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Subband Filling and Mott Transition in $Ca_{2-x}Sr_xRuO_4$

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A new concept is proposed for the paramagnetic metal insulator transition in the layer perovskite $Ca_{2-x}Sr_xRuO_4$. Whereas the pure Sr compound is metallic up to large Coulomb energies due to strong orbital fluctuations, structural changes induced by doping with Ca give rise to an interorbital charge transfer which makes the material extremely sensitive to local correlations. Using dynamical mean field theory based on finite temperature multiband exact diagonalization, it is shown that the combination of crystal field splitting and on-site Coulomb interactions leads to complete filling of the d_{xy} band and to a Mott transition in the half-filled $d_{xz,yz}$ bands.

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The layer perovskite $Ca_{2-x}Sr_xRuO_4$ has attracted wide interest during recent years because of the complex sequence of electronic and magnetic phases which arise when Sr is isoelectronically substituted by Ca [1–3]. While the pure Sr compound exhibits unconventional superconductivity [4], the structural distortions induced by the smaller Ca ions ultimately lead to an antiferromagnetic Mott insulator. The physical mechanism of how this multiband material with four electrons per Ru ion evolves from the metal Sr_2RuO_4 towards the insulator Ca_2RuO_4 is presently not well understood.

According to band structure calculations [5], the t_{2g} orbitals in Sr_2RuO_4 are approximately equally occupied. Because of the planar geometry, these bands split into a wide, nearly two-dimensional d_{xy} band and two narrow, nearly one-dimensional $d_{xz,yz}$ bands. Clearly, the Mott transition in such a highly anisotropic system cannot be understood in terms of single-band models or multiband extensions assuming degenerate subbands. To analyze the role of local Coulomb interactions in $Ca_{2-x}Sr_xRuO_4$, several aspects were investigated within dynamical mean field theory (DMFT) [6], using a variety of impurity solvers to treat on-site correlations [7–12].

While it is generally agreed upon that Coulomb interactions in Sr_2RuO_4 lead to a sizeable band narrowing and effective mass enhancement, and a shift of the d_{xy} van Hove singularity towards the Fermi level due to $d_{xz,yz} \rightarrow d_{xy}$ charge transfer [7,9–11], the Mott transition near the Ca end of the phase diagram is complicated because of the charge rearrangement among t_{2g} orbitals when the Ca/Sr concentration is varied. Using the noncrossing approximation [13], Anisimov *et al.* [8] obtained successive, "orbital-selective" Mott transitions upon increasing the on-site Coulomb energy U: first for the narrow $d_{xz,yz}$ bands and subsequently for the wide d_{xy} band. These transitions arise via a $d_{xy} \rightarrow d_{xz,yz}$ charge transfer, i.e., $(n_{xy}, n_{xz}, n_{yz}) \approx (2/3, 2/3, 2/3) \rightarrow (0.5, 0.75, 0.75)$. Orbital-selective Mott transitions, with the same interorbital charge transfer, were found also by Dai *et al.* [12] within slave boson mean field calculations for a three-band model consisting of wide and narrow semicircular densities of states. To account for the Ca induced octahedral distortions [14], the d_{xy} band was assumed to be narrower than the $d_{xz,yz}$ bands. Accordingly, in contrast to Ref. [8], d_{xy} is the first band to become insulating with increasing U. An important parameter in this work is the *negative* crystal field splitting $\Delta = \epsilon_{xz,yz} - \epsilon_{xy}$, which *decreases* the relative d_{xy} occupancy. The Mott transitions then occur at smaller values of U than for $\Delta = 0$. In both models, a second, opposite interorbital charge transfer due to further structural modifications, i.e., $(n_{xy}, n_{xz}, n_{yz}) = (0.5, 0.75, 0.75) \rightarrow (1.0, 0.5, 0.5)$, is required in the limit $x \rightarrow 0$ to yield the antiferromagnetic insulating properties of Ca_2RuO_4 [8].

In the present work, we use finite temperature exact diagonalization (ED) DMFT [15] to study the nature of the Mott transition in $Ca_{2-x}Sr_xRuO_4$. Since a t_{2g} tight-binding Hamiltonian including the full complexity of the octahedral distortions as a function of Ca/Sr concentration is not yet available, we use the Sr_2RuO_4 density of states components as a single-particle starting point (see Fig. 1).

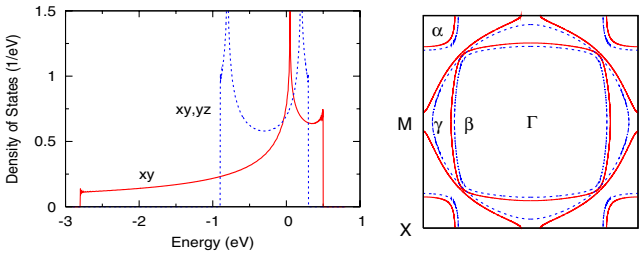

FIG. 1 (color online). Left panel: density of states of Sr_2RuO_4. Solid (red) curve: wide d_{xy} band; dashed (blue) curve: narrow $d_{xz,yz}$ bands ($E_F = 0$). Right panel: Fermi surface (schematic) of Sr_2RuO_4 (dashed blue curve) and $Ca_{1.5}Sr_{0.5}RuO_4$ (solid red curve). In the former (latter) case, the d_{xy} van Hove singularity at M is above (below) E_F.

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As shown by Fang *et al.* [14], rotation, tilting, and flattening of oxygen octahedra gives rise to *increasing* d_{xy} orbital occupancy with increasing Ca concentration: in the limit $x = 0$, the spin-averaged occupancy is $n_{xy} \approx 0.83$, compared to $n_{xy} \approx 0.63$ for $x = 2$. To account for this charge transfer, we allow, in contrast to Ref. [12], for a *positive* crystal field splitting between $d_{xz,yz}$ and d_{xy} states. For instance, a lowering of the d_{xy} bands by $\Delta = 0.2(0.4)$ eV yields $n_{xy} \approx 0.74(0.83)$.

The main result of this work is a new mechanism for the Mott transition in this multiband system: for realistic values of the Coulomb energy U and crystal field splitting Δ, we find an enhanced filling of the d_{xy} band with increasing U. Once the $d_{xz,yz} \rightarrow d_{xy}$ charge transfer is complete, i.e., $(n_{xy}, n_{xz}, n_{yz}) \rightarrow (1.0, 0.5, 0.5)$, a Mott transition takes place in the remaining half-filled $d_{xz,yz}$ bands. The key quantity in this picture is the structure induced occupancy of the d_{xy} band rather than its width.

This scenario differs qualitatively from the ones proposed in Refs. [8,12]: instead of successive transitions in the half-filled d_{xy} band and in the 3/4-filled $d_{xz,yz}$ bands, we find a common d_{xy} band filling and $d_{xz,yz}$ Mott transition. The d_{xy} band filling, induced by the combined effect of crystal field and Coulomb interactions, signifies a change from a correlated metallic state to a correlated band insulating state and does not correspond to a Mott transition. On the other hand, since a full d_{xy} band implies half-filled $d_{xz,yz}$ bands, the latter readily undergo a standard metal insulator transition. Thus, the present three-band system does not exhibit orbital-selective Mott transitions. Our solution solely relies on the structure induced increase in d_{xy} occupancy [14] and is consistent with the $(n_{xy}, n_{xz}, n_{yz}) = (1.0, 0.5, 0.5)$ configuration obtained for Ca_2RuO_4 within LDA + U [8]. Thus, we do not require the more complex path $n_{xy} \approx 2/3 \rightarrow 1/2 \rightarrow 1$ as Sr is replaced by Ca.

The details of our multiband ED approach are given in Ref. [15]. All calculations are carried out for full Hund exchange J. To obtain the orbital occupancy n_i as a function of U, we assume $J = U/4$. The interorbital Coulomb energy is $U' = U - 2J$. To achieve fast convergence we use the cluster size $n_s = 9$ (2 bath levels per impurity orbital); for greater precision, specific points are calculated with $n_s = 12$. The temperature is assumed to be $T = 20$ meV. We focus here on the paramagnetic Mott transition.

Figure 1 shows the t_{2g} density of states components for Sr_2RuO_4, derived from a tight-binding Hamiltonian [7] fitted to the local density approximation band structure of Ref. [5]. The band extrema were adjusted slightly in order to accommodate four electrons below E_F. The d_{xy} van Hove singularity lies about 60 meV above E_F. The right panel shows the Fermi surface. The γ sheet corresponds to d_{xy}, the α and β sheets to $d_{xz,yz}$. The latter do not cross because of a small hybridization term. Also shown is the Fermi surface for a crystal field $\Delta = 0.1$ eV. Since the d_{xy} van Hove singularity now lies below E_F, the γ sheet has turned from electronlike to holelike.

Figure 2 summarizes the variation of the t_{2g} orbital occupancies with on-site Coulomb energy U. In the case of Sr_2RuO_4 ($\Delta = 0$), a gradual charge transfer from $d_{xz,yz}$ to d_{xy} states is found, in agreement with the trend found within quantum Monte Carlo DMFT for small U [7]. The system is seen to remain metallic up to large U. This result is consistent with previous calculations [9] which revealed no Mott transition up to $U = 4$ eV. Near $U_c \approx 10$ eV the interorbital charge transfer is complete with $n_{xy} = 1$. The remaining half-filled $d_{xz,yz}$ bands then undergo a Mott transition (see below).

Note that the filling of the d_{xy} band for $\Delta = 0$ accelerates towards increasing U. The reason for this trend is that the larger d_{xy} occupancy reduces the intra-t_{2g} screening of U. Since at the same time the occupancy of the $d_{xz,yz}$ bands approaches one half, the tendency for the latter bands to undergo a Mott transition becomes rapidly favorable. In the absence of the d_{xy} band, the half-filled $d_{xz,yz}$ bands (width $W = 1.2$ eV) would exhibit a common metal insulator transition at $U_c = 1.4$ eV ($U_c \approx 0.8W$ for twofold degenerate semicircular bands and $J = U/4$ [16]). Thus the results for $\Delta = 0$ may be interpreted as $d_{xz,yz}$ Mott transition delayed by strong orbital fluctuations [17].

In view of this picture it is plausible that, at finite Ca concentrations, the greater initial occupancy of the d_{xy} band associated with $\Delta > 0$ gives rise to complete d_{xy} filling and a $d_{xz,yz}$ Mott transition at progressively lower values of U_c. This is confirmed by the results shown in Fig. 2. According to Fang *et al.* [14] the crystal field

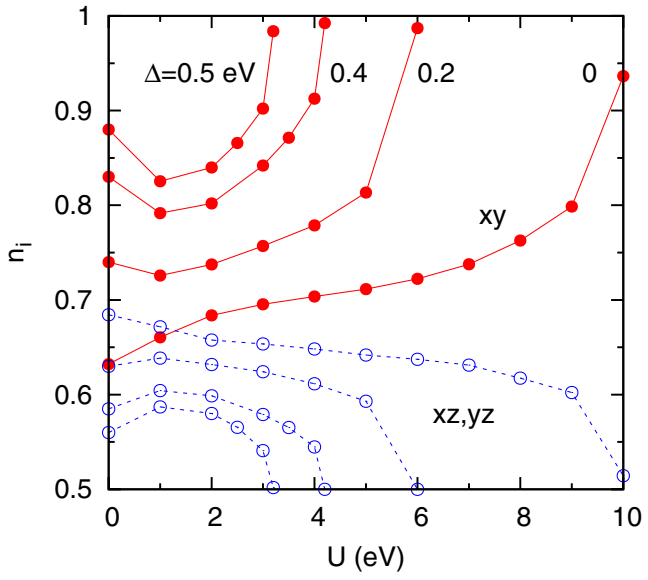

FIG. 2 (color online). Orbital occupancy n_i as a function of Coulomb energy for various crystal field splittings Δ, derived within ED/DMFT for $T = 20$ meV. Solid (red) dots: n_{xy}, empty (blue) dots: $n_{xz,yz}$. The lines are guides to the eye.

splitting for Ca_2RuO_4 induced by octahedral distortions is about 0.4 eV. The d_{xy} band filling and $d_{xz,yz}$ Mott transition is then shifted to $U_c \approx 4$ eV. Thus, the reduced orbital fluctuations greatly diminish the delay of the Mott transition in the half-filled $d_{xz,yz}$ bands.

In the range $0.5 \leq x \leq 2.0$ the octahedral distortions consist mainly of rotations about the z axis. The associated lowering of the d_{xy} band is rather small, giving $\Delta < 0.2$ eV [14]. According to the results shown in Fig. 2, the correlation induced d_{xy} filling and $d_{xz,yz}$ Mott transition then occur at $U_c > 6$ eV. In this doping region the system therefore remains metallic. This result is consistent with angle resolved photoemission data [2] and optical data [3] which show that near $x = 0.5$, all t_{2g} states are itinerant.

A crystal field $\Delta = 0.1$ eV is large enough to push the d_{xy} van Hove singularity below E_F. This also agrees with the photoemission results [2] which yield nearly the same Fermi surface for $Ca_{1.5}Sr_{0.5}RuO_4$ and Sr_2RuO_4, except that, because of the lowering of the van Hove singularity, the γ sheet has changed from electronlike to holelike, as indicated in Fig. 1. These data are naturally explained by the results shown in Fig. 2, whereas they are difficult to reconcile with the trend towards a half-filled d_{xy} band proposed in Refs. [8,12].

As shown in Ref. [14], Sr substitution via Ca does not only enhance the d_{xy} occupancy, but also gives rise to d_{xy} band narrowing as a result of the less effective hopping via the displaced intraplanar O neighbors. To account for this effect we have evaluated the phase diagram shown in Fig. 2 for W_{xy} reduced by a factor of 2. Qualitatively the same picture is obtained as before, demonstrating that the $d_{xz,yz}$ Mott transition is primarily affected by the occupancy of the d_{xy} band and not by its width.

To prove that d_{xy} band filling and $d_{xz,yz}$ Mott transition coincide in the present system we show in Fig. 3 the t_{2g} quasiparticle spectra for $\Delta = 0.4$ eV. To avoid uncertainties stemming from the extrapolation from Matsubara frequencies to real frequencies we give here the spectra of the cluster Green's functions, $A_i(\omega) = -\frac{1}{\pi}\mathrm{Im}\, G_i(\omega + i\delta)$, with $\delta = 50$ meV. While spectral details differ from those of the solid [15], the cluster results are adequate for the distinction between metallic and insulating behavior. The spectra for $U = 3.0$ eV reveal that all subbands are metallic and exhibit appreciable spectral weight below the single-particle bands, associated with lower Hubbard bands. In contrast, at $U = 4.5$ eV the d_{xy} band is filled and the half-filled $d_{xz,yz}$ bands exhibit a clear separation into upper and lower Hubbard bands. The transition between these two regions occurs at $U_c \approx 4.2$ eV. Note that the insulating gap arises between the filled d_{xy} band and the upper Hubbard bands of the half-filled $d_{xz,yz}$ bands.

We point out that, in general, the d_{xy} band filling and $d_{xz,yz}$ Mott transition do not need to take place at the same U. For instance, if the $d_{xz,yz}$ bands were much wider, their Mott transition would occur above the d_{xy} band filling. Also, a stronger crystal field could give a d_{xy} filling at very small U and a Mott transition in the half-filled $d_{xz,yz}$ bands at a larger U. Because of the small width of these bands, the trend seen in Fig. 2 suggests that this possibility should arise only for $\Delta > 0.5$ eV. An analogous effect was discussed by Manini *et al.* [18] for a two-band model with equal bands of semicircular density of states, offset via a

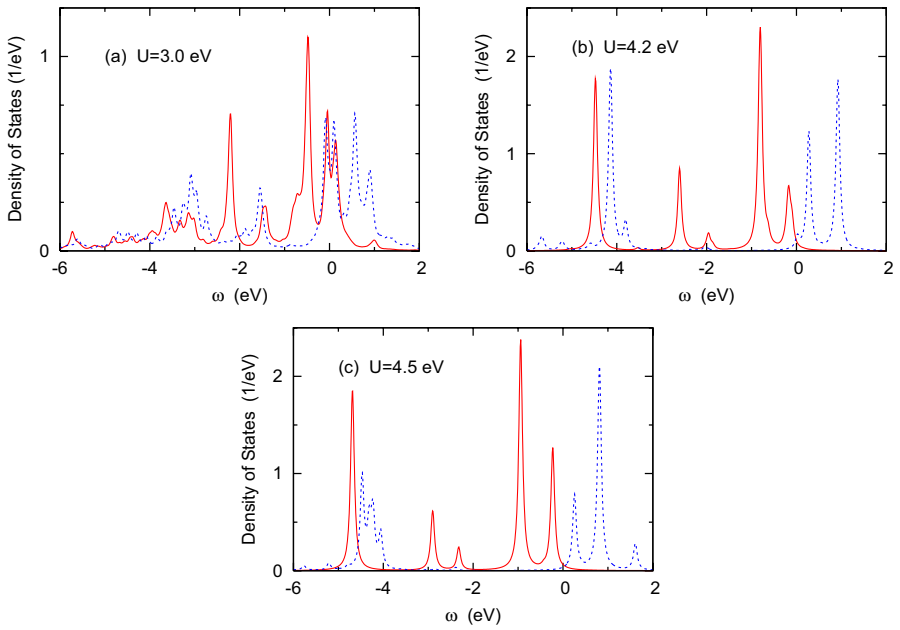

FIG. 3 (color online). Quasiparticle spectra calculated using ED/DMFT for crystal field splitting $\Delta = 0.4$ eV; $T = 20$ meV. (a) Metallic region $U = 3.0$ eV; (b) transition near $U_c \approx 4.2$ eV; (c) insulating region $U = 4.5$ eV. Solid (red) curves: d_{xy} band; dashed (blue) curves: $d_{xz,yz}$ bands.

crystal field Δ. For unit total occupancy and small Δ, a single transition was found where one band is pushed above E_F and the other (then half-filled) exhibits a Mott transition. For larger Δ, one band is emptied at small U while the second remains metallic up to a Mott transition at larger U.

We also note that the Mott transitions in the $3d^1$ perovskites $LaTiO_3$ and $YTiO_3$ reveal an almost complete emptying of two t_{2g} subbands and a metal insulator transition in the remaining nearly half-filled band [19]. Moreover, in V_2O_3 ($3d^2$) the Mott transition occurs for nearly half-filled e_g' subbands and an almost empty a_g band [20]. Evidently, in these multiband systems the Mott transition is made feasible by a striking suppression of orbital fluctuations.

In the work discussed above the $d_{xz,yz}$ bands are degenerate. In real Sr_2RuO_4 these orbitals interact weakly, giving slightly different subband densities of states $N_{xz\pm yz}(\omega)$ of identical width. Ca induced octahedral distortions will enhance these differences, so that the Mott transition in these subbands becomes nontrivial. This will be addressed in future studies.

To analyze the Mott transition in $Ca_{2-x}Sr_xRuO_4$ we have focused on the variation of the subband occupancies with Coulomb energy. In reality, U should be roughly constant as a function of x, with $U \approx 3.1$ eV and $J \approx 0.7$ eV according to constrained local density approximation calculations for $x = 2$ [11]. Thus, in Fig. 2 a vertical line near $U = 3$ eV qualitatively covers the low temperature phase diagram. $\Delta = 0$ corresponds to metallic Sr_2RuO_4. $\Delta \approx 0.1$ eV represents $Ca_{1.5}Sr_{0.5}RuO_4$, which is also metallic. Finally, the results for $\Delta \geq 0.4$ eV indicate that the metal becomes unstable since n_{xy} rapidly approaches unity and $n_{xz,yz}$ one half: the favorable electronic configuration for a Mott transition [21].

In summary, the paramagnetic metal insulator transition in the layer perovskite $Ca_{2-x}Sr_xRuO_4$ has been investigated within multiband finite temperature ED/DMFT. The results suggest a new concept following from the enhanced d_{xy} occupancy induced by Ca doping. Instead of orbital-selective Mott transitions, we find a common transition where the d_{xy} is completely filled and the remaining half-filled $d_{xz,yz}$ bands undergo a standard metal insulator transition. In the pure Sr compound strong orbital fluctuations preclude this transition, despite the narrow width of the t_{2g} subbands. Thus, realistic Coulomb energies give rise only to a weak $d_{xz,yz} \rightarrow d_{xy}$ charge transfer. This transfer is enhanced by the structural changes due to $Sr \rightarrow Ca$ substitution. Accordingly, orbital fluctuations are reduced and the material becomes highly sensitive to local correlations. In the Ca rich compound orbital fluctuations are sufficiently weak that the Mott transition occurs at realistic values of U. On the basis of this picture it would be very interesting to study the region $x \leq 0.5$ more closely in order to understand the orbital-selective mass enhancement [3] and the rich magnetic phases of this material [1].

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