ($p \sim 0.85$ at 390 K). For $x = 0.15$ (L-Pbca) we find a metal at 390 K with $p \sim -0.07$.
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