

Electron-lattice coupling, orbital stability, and the phase diagram of $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$

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Hartree-Fock calculations are presented of a theoretical model describing the $(\text{Sr,Ca})_2\text{RuO}_4$ family of compounds. Both commensurate and incommensurate magnetic states are considered, along with orbital ordering and the effect of lattice distortions. The concept of interaction-driven orbital stability is introduced. A coherent description of the observed phase diagram is obtained involving relatively weak correlations and an insulating state stabilized by lattice distortions.

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I. INTRODUCTION

The two dimensional perovskite ruthenate series $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ presents a rich phase diagram,¹ evolving as x is varied from the Fermi-liquid-triplet superconductor Sr_2RuO_4 to the antiferromagnetic (Mott) insulator Ca_2RuO_4 . The origin and indeed the nature of some of the phases remains the subject of controversy. A further element of interest has been added by surface studies,² which indicate that (perhaps contrary to intuition) the Mott insulating state is less stable on the surface than in the bulk. In particular, bulk $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ exhibits a metal to insulator transition as the temperature is decreased below 150 K,¹ whereas surface sensitive probes place the transition at ≈ 125 K.²

In this paper, we present systematic Hartree-Fock calculations which shed new light on the physics of $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$. While a prior theoretical literature exists,³⁻⁸ our analysis involves new features, including the study of heretofore unexplored parameter ranges, of incommensurate magnetic phases, and of Jahn-Teller coupling to the apical oxygen. We also show that interaction effects, in particular a Hund's coupling, can act to stabilize a system against orbital disproportionation. This phenomenon has apparently been overlooked in the previous literature on orbitally degenerate transition metal oxides. We argue that it is important in the ruthenate materials, explaining among other things why the ‘‘orbitally selective Mott transition’’ proposed by Ref. 7 apparently does not occur and why the surface ferromagnetism observed in ‘‘GGA’’ calculations⁴ does not seem to occur in the actual compounds. This physics may be expected to be of importance in other orbitally degenerate transition metal oxides as well.

The Hartree-Fock method used here has the advantage of simplicity and flexibility, permitting the study of a wide variety of parameter ranges and physical effects. The method of course has well-known deficiencies, including a very poor representation of $T > 0$ physics and an inability to capture the correlations associated with the Mott metal-insulator transition or with low dimensional fluctuations. However, for materials in which correlation effects are not too strong it may be expected to provide a reasonable view of the ground state phase diagram, which is the object of study here.

The rest of this paper is organized as follows. In Sec. II we present the Hamiltonian and approximations used. Section III explicates, via a simple model calculation, the phys-

ics of ‘‘interaction-driven orbital stability.’’ In Sec. IV we present our calculated phase diagrams, and Sec. V relates the results to the behavior of the actual materials. Section VI is a conclusion and a discussion of further implications of our results.

II. MODEL AND METHOD

We study a model Hamiltonian derived from a tight-binding approximation to the calculated band structure⁹ and supplemented by electron-electron and electron-lattice interactions:

$$H = H_{band} + H_{e-e} + H_{e-latt} + H_{latt}. \quad (1)$$

The near-Fermi-level states are derived from Ru t_{2g} symmetry d -states (admixed with oxygen) and are well described by a tight-binding dispersion $H_{band} = H_{xy} + H_{xz,yz}$ with

$$H_{xy} = \sum_{k\sigma} \varepsilon_k^{xy} d_{k\sigma xy}^\dagger d_{k\sigma xy}, \quad (2)$$

$$H_{xz,yz} = \sum_{k\sigma} (d_{k\sigma xz}^\dagger d_{k\sigma yz}^\dagger) \begin{pmatrix} \varepsilon_k^{xz} & \varepsilon_k' \\ \varepsilon_k' & \varepsilon_k^{yz} \end{pmatrix} \begin{pmatrix} d_{k\sigma xz} \\ d_{k\sigma yz} \end{pmatrix}, \quad (3)$$

where $\varepsilon_k^{xy} = \varepsilon_0^{xy} - 2t(\cos k_x + \cos k_y) - 4t_1 \cos k_x \cos k_y$, $\varepsilon_k^{xz} = \varepsilon_0^{xz,yz} - 2t_2 \cos k_x - 2t_3 \cos k_y$, $\varepsilon_k' = -4t_4 \sin k_x \sin k_y$ and $\varepsilon_k^{yz}(k_x, k_y) = \varepsilon_k^{xz}(k_y, k_x)$. Quantum oscillation measurements imply that $\varepsilon_0^{xy} = 0.62$, $\varepsilon_0^{xz,yz} = 0.32$, $t = 0.42$, $t_1 = 0.17$, $t_2 = 0.30$, $t_3 = 0.03$ and $t_4 = 0.04$ (eV).¹⁰ These band parameters give $n_{xy} = 1.31$ and $n_{xz} = n_{yz} = 1.35$, almost $4/3$. A crucial question, discussed in more detail later, is how the orbital occupancies change as parameters are varied.

The electron-electron term, $H_{e-e} = \sum_i H_{e-e}^{(i)}$, is

$$H_{e-e}^{(i)} = U \sum_a n_{ia\uparrow} n_{ia\downarrow} + (U' - J) \sum_{a>b,\sigma} n_{ia\sigma} n_{ib\sigma} + U' \sum_{a\neq b} n_{ia\uparrow} n_{ib\downarrow} + J \sum_{a\neq b} d_{ia\uparrow}^\dagger d_{ib\uparrow}^\dagger d_{ib\downarrow}^\dagger d_{ia\downarrow}. \quad (4)$$

We have written in Eq. (4) in the conventional notation¹¹ in which U , U' , J , are the intraorbital Coulomb, interorbital Coulomb, interorbital exchange interactions, respectively, and we have omitted a pair-transfer (J') interaction which does not affect the Hartree-Fock results. For d -orbitals, U ,

U' , and J are functions of only two of independent linear combinations of the fundamental atomic physics (Slater) parameters F_0, F_2, F_4 . One combination involves the multiplet averaged interaction F_0 , along with a small admixture of F_2 and F_4 and is expected to be strongly renormalized by solid state effects;¹² the other involves the combination of F_2 and F_4 which determines J and is expected¹² to be much less influenced by solid state effects. The precise linear combinations of F_2 and F_4 depend on the strength of the ligand field and are not important here, but in cubic symmetry $U=U'+2J$. (In a tetragonal environment small corrections occur, neglected here for simplicity.) We therefore set $U=U'+2J$ and explore a range of U and J values, which is equivalent to changing F_0 and electronic bandwidth.

Finally, the electron-lattice coupling and lattice distortion energy are given by

$$H_{e-latt} + H_{latt} = \lambda \sum_i \tau_{3i} Q_i + \frac{1}{2} K \sum_i Q_i^2. \quad (5)$$

Here, $\tau_3 = n_{xy} - \frac{1}{2}(n_{xz} + n_{yz})$, and Q represents a normal coordinate of the RuO₆ distortion (apical oxygen displacement). λ and K are the electron-lattice coupling constant and the spring constant, respectively. The electron-lattice coupling considered here is a Jahn-Teller coupling.

We use the Hartree-Fock approximation to determine the ground state phase diagram of the model. This approximation is useful because it permits the examination of wide parameter ranges. While it is known to provide a very poor account of $T > 0$ phenomena such as magnetic transition temperatures, it provides a reasonable description of the possible ground state phases, especially of more weakly correlated materials. The main qualitative $T=0$ deficiency of the Hartree-Fock approximation is an inability to describe the physics associated with the Mott metal-insulator transition. We will argue below that the ruthenates should be understood as relatively weakly correlated materials in the sense that Mott physics is not the dominant effect over most of the phase diagram.

III. ORBITAL STABILITY

The Hartree-Fock results to be presented later reveal an apparently previously unnoticed effect, namely that in appropriate circumstances interactions, which are usually thought to favor orbitally ordered states, can in fact favor orbitally symmetric states. In this section we present a simple one-atom calculation which reveals the generality of the idea.

In conventional atomic physics one deals with an isolated atom for which the relevant states have definite values of particle number. Minimization of the atomic energy at a fixed particle number leads to a ground state with the maximal angular momentum, with excited state energies are determined by the higher Slater parameters, F_2, F_4 , i.e., by J . In other words, in the standard atomic physics ground state, the available particles are typically not distributed evenly over the available orbitals: the state is orbitally disproportionated.

For an atom in a metallic environment the electron number on a given site is not a good quantum number, although

the mean electron occupancy is fixed by the chemical composition of the material in question. In this case it is more appropriate to compute the interaction energy using a density matrix. For comparison to the Hartree-Fock calculations presented below, we consider minimizing the interaction energy, Eq. (4), with respect to a density matrix corresponding to a mean charge density per orbital n_a and spin density per orbital m_a . We find $(n/m)_{tot} = \sum_a (n/m)_a$

$$E_{ee}[n_a, m_a] = \frac{U(n_{tot}^2 - m_{tot}^2)}{4} + \frac{U-5J}{2} \sum_{a>b} n_a n_b + \frac{U-J}{2} \sum_{a>b} m_a m_b. \quad (6)$$

One sees that unlike in the isolated atom case the F_0 (i.e., U) parameter contributes to interaction energy differences between states with the same average charge and spin density. At fixed total density n_{tot} and for a given number of orbitals n_{orb} , the term $\sum_{a>b} n_a n_b$ is maximized by the uniform density $n_a = n_{tot}/n_{orb}$. Thus in a paramagnetic state ($m_a=0$ for all a) for $J/U < 1/5$ an orbitally disproportionated state minimizes the interaction energy, whereas for $J/U > 1/5$ a state of uniformly occupied orbitals minimizes the interaction energy. For spin polarized states the situation becomes more complicated, because the m_a and n_a are not independent ($m_a \leq n_a$). For fully spin polarized states ($m_a = n_a$), the condition for disproportionation becomes $J/U > 1/3$.

These arguments are merely illustrative, because of course other terms including hybridization and ligand field splittings contribute to energy differences. They indicate, however, that in a solid state environment interactions may sometimes inhibit orbital disproportionations that the phenomenon has validity beyond the present, Hartree-Fock approximation (although of course the precise values of Slater/Kanamori parameters at which the interactions change from promoting to inhibiting disproportionation depend on the approximation considered) and that the phenomenon is of relevance beyond the present, ruthenate, context to a wide range of transition metal oxides. As an example of the types of behavior which may occur in more realistic situations we show in Fig. 1 the U dependence of the orbital occupancies computed via the Hartree-Fock approximation to the paramagnetic phase of Eq. (1) at different J , assuming a level energy difference such that at $U=0$ there is a small disproportionation, $n_{xy}=1.4$ and $n_{xz,yz}=1.3$. One sees that for small J the interaction amplifies the disproportionation whereas for $J > U/5$ the interaction suppresses the disproportionation. These results suggest that caution should be exercised in using calculations which neglect the “ J ” term in the interaction Hamiltonian^{5,7} to interpret data.

IV. PHASE DIAGRAM

The ground state phase diagram is calculated by comparing energies of different phases including paramagnetic (PM), a ferromagnetic (FM) state, commensurate antiferromagnetic states with $\vec{q}_C = (\pi, 0)$ (C-AFM) and $\vec{q}_G = (\pi, \pi)$ (G-AFM), and incommensurate magnetic (ICM) states. The

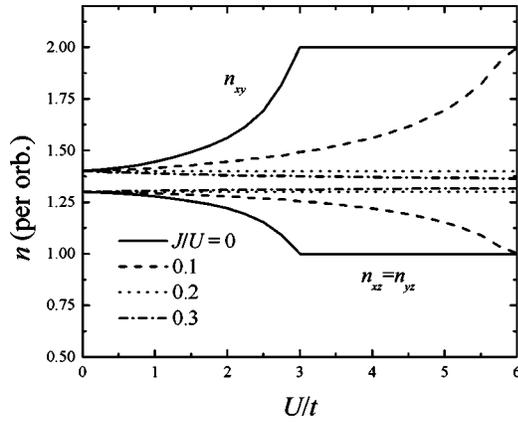


FIG. 1. Orbital occupancies in PM phase as functions of U/t for a band structure $n_{xy}=1.4$ and $n_{xz}=n_{yz}=1.3$ at $U=0$.

G-AFM state is the one proposed by Nakatsuji and Maeno¹ for Ca_2RuO_4 . A variety of incommensurate states were considered. Within Hartree-Fock, the favored ICM states have wavevector very close to $\vec{q}_{IC}=(2\pi/3, 2\pi/3)$ [the leading instability is at $q^* \simeq (0.69\pi, 0.69\pi)$]. This wavevector regime is selected by a susceptibility maximum arising from the near nesting of the quasi-one-dimensional $\{xz, yz\}$ bands. Strong magnetic scattering peaked near q^* has been experimentally observed in Sr_2RuO_4 ,¹³ however, for more calcium-rich compounds ($\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ with $x=0.5$ or 0.4) stronger fluctuations are observed at other wave vectors^{14,15} (although incommensurate magnetic order is apparently never observed). We believe that the qualitative properties we find for the state we studied are representative of those found for other states.

We also considered the possibility of orbital ordering (OO), i.e., changing the relative occupancy of xy , xz and yz states. Uniform states were found in which $n_{xy} \neq n_{xz, yz}$, but two-sublattice states similar to those reported in Ref. 6 were never found to minimize the energy in the parameter ranges studied here. One possible reason for the difference in results is that the systems studied in Ref. 6 were very small (typically 2×2 with open boundary conditions), and therefore perhaps influenced by finite size effects, which would tend to favor two sublattice states.

Figure 2 shows the numerically obtained ground-state phase diagram for the model without electron-phonon coupling as a function of U/t and J/U . At large U , two phases are observed; a ferromagnetic metal with a small degree of orbital disproportionation (FM) and an insulating antiferromagnetic phase (G-AFMOO). In the G-AFMOO state, the xy -orbital is occupied by two electrons and the other two electrons sit on the $\{xz, yz\}$ -orbitals forming a half-filled band gapped by the AF order. Even in the absence of long range order, the strong correlations and commensurate filling of the $\{xz, yz\}$ -bands would lead to Mott insulating behavior, although this behavior of course cannot be produced by the Hartree-Fock approximation considered here. Because it involves orbital disproportionation the G-AF phase is only stable for small J/U . Turning now to the small U regime, we find that as U/t is increased the first phase transition is of second order, and is to an ICM state characterized by a wave

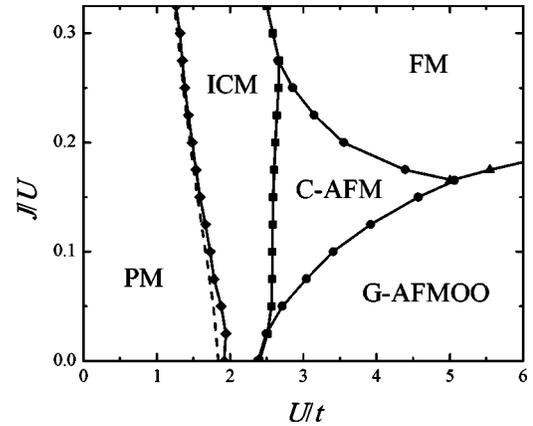


FIG. 2. Phase diagram without electron-phonon coupling for band parameters corresponding to $n_{xy}=n_{xz}=n_{yz}=4/3$ at $U=0$. PM: paramagnetic state, FM: ferromagnetic state, C-AFM: C-type antiferromagnetic state [$\vec{q}_C=(\pi, 0)$], G-AFM: G-type antiferromagnetic state [$\vec{q}_G=(\pi, \pi)$], ICM: incommensurate magnetic state [$\vec{q}_{IC}=(2\pi/3, 2\pi/3)$], OO: orbital disproportionation with $n_{xy} \neq n_{xz, yz}$. Only the G-AFM state is insulating. Symbols connected by solid lines indicate phase boundaries (first order, except for the ICM/PM boundary) between the indicated states. Dotted line: second-order phase transition from PM to ICM with \vec{q}^* determined by the susceptibility maximum in the linearized Hartree-Fock equation. As $U/t \rightarrow \infty$ the G-AFMOO-FM phase boundary asymptotes to $J/U = 1/3$ as discussed in the text.

vector $q^* \simeq (0.69\pi, 0.69\pi)$ determined by near nesting of the $\{xz, yz\}$ bands. As U is further increased a first order transition occurs to a phase which is FM or C-AFM depending on J/U . Note that in computing the energy of the ICM phase we approximated the ICM vector by $\vec{q}_{IC}=(2\pi/3, 2\pi/3)$. The errors due to this approximation may be estimated from the difference between the dotted and solid lines in Fig. 2. At weak coupling the wave vector characterizing the magnetic phase is found to be determined by the maximum in the calculated susceptibility. We note that in addition to the peak at q^* which leads to the order found in the calculations, the susceptibility χ implied by the tight-binding parameters also has a strong peak at a smaller $\vec{q}_{IC2} \sim (0.5, 0.5)$, arising from the xy band, so that ICM order at this wave vector is also possible in principle. In the present calculation the q^* instability always wins. However the energy differences are small, raising the possibility that beyond-Hartree-Fock corrections could switch the ordering wave vector to \vec{q}_{IC2} .

We now consider the robustness of these results to beyond-Hartree-Fock physics. Of course the precise locations of phase boundaries will change by factors of order unity. The important question is the robustness of the qualitative features. The strong coupling phases have a transparent interpretation in terms of minimizing E_{ee} , Eq. (6), and seem unlikely to change. The smaller U phases present additional issues. One question is whether beyond-Hartree-Fock effects could eliminate the incommensurate phase altogether. We note that a dynamical mean field study of a simple one-band model of carriers Hunds-coupled to classical core spins found that at intermediate dopings and small

values of the Hunds coupling the ground state was an incommensurate magnet with a wave vector given by the Hartree-Fock estimate, but that as the Hunds coupling increased the ferromagnetic phase grew at the expense of the incommensurate phase.¹⁶ Further study, especially of the larger J region of the phase diagram, using beyond-Hartree-Fock methods which allow for the possibility of ICM ordering would be very desirable.

The crucial feature of the no-phonon Hartree-Fock phase diagram is that the G-AFM phase exists only at relatively small Hunds coupling J and is separated from the paramagnetic metal phase describing Sr_2RuO_4 by a sequence of intermediate phases. The G-AFM phase is, as first proposed by Nakatsuji and Maeno,¹ likely to be the phase observed in Ca_2RuO_4 . As we shall discuss below, there is evidence that J is not small in the actual materials. Further, the predicted intermediate phases are not observed. These observations suggest that the no-phonons model is an incomplete description of the $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ system, and that an additional coupling which favors orbital disproportionation is present in the materials. A very natural possibility is a Jahn-Teller coupling to a “ Q_3 -type” lattice distortion (a volume-preserving increase in the Ru-apical-oxygen distance and a decrease in the Ru-planer-oxygen distance).

Figure 3 shows results obtained keeping the electron-lattice coupling equation (5) for $J=0.1U$ [panel (a)], $J=0.2U$ [panel (b)], and $J=0.25U$ [panel (c)]. In each case increasing the Jahn-Teller coupling increases the range over which the G-AFM phase is found. For sufficiently strong electron-phonon coupling and sufficiently weak correlations an additional orbitally ordered phase (PM-OO) is found. This phase is essentially the G-AFM phase, but with only partial orbital polarization and without magnetic order. We also note that for strong enough electron-phonon coupling, direct transitions either from a paramagnetic state to the G-AFM or from the ICM state to the G-AFM state are possible.

V. RELATION TO DATA

In this section we discuss the relation between the Hartree-Fock calculation and experiments in $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$, beginning with Sr_2RuO_4 . This material is a paramagnetic metal and at very low temperatures is believed to become a triplet superconductor.¹⁷ The high purity and large size of available samples has allowed the accumulation of a very extensive set of data. In particular, quantum oscillation measurements (Table 6 in Ref. 10) have directly determined the Fermi surface, the “thermodynamic” quasiparticle mass enhancement, the spin polarization as a function of the applied field, and (with perhaps less certainty) the dynamical mass enhancement (the renormalization of cyclotron frequency). All of the masses are enhanced over the predictions of band theory, suggesting the importance of correlations, but the degree of mass enhancement exhibits a revealing dependence on the type of mass and the Fermi surface sheet. The cyclotron mass pertains to the low frequency current-current correlation function. In a Galilean-invariant compound it would not be renormalized at all¹⁸ but of course the narrow d -bands important in transition metal oxides are very far from the

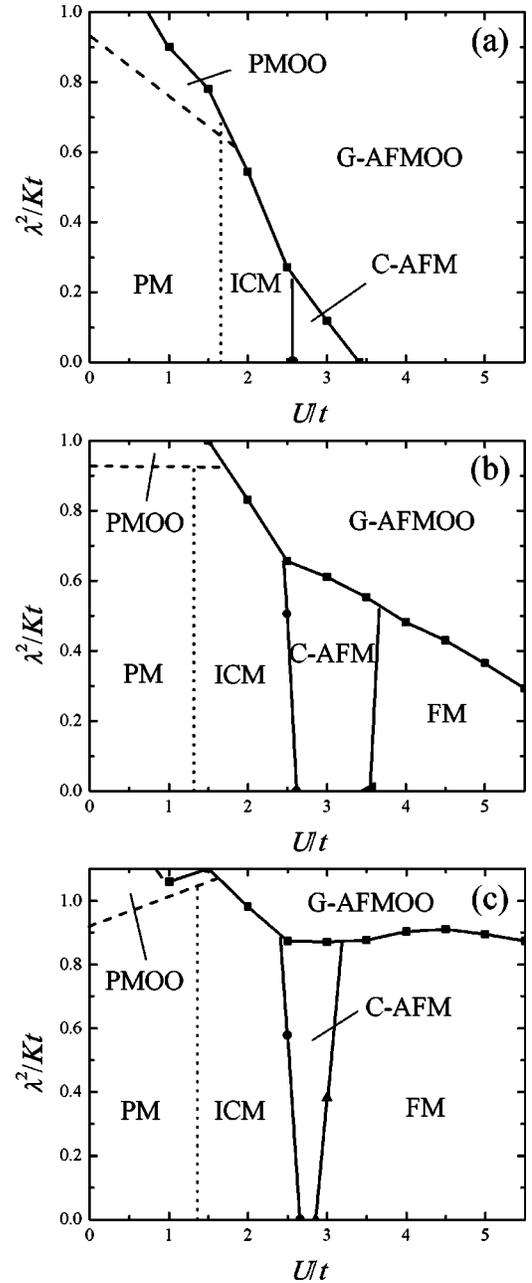


FIG. 3. Phase diagram as a function of U/t and λ^2/Kt for $J/U=0.1$ [panel (a)], $J/U=0.2$ [panel (b)], $J/U=0.25$ [panel (c)]. Solid lines: first-order phase transitions. Dotted line: second-order transition from PM to ICM. Broken line: transition to quadrupole ordering with $\tau_3 > 0$; weakly first-order because cubic terms are allowed in the free energy.

Galilean-invariant limit. One expects the mass associated with current fluctuations to be renormalized by the on-site fluctuations associated with proximity to a Mott transition. The Fermi sheet independence (the enhancement is about a factor of two on all sheets) is consistent with this interpretation. The relative weakness of this contribution to the mass enhancement suggests that these correlations, while clearly present, are not dominant. The thermodynamic and susceptibility mass enhancements are larger and more strongly sheet dependent: the ratio of the thermodynamic mass to the cy-

clotron mass is about 1.5–1 on the α, β sheets and 3–1 on the γ sheet, and the ratio of the susceptibility mass to the cyclotron mass is about 2–1 on the α, β sheets and 5–1 on the γ sheet. These data strongly suggest that much of the observed mass enhancements come from long wavelength fluctuations, which do not affect the current and hence the cyclotron mass very much, and that the important long wavelength fluctuations are ferromagnetic and due mainly to fluctuations on the γ sheet.

We therefore suggest that the cyclotron mass enhancement be interpreted as arising from a local (and orbital) independent self energy, in the spirit of the dynamical mean field or Brinkman-Rice approximation and leading to an intermediate energy Fermi liquid state characterized by a factor of two reduction in bandwidth. The remaining correlations are proposed to arise from spin fluctuations. A widely used measure of the strength of ferromagnetic correlations is the Wilson ratio of the susceptibility to the specific heat. This measure can be misleading in quasi-two dimensional materials with strong ferromagnetic enhancements. If the degree of ferromagnetic enhancement r^{-1} is defined as the ratio of the uniform susceptibility to the average of $\chi(q)$ over the Brillouin zone, then in an electronically two dimensional material the contribution of ferromagnetic spin fluctuations to the specific heat is $\sim r^{-1/2}$, and in a three dimensional material as $\ln(1/r)$ so the Wilson ratio diverges more slowly than the susceptibility. We therefore suggest that the increase of the susceptibility mass over the cyclotron mass be interpreted as the “Stoner factor” of the usual theory of itinerant electron magnetism, which can be used to position Sr_2RuO_4 on the phase diagram calculated above. The quantum oscillation measurements then reveal a γ -band Stoner factor of 4 or so. Within the Hartree-Fock approximation this corresponds to an effective interaction with $2 < U_{\text{eff}}/t_{\text{eff}} < 2.3$ (weakly dependent on J/U), i.e., to a $U/t \approx 0.8$ of the critical value for a ferromagnetic instability. Within Hartree-Fock we also find that the three dimensional model has a second order PM-FM transition at $U+2J \approx 2.5t$ and for $U+2J \approx 3t$, $m \sim 1\mu_B$ consistent with observation.¹⁹ To summarize, we believe that the quantum oscillations data show unambiguously that Sr_2RuO_4 is a material with moderate correlations, not close to a Mott transition but with very substantial “Stoner” ferromagnetic enhancements. The low energy theory for Sr_2RuO_4 is characterized by a moderate effective interaction, e.g., $U \approx 2t$ $J \approx 0.6t$, provides a good description of the Sr-ruthenates.

We next turn to the behavior as Sr is replaced by Ca, focusing first on $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ in the range $x > 0.5$. The main effect of the substitution is to buckle the Ru-O-Ru bonds, thereby reducing the bandwidths. In addition, changes occur in the ratio of the Ru-(apical oxygen) distance to the Ru-(in plane oxygen) distance, changing the relative energies of the xy and xz, yz levels. However, very interesting recent photoemission data²⁰ strongly suggest that at $x=0.5$ one still has $n_{xy} \approx n_{xz} \approx n_{yz} \approx 4/3$, suggesting that the material is in the $J > U/5$ regime where interaction effects suppress orbital disproportionation. The main observed effect on the electronic properties is a dramatic increase in the magnetic susceptibility and a less rapid increase in the specific heat coefficient, at least qualitatively consistent with behavior

expected as a quantum ferromagnetic transition is approached. This strongly suggests that main effect of Ca substitution is to drive the system very close to a Stoner (or itinerant electron) ferromagnetic transition, by reducing the bandwidth and thereby increasing the relative strength of the interactions. The estimate of the interaction strength given in the previous paragraph implies that an $\sim 10\%$ decrease in t (a change of the magnitude expected when Sr is replaced by Ca^{5+}) would be enough to drive a transition into an ordered state.

At this stage a difficulty arises: over a wide range of the phase diagram, the Hartree-Fock approximation indicates that the first instability is to an ICM state driven by Fermi surface nesting, and that this should be followed by a first order transition to a C-AFM phase. Indeed Hartree-Fock indicates that the instability to an ICM phase occurs at $U/t < 2$, i.e., where the Stoner factor is less than the value 4 apparently implied by the quantum oscillations measurement. The absence of the ICM phase is perhaps not surprising: as noted above, beyond-Hartree-Fock corrections are expected to shift the ICM phase boundary substantially, both because we are dealing with low dimensional magnetism, on which quantum fluctuations have a substantial effect, and because inelastic scattering will weaken the susceptibility peaks, with the weakening being much more severe at large q than at $q=0$. A perhaps more serious discrepancy is that no sign is found of the C-AFM phase found in wide regions of the phase diagram. Because this phase occurs via a first-order phase transition and has a large amplitude ordered moment, it should be relatively stable against fluctuation effects. That it is not observed suggests that either J is very small or that $J \geq 0.25U$, so that the materials are in a region of the phase diagram in which the C-AF phase is absent. The apparent persistence of the (approximately) symmetric orbital occupancy argues for the larger J values.

In the actual materials, the doping $x=0.5$, while clearly very close to a ferromagnetic instability, marks the onset of a lattice distortion²¹ which distinguishes the $[1,1]$ and $[1, \bar{1}]$ directions of the $2d$ lattice. While band calculations suggest that this distortion has a negligible effect on the electronic structure,⁵ it apparently moves the system farther from the ferromagnetic instability, reducing as x is decreased both the uniform susceptibility and the specific heat coefficient. Within the Hartree-Fock phase diagram, a natural interpretation would be the onset of an incommensurate magnetic phase, but magnetism is apparently not observed. Rather the subtle effects of the structural distortion apparently act to reduce the Fermi surface density of states in a manner which overcompensates the continuing bandwidth narrowing due to Ca doping, thereby weakening the ferromagnetic fluctuations and reducing both the susceptibility and the magnetic contribution to the specific heat.

An alternative interpretation^{1,7} is that some of the electronic degrees of freedom become localized, leading among other things to the emergence of an antiferromagnetic exchange which reduces the ferromagnetic tendency. The approximately Curie behavior, with a large effective moment, of the temperature dependent susceptibility is argued to support this interpretation. However, we note that the results of

Ref. 20 suggest that orbital disproportionation does not occur at $x=0.5$, and that measurements on $\text{Sr}_3\text{Ru}_2\text{O}_7$,²² a clearly itinerant-electron system on the verge of ferromagnetism also reveal a Curie-Weiss susceptibility with a large effective moment.

A further increase of Ca concentration leads to a first-order transition to a strongly insulating state, believed¹ to be the G-AF state discussed above. The apparent direct transition from a paramagnetic to a G-AF state is in the present calculations found only for relatively large electron-phonon couplings, and only for relatively large J . We take this as evidence for the importance of electron-lattice coupling. Further consequences of our calculation, namely the association of the transition with a lattice distortion and a hardening of the phonon frequency, have been observed experimentally.²³ Pressure experiments on Ca_2RuO_4 observe a transformation to a metallic phase with a small FM moment. Pressure increases t and K , corresponding to diagonal motion in Fig. 3 but our FM phase is fully polarized in contrast to that found in Ref. 24.

Our results suggest a possible interpretation of the puzzling surface experiments by Moore *et al.* who find that the surface of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ remains metallic down to a lower temperature (125 K) than does the bulk material (150 K) and that both on the surface and in bulk the metal-insulator transition is accompanied by a Q_3 -type distortion of magnitude ~ 0.02 . However, the surface phonon frequency corresponding to apical oxygen motion is larger than the bulk phonon frequency, implying that the stiffness K is larger so that as seen in Fig. 3 the insulating phase is more difficult to access. However, many issues remain unresolved. The distance between the Ru and the surface layer apical oxygen is found to be much less than the bulk Ru-apical oxygen distance. Unless compensated by a change in the Ru-first subsurface apical oxygen distance, this would imply large frozen-in Q_3 and Q_0 type distortions, which would be expected to change the surface layer properties substantially. Further, the bulk metal-insulator transition involves a 2% increase in the in-plane bond length, and elementary elastic compatibility arguments suggests that the surface in-plane bond should follow the bulk. Why this does not drive a metal-insulator transition is unclear.

VI. SUMMARY AND CONCLUSION

We have performed Hartree-Fock calculations of a model believed to be relevant to the still mysterious physics of $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ series of compounds. Two key results, which seem likely to have validity beyond the Hartree-Fock approximation, are that a correct treatment of the multiplet interaction parameters (especially the J) is crucial, because J can stabilize the system against orbital disproportionation,

and that an electron-lattice interaction is likely to be important in stabilizing the observed G-AFM state. Our approach is most similar to that of Nomura and Yamada,³ who performed Hartree-Fock studies of essentially the same model studied here, but with band parameters corresponding to slightly broader $1d$ bands and $U'/U=0.5$, $J/U=0.25$ (“orbitally stable”). These authors considered only G-AFM and FM ordered phases and did not include electron-lattice coupling, but did investigate effects of changes in relative energy level. In a closely related work, Fang and Terakura used LSDA band theory methods to investigate FM and G-AFM states.⁵ Their results, in particular their prediction of a direct PM-FM transition as the bandwidth is reduced, correspond reasonably well to the Hartree-Fock results with $J/U \approx 0.3$, the ICM phase omitted and no lattice distortion. Very recently,⁵ the calculation was refined to include a LDA+ U treatment of Ca_2RuO_4 along with the band theory corresponding to the experimental lattice structure, and results for optical absorption was presented. Our results lead us to wonder if adding a U but not a J to the LDA energies is appropriate. Hotta and Dagotto⁶ studied the model via a combination of mean-field results and numerical studies of small systems and showed the importance of coupling to the shape changes of the RuO_6 octahedron. However, their phase diagrams feature phases with complicated spatial structures which we are unable to stabilize. It is possible that the spatial structures found in Ref. 6 are due to boundary effects in small size systems accessible numerically. Anisimov and co-workers⁷ used a “dynamical mean-field” method to study a $J=0$ model. At large U they found an insulating “(2,2)” phase which is essentially the same as the G-AFMOO phase we find. At slightly lesser correlation strengths, Anisimov *et al.* find an interesting “(3,1)” phase in which 3 electrons are in the $\{xz, yz\}$ bands in a Mott insulating state, while the xy band remains metallic. Liebsch⁸ argues that this is impossible in models in which magnetic order is neglected, but these results have themselves been questioned.²⁵ In any event, the Hartree-Fock analog (an antiferromagnet with one electron in the xy orbital) is not found in our calculations.

To summarize, we have shown that moderate interactions, a reasonable J/U and electron-lattice interactions can account for the $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ phase diagram. We argued that the materials are in the regime in which disproportionation is suppressed by interactions. Determining the susceptibility to orbital disproportionation in other compounds and other multiplet structures is an important open issue. An investigation, using dynamical mean field methods, of the G-AFM boundary is an important direction for future research.

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