

Magnetic and orbital ordering of RuO₂ planes in RuSr₂(Eu, Gd)Cu₂O₈

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We start from an effective Hamiltonian for Ru ions in a square lattice, which includes the on-site interactions between t_{2g} orbitals derived from Coulomb repulsion, and a tetragonal crystal-field splitting. Using perturbation theory in the hopping terms, we derive effective Hamiltonians to describe the RuO₂ planes of RuSr₂(Eu, Gd)Cu₂O₈. For undoped planes (formal valence Ru⁺⁵), depending on the parameters we find three possible orderings of spin and orbitals, and construct a phase diagram. This allows us to put constraints on the parameters based on experimental data. When electron doping consistent with the hole doping of the superconducting RuO₂ planes is included, we obtain (for reasonable parameters) a double-exchange model with infinite antiferromagnetic coupling between itinerant electrons and localized spins. This model is equivalent to one used before [H. Aliaga and A. A. Aligia, *Physica B* **320**, 34 (2002)], which consistently explains the seemingly contradictory magnetic properties of RuSr₂(Eu, Gd)Cu₂O₈.

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I. INTRODUCTION

In recent years, there has been much interest in ruthenates because of their interesting magnetic and superconducting properties. For example, SrRuO₃ is a ferromagnet that orders at $T_M=165$ K,¹ Sr₂RuO₄ is an exotic p -wave superconductor with transition temperature $T_S=1.5$ K,² and Sr₃Ru₂O₇ presents a metamagnetic transition³ and non-Fermi liquid behavior.⁴ A close relationship between ferromagnetic (FM) exchange and triplet p -wave superconductivity is expected in analogy with ³He (Ref. 5) or from bosonization studies in one dimension.^{6,7}

RuSr₂(Eu, Gd)Cu₂O₈ has a magnetic transition at $T_M \sim 133$ K, and a superconducting transition at $T_S \sim 33$ K for Eu or $T_S \sim 15-40$ K for Gd (depending on the conditions of preparation and annealing).^{8,9} Below T_S , superconductivity coexists with magnetic order, which was first believed to be FM,⁹⁻¹² since the magnetization shows a rapid increase with magnetic field for fields below 5 T, and the inverse magnetic susceptibility at high temperatures yields a positive Curie constant $\Theta=100 \pm 3$ K.¹² However, neutron diffraction experiments found superlattice reflections consistent with an usual antiferromagnetic (AF) order with nearest-neighbor spins antiparallel in all three directions.¹³ This seems difficult to reconcile with the above-mentioned magnetic properties, in particular with a positive Curie constant. Nevertheless, a double-exchange model could consistently account for these observations.¹⁴

The crystal structure of RuSr₂(Eu, Gd)Cu₂O₈ is similar to that of YBa₂Cu₃O₇, except that Y is replaced by Eu or Gd, and the CuO chain layer is replaced by a square planar RuO₂ layer, with resulting tetragonal symmetry, except for small distortions typical of perovskites.⁹ The sequence of layers perpendicular to the tetragonal axis is RuO₂/SrO/CuO₂/(Eu or Gd)/CuO₂/SrO. Several experiments, like muon spin rotation,⁹ magnetization,^{9,12} electron paramagnetic resonance, and ferromagnetic resonance,¹⁰ demonstrate that the development of superconductivity does not affect the mag-

netic order. This suggests that, at least as a first approximation, the superconducting CuO₂ planes and the magnetic RuO₂ planes behave as separate entities related only by charge transfer, as it happens with CuO planes and chains in YBa₂Cu₃O_{6+x}.¹⁵ Band structure calculations are consistent with this picture.¹¹ From what is known for YBa₂Cu₃O_{6+x},^{15,16} a superconducting critical temperature $T_S \sim 30-40$ K suggests a doping of slightly less than 0.1 holes per CuO₂ plane. This implies a doping of ≤ 0.2 electrons to the RuO₂ planes with respect to the formal oxidation states Ru⁺⁵ and O⁻². Taking into account a certain degree of Ru-O covalence, this doping is consistent with x-ray absorption near-edge structure experiments, which suggest a Ru valence near 4.6.¹⁷ This situation is at variance with the compounds of the Ruddlesden-Popper series (Cu, Sr)_{n+1}Ru_nO_{3n+1} (like those mentioned above) for which the formal oxidation state of Ru is Ru⁺⁴.

The main features of the puzzling magnetic behavior of RuO₂ planes in RuSr₂(Eu, Gd)Cu₂O₈ were explained in terms of a double-exchange model in which Ru⁺⁵ spins have a strong Hund coupling with a band of itinerant electrons.¹⁴ Within this picture, the undoped system presents usual AF ordering. Additional electrons form FM polarons that tend to align easily in the direction of an applied magnetic field. Consequently, in spite of the AF order, the magnetic susceptibility at temperatures $T > T_M$ can be well described by $\chi = C/(T - \Theta)$, with $\Theta > 0$, in agreement with experiment.¹² Further support to the double-exchange model is brought by the negative magnetoresistance above T_M , or below T_M for high enough magnetic field.^{18,19} While this model has been successful in explaining several properties of manganites,^{20,21} where the itinerant electrons are in $3d e_g$ orbitals, there is so far no justification for its application to ruthenates, where the relevant orbitals are the $4d t_{2g}$ ones,^{11,22,23} in which case crystal-field effects are expected to be more important, and correlations should be smaller due to the larger extent of the Ru $4d$ orbitals, in comparison with Mn $3d$ ones.

In this work, we start from an effective Hamiltonian H for the Ru $4d$ t_{2g} orbitals in a square lattice, after integrating out the O orbitals. H includes all atomic Coulomb interactions, and a tetragonal crystal-field splitting Δ . We treat H in perturbation theory in the effective Ru-Ru hopping. Since the effective parameters are difficult to estimate, the quantitative validity of this strong-coupling approach is difficult to address. However, for reasonable parameters our results are consistent with experiment, and confirm results previously obtained with the double-exchange model. In the case of Sr_2RuO_4 , which has been studied in more detail, there is a wide range of proposed parameters, but it is clear that the correlations are significant, and the system is believed to be in the intermediate-coupling regime.^{24,25} Notice that approaches that neglect quantum fluctuations should assume smaller interactions to avoid magnetic ordering in Sr_2RuO_4 , while instead RuO_2 planes in $\text{RuSr}_2(\text{Eu}, \text{Gd})\text{Cu}_2\text{O}_8$ do order magnetically at T_M .

The paper is organized as follows. In Sec. II, we present the model and discuss its parameters. In Sec. III, we describe the eigenstates and energies of the local Hamiltonian. In Sec. IV, we derive effective Hamiltonians that describe spin and orbital degrees of freedom in the undoped case, after integrating out the charge fluctuations. Section V contains the phase diagram for this case. In Sec. VI, we discuss the effective Hamiltonians for the doped case, and their relation to the double-exchange model. Our results are summarized and discussed in Sec. VII.

II. THE MODEL

We start with an effective model for the $4d$ t_{2g} orbitals of Ru ions in a square lattice. It can be derived from an appropriate multiband model for RuO_2 planes by a canonical transformation eliminating Ru-O hopping terms,²⁶ or by the cell perturbation method if Ru-O covalence were important.^{27,28} The Hamiltonian is

$$H = \sum_i (H_i^i + H_{\text{CF}}^i) + H_h, \quad (1)$$

where H_i^i contains the local interaction terms at site i , H_{CF}^i is a tetragonal crystal-field splitting, and H_h contains the hopping terms which we restrict to nearest neighbors. Since H_i^i contains only intrasite interactions, we assume for it the same form as for an isolated Ru ion, neglecting spin-orbit coupling. This form can be calculated in a straightforward way using known methods of atomic physics.^{29,30} Expanding the Coulomb interaction term $e^2/|\mathbf{r}_1 - \mathbf{r}_2|$ in spherical harmonics, all Coulomb integrals can be expressed in terms of Slater parameters F_0 , F_2 , and F_4 (as done earlier³¹ for e_g orbitals). Here, we write H_i^i using the Kanamori parameters (which seem to be more popular in condensed matter^{32,33}) for t_{2g} orbitals: $U = F_0 + 4F_2 + 36F_4$, $J = J' = 3F_2 + 20F_4$, and $U' = U - 2J$. Then,

$$H_i^i = U \sum_{\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} + \frac{1}{2} \sum_{\alpha \neq \beta, \sigma \sigma'} (U' n_{i\alpha\sigma} n_{i\beta\sigma'} + J d_{i\alpha\sigma}^\dagger d_{i\beta\sigma'}^\dagger d_{i\alpha\sigma'} d_{i\beta\sigma}) + J' \sum_{\alpha \neq \beta} d_{i\alpha\uparrow}^\dagger d_{i\alpha\downarrow}^\dagger d_{i\beta\downarrow} d_{i\beta\uparrow}, \quad (2)$$

where $n_{i\alpha\sigma} = d_{i\alpha\sigma}^\dagger d_{i\alpha\sigma}$, and $d_{i\alpha\sigma}^\dagger$ creates an electron in the t_{2g}

orbital α (xy , yz , or zx), with spin σ at site i .

Choosing z as the tetragonal axis, we write the crystal field term in the form

$$H_{\text{CF}}^i = \Delta \left(\sum_{\sigma} d_{i\alpha\sigma}^\dagger d_{i\alpha\sigma} - 1 \right), \quad (3)$$

in such a way that it changes sign under an electron-hole transformation.

Denoting by $\delta = \pm \hat{x}$, $\pm \hat{y}$ the four vectors that connect a site with its four nearest neighbors, the hopping term has the form

$$H_h = -t \sum_{i\sigma} (d_{i+\hat{x},z\sigma}^\dagger d_{iz\sigma} + d_{i+\hat{y},yz\sigma}^\dagger d_{iy\sigma} + \text{H.c.}) - t' \sum_{i\delta\sigma} d_{i+\delta,xy\sigma}^\dagger d_{i\sigma}. \quad (4)$$

Notice that, since we neglect the distortions, electrons occupying zx (yz) orbitals do not hop in the y (x) direction due to the symmetry of the intermediate O $2p$ orbitals.^{26,28}

While the parameters of H are difficult to estimate, we expect that the order of magnitude of t and t' is near $1/4$ eV^{14,24–26,28} (see also Sec. VII). Since the exchange interactions are not expected to be strongly screened in the solid, one may estimate J from atomic spectra.³⁴ From the low-lying levels of Ru^+ (with three holes in the $4d$ shell), we obtain $F_2 \sim 863$ cm⁻¹ and $F_4 \sim 78$ cm⁻¹, leading to $J \sim 0.5$ eV. Optical experiments in Sr_2RuO_4 suggest that $U \sim 1.5$ eV.³⁵ Notice that the expectation value of the Coulomb repulsion in any state with two electrons and total spin $S = 1$ should be positive. This implies, for two different t_{2g} orbitals in the atomic case, $F_0 - 5F_2 - 24F_4 > 0$, or

$$U - 3J = U' - J > 0. \quad (5)$$

For a Slater determinant with both e_g orbitals, one obtains $F_0 - 8F_2 - 9F_4 > 0$.³¹ This condition is expected to be more restrictive than Eq. (5), since F_2 is usually more than one order of magnitude larger than F_4 . For example, using the above estimates for F_2 and F_4 , this gives $F_0 > 0.94$ eV and $U' - J > 0.17$ eV. We assume Eq. (5) to be valid in general. Otherwise, for large $|\Delta|$, there is a charge-transfer instability of the ground state for the undoped system. The physics of Sr_2RuO_4 suggests that Δ is small and negative.²⁵

III. EIGENSTATES OF THE LOCAL HAMILTONIAN

The local part $H_i^i + H_{\text{CF}}^i$ can be easily diagonalized. To describe the undoped system, we need the eigenstates with three electrons, and those with two and four electrons are needed when the effects of the hopping term H_h or doping are included. We denote the eigenstates by $|in\Gamma SM\rangle$, where i is the site index, n is the number of electrons, Γ denotes the symmetry (irreducible representation of the point group D_{4h} or symmetry of the basis function for the two-dimensional representation), S is the total spin and M its projection on the tetragonal axis z . If $S=0$, M is suppressed. For simplicity, we drop the site index in this section. The subscript g is also dropped in the irreducible representations. Some eigenstates and their energies are listed in Table I. The remaining ones

TABLE I. Eigenstates and energies of $H_I^i + H_{\text{CF}}^i$ for two and three particles. Here $u_j, v_j > 0$, $u_j^2 + v_j^2 = 1$, $u_2^2 = [1 - (\Delta - J'/2)/r_2]/2$, $r_2 = [(\Delta - J'/2)^2 + 2(J')^2]^{1/2}$, $u_3^2 = [1 - \Delta/r_3]/2$, and $r_3 = [\Delta^2 + (J')^2]^{1/2}$. A prime indicates a new appearance of the same irreducible representation of the point group. States obtained by applying the spin lowering operator S^- or rotation of $\pi/2$ in the xy plane are not shown.

| Notation | Eigenstate | Energy |
|--|--|---------------------|
| $ 2a_1 0\rangle$ | $[u_2 d_{xy\downarrow}^\dagger d_{xy\uparrow}^\dagger - 1/\sqrt{2} v_2 (d_{zx\downarrow}^\dagger d_{zx\uparrow}^\dagger + d_{yz\downarrow}^\dagger d_{yz\uparrow}^\dagger)] 0\rangle$ | $U + J'/2 - r_2$ |
| $ 2a_1' 0\rangle$ | $[u_2 d_{xy\downarrow}^\dagger d_{xy\uparrow}^\dagger + 1/\sqrt{2} v_2 (d_{zx\downarrow}^\dagger d_{zx\uparrow}^\dagger + d_{yz\downarrow}^\dagger d_{yz\uparrow}^\dagger)] 0\rangle$ | $U + J'/2 + r_2$ |
| $ 2b_1 0\rangle$ | $1/\sqrt{2} (d_{zx\downarrow}^\dagger d_{zx\uparrow}^\dagger - d_{yz\downarrow}^\dagger d_{yz\uparrow}^\dagger) 0\rangle$ | $U - J' - \Delta$ |
| $ 2b_2 0\rangle$ | $1/\sqrt{2} (d_{yz\downarrow}^\dagger d_{yz\uparrow}^\dagger - d_{zx\downarrow}^\dagger d_{zx\uparrow}^\dagger) 0\rangle$ | $U' + J - \Delta$ |
| $ 2x 0\rangle$ | $1/\sqrt{2} (d_{xy\downarrow}^\dagger d_{yz\uparrow}^\dagger - d_{xy\uparrow}^\dagger d_{yz\downarrow}^\dagger) 0\rangle$ | $U' + J$ |
| $ 2a_2 11\rangle$ | $d_{yz\uparrow}^\dagger d_{zx\uparrow}^\dagger 0\rangle$ | $U' - J - \Delta$ |
| $ 2x 11\rangle$ | $d_{xy\uparrow}^\dagger d_{yz\uparrow}^\dagger 0\rangle$ | $U' - J$ |
| $ 3a_1 \frac{1}{2} \frac{1}{2}\rangle$ | $1/\sqrt{2} d_{xy\uparrow}^\dagger (d_{yz\uparrow}^\dagger d_{zx\downarrow}^\dagger - d_{yz\downarrow}^\dagger d_{zx\uparrow}^\dagger) 0\rangle$ | $3U'$ |
| $ 3a_2 \frac{1}{2} \frac{1}{2}\rangle$ | $1/\sqrt{2} d_{xy\uparrow}^\dagger (d_{zx\downarrow}^\dagger d_{zx\uparrow}^\dagger - d_{yz\downarrow}^\dagger d_{yz\uparrow}^\dagger) 0\rangle$ | $U + 2U' - J - J'$ |
| $ 3b_1 \frac{1}{2} \frac{1}{2}\rangle$ | $1/\sqrt{6} [d_{xy\uparrow}^\dagger (d_{yz\uparrow}^\dagger d_{zx\downarrow}^\dagger + d_{yz\downarrow}^\dagger d_{zx\uparrow}^\dagger) - 2d_{xy\downarrow}^\dagger d_{yz\uparrow}^\dagger d_{zx\uparrow}^\dagger] 0\rangle$ | $3U'$ |
| $ 3b_2 \frac{1}{2} \frac{1}{2}\rangle$ | $1/\sqrt{2} d_{xy\uparrow}^\dagger (d_{zx\downarrow}^\dagger d_{zx\uparrow}^\dagger + d_{yz\downarrow}^\dagger d_{yz\uparrow}^\dagger) 0\rangle$ | $U + 2U'$ |
| $ 3x \frac{1}{2} \frac{1}{2}\rangle$ | $(u_3 d_{xy\downarrow}^\dagger d_{xy\uparrow}^\dagger - v_3 d_{yz\downarrow}^\dagger d_{yz\uparrow}^\dagger) d_{zx\uparrow}^\dagger 0\rangle$ | $U + 2U' - J - r_3$ |
| $ 3x' \frac{1}{2} \frac{1}{2}\rangle$ | $(v_3 d_{xy\downarrow}^\dagger d_{xy\uparrow}^\dagger + u_3 d_{yz\downarrow}^\dagger d_{yz\uparrow}^\dagger) d_{zx\uparrow}^\dagger 0\rangle$ | $U + 2U' - J + r_3$ |
| $ 3b_1 \frac{3}{2} \frac{3}{2}\rangle$ | $d_{xy\uparrow}^\dagger d_{yz\uparrow}^\dagger d_{zx\uparrow}^\dagger 0\rangle$ | $3U' - 3J$ |

for $n=3$ and $n=2$ are obtained by applying the operator S^- or a rotation of $\pi/2$ around z to those listed. The corresponding results for $n=4$ can be obtained from those of $n=2$ using electron-hole symmetry: replace creation by annihilation operators with the opposite spin, $d_{i\alpha\sigma}^\dagger \rightarrow d_{i\alpha,-\sigma}$, replace the vacuum by the state with all t_{2g} orbitals occupied, change the sign of Δ , and add $U + 4U' - 2J = 5U'$ to the resulting energies.

Since we started with a local interaction Hamiltonian H_I^i with full rotational symmetry, the symmetry group of $H_I^i + H_{\text{CF}}^i$ is actually higher than D_{4h} . For example, rotations around z of the orbitals yz and zx keeping the xy fixed leave $H_I^i + H_{\text{CF}}^i$ invariant. As a consequence, the state $|2b_1 0\rangle$ is degenerate with $|2b_2 0\rangle$, and the states $|3a_1 \frac{1}{2} M\rangle$ and $|3a_2 \frac{1}{2} M'\rangle$ also become degenerate. This degeneracy is broken if the conditions $U = U' + 2J$, $J' = J$ are relaxed, but a degeneracy between $|3a_1 \frac{1}{2} M\rangle$ and $|3b_1 \frac{1}{2} M'\rangle$ persists, which is broken only if an exchange interaction J between the orbitals yz and zx different from the other two is introduced.

For $n=3$, the ground state is the spin quadruplet $|3b_1 \frac{3}{2} M\rangle$ if $|\Delta| \leq \sqrt{15}J$, while for $|\Delta| \geq \sqrt{15}J$ the ground state is also fourfold degenerate, but it is the spin and orbital E_g doublet $|3x \frac{1}{2} M\rangle$, $|3y \frac{1}{2} M\rangle$. These two possibilities lead to two different effective Hamiltonians in the undoped case, after integrating out the charge degrees of freedom.

IV. EFFECTIVE HAMILTONIANS FOR UNDOPED PLANES

In this section, we construct effective Hamiltonians H_{eff} for the undoped case, using second-order degenerate perturbation theory in H_h . Depending on the ground state of $H - H_h$, there are two possibilities for H_{eff} .

A. $\Delta^2 < 15J$

In this case, the ground-state manifold of $H - H_h$ is the spin quadruplet $|i3b_1 \frac{3}{2} M\rangle$ at each site i . The degeneracy is

lifted by second-order contributions in which the intermediate states have two nearest-neighbor sites with two and four electrons, both with total spin $S=1$ and both with the same symmetry B_{2g} , x or y . The different matrix elements are easily calculated using Eq. (4) and Table I. We omit the details. The resulting H_{eff} is a Heisenberg model for the effective $S=3/2$ spins:

$$H_{\text{eff}}^a = K \sum_{\langle ij \rangle} \left(\mathbf{S}_i \cdot \mathbf{S}_j - \frac{9}{4} \right); \quad K = \frac{4(t^2 + t'^2)}{9(U + 2J)}. \quad (6)$$

The coupling constant K turns out to be independent of Δ . The ground state of this model is a two-sublattice antiferromagnet with antiparallel nearest-neighboring spins. We call it AFI. The energy per site can be calculated accurately enough using spin waves, and is given by³⁶

$$E_{\text{AFI}} - E_{3b_1 3/2} \approx -2KS(S + 0.158) = -4.974K, \quad (7)$$

where $E_{3b_1 3/2}$ is the energy of the state $|i3b_1 \frac{3}{2} M\rangle$ given in Table I.

B. Large Δ^2

For $\Delta^2 > 15J$, the ground state of $H_I^i + H_{\text{CF}}^i$ is the spin and orbital doublet $|i3\gamma \frac{1}{2} M\rangle$, with $\gamma=x$ or y , which we denote briefly as $|i\gamma\sigma\rangle$. The number of intermediate states is much larger than in the previous case, and H_{eff} becomes very complicated. Since for $\Delta^2 > 15J$ the structure of the states involved in the derivation is already very similar to that for $\Delta \rightarrow \pm\infty$ (as can be checked by inspection of Table I), we restrict the calculation to this case. The result is

$$H_{\text{eff}}^b = \sum_i \left\{ J_A \sum_{\gamma} P_{i\gamma} P_{i+\hat{\gamma},\gamma} \left(\mathbf{S}_i \cdot \mathbf{S}_{i+\hat{\gamma}} - \frac{1}{4} \right) - \sum_{\delta} P_{ix} P_{i+\delta,y} (J_F \mathbf{S}_i \cdot \mathbf{S}_{i+\delta} + A) \right\}, \quad (8)$$

where now \mathbf{S}_i are spin-1/2 operators, $P_{i\gamma}$ are the orbital projectors

$$P_{i\gamma} = \sum_{\sigma} |i\gamma\sigma\rangle \langle i\gamma\sigma|, \quad (9)$$

and

$$J_A = 2t^2 \left(\frac{1}{U' + J} + \frac{1}{U' + 3J} \right), \quad J_F = \frac{2Jt^2}{U'^2 - J^2},$$

$$A = \frac{t^2}{U' - J} - \frac{J_F}{4}. \quad (10)$$

The first term of H_{eff}^b is a one-dimensional interaction, FM in the orbital degrees of freedom, and AF in spin. The term proportional to A is a spin-independent AF orbital interaction, while the J_F term is FM in spin and AF in orbital variables.

Clearly, there are two possible competing ground states of H_{eff}^b : (i) a FM orbital ordering (all sites $|ix\sigma\rangle$, for example), with spin degrees of freedom determined by the critical one-dimensional AF Heisenberg model; and (ii) a spin FM and orbital Néel ordered phase (for example $|ix\uparrow\rangle$ in one sublattice and $|iy\uparrow\rangle$ in the other). In the first case, for finite Δ , a small AF coupling J_{\perp} between the chains appears [see Eqs. (13) and (14)], which yields long-range order at $T=0$. We call this phase AFII. From Bethe ansatz results,³⁷ the energy of this phase for $\Delta \rightarrow \pm\infty$ is

$$E_{\text{AFII}} = E_{3x1/2} - J_A \ln 2. \quad (11)$$

The second phase will be denoted FM-AFO, and its ground-state energy is given by

$$E_{\text{FM-AFO}} - E_{3x1/2} = -2 \left(A + \frac{J_F}{4} \right) = -\frac{2t^2}{U' - J}. \quad (12)$$

V. THE PHASE DIAGRAM

We now turn to the construction of a phase diagram for undoped planes, comparing the energies of the phases described in Sec. IV, but now for arbitrary Δ . Since the correction terms for $\sqrt{15}J < |\Delta| < +\infty$ are small, we do not expect any new phases to appear in this interval, except perhaps near the borderline between two phases, as we will discuss at the end of this section.

The energy of the AFI phase is still given by Eq. (7), due to the independence of H_{eff}^a [Eq. (6)] on the crystal-field splitting. The most important change occurs in the part of H_{eff}^b [Eq. (8)] that describes the AFII phase, in which an interchain coupling is generated. Thus, the effective Hamiltonian of the AFII phase, assuming that the chains are oriented along the x direction, is

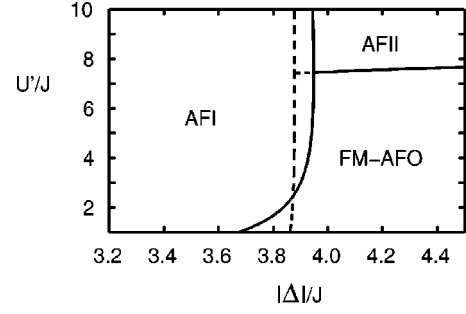


FIG. 1. Phase diagram of undoped RuO_2 planes for $t=t'=J/4$ (thin line) and $t=t'=J$ (thick line).

$$H_{\text{eff}}^{b2} = \sum_i \left\{ J'_A \left(\mathbf{S}_i \cdot \mathbf{S}_{i+\hat{x}} - \frac{1}{4} \right) + J_{\perp} \mathbf{S}_i \cdot \mathbf{S}_{i+\hat{y}} + C \right\}, \quad (13)$$

where J'_A is the AF coupling along the chains, which coincides with J_A for $|\Delta| \rightarrow \infty$, $J_{\perp} = 4(C_{\uparrow\uparrow} - C_{\downarrow\downarrow})$, $C = C_{\uparrow\uparrow} + C_{\downarrow\downarrow}$, and $C_{\uparrow\uparrow}(C_{\downarrow\downarrow})$ is the negative correction of the energy due to virtual hoppings from site i to $i+\hat{y}$ and back when the spin of both sites are equal (opposite). The expressions for J'_A , $C_{\sigma\sigma'}$, as well as the energy of the FM-AFO phase are lengthy but straightforward to obtain, and we do not reproduce them here. Instead, J_{\perp} takes a simpler form, given by

$$J_{\perp} = \frac{2J^4(t^2 + t'^2)}{(\Delta^2 + J^2)[u' + 2(r_3 - J)]\{U'^2 + 4[\Delta^2 + J^2 + U'(2r_3 - J)]\}}, \quad (14)$$

where $r_3 = (\Delta^2 + J^2)^{1/2}$. Equation (5) and the stability condition of the AFII phase against AFI for vanishing t and t' ($\Delta^2 > 15J$) imply $J_{\perp}/J_A < 6.80 \times 10^{-4}$.

The energy of the AFII phase up to second order in H_h is given by

$$E'_{\text{AFII}} = E_{3x1/2} - J'_A \ln 2 + C + E_{J_{\perp}}, \quad (15)$$

where $E_{J_{\perp}}$ is the correction due to the interchain coupling. This correction can be calculated treating the J_{\perp} term in a mean-field approximation, by a straightforward generalization of Schulz's results³⁸ for the case in which each chain has z nearest-neighboring chains (he considered $z=4$ while we have $z=2$). The energy gain due to the appearance of a spontaneous staggered expectation value of the spin projection in the chain direction $m = (-1)^i \langle S_i^z \rangle$ is (for any sign of J_{\perp})

$$E_{J_{\perp}} = z|J_{\perp}|m^2 - \frac{7}{10}(\pi J'_A)^{-1/3}(z|J_{\perp}|m)^{4/3}. \quad (16)$$

Minimizing with respect to m , one obtains the equilibrium value of the sublattice magnetization

$$m = \left(\frac{14}{15} \right)^{3/2} \left(\frac{z|J_{\perp}|}{\pi J'_A} \right)^{1/2}. \quad (17)$$

The resulting phase diagram is shown in Fig. 1. Due to electron-hole symmetry, the boundaries between the phases do not depend on the sign of Δ . The spin AF phase AFI, and

the spin FM and orbital AF (FM-AFO) phase dominate the phase diagram. Comparing Eqs. (11) and (12), one obtains a critical value $U'_c \approx 8.52J$ for the boundary between the AFII phase and the FM-AFO in the limit $|\Delta| \rightarrow \infty$. For $U' > U'_c$, the only stable phases are the spin AF ones. The main difference between these phases is that the staggered magnetization is very small in the AFII phase. In fact, from Eq. (17), we obtain $m < 0.03$ for the parameters of Fig. 1.

Within our perturbation theory up to second order in t and t' , the boundary between the FM-AFO phase and the AFII phase is independent of t and t' . The boundary of the AFII phase is also weakly dependent on hopping. For $U'/J > 2$, the stability region of the AFII phase is slightly enlarged by increasing the hopping parameters, as can be seen in Fig. 1. For smaller values of U'/J , the energy of the FM-AFO phase decreases due to the proximity of a charge instability near which our perturbative treatment becomes invalid. The main effect of increasing t and t' is to enhance the energy difference between the stable and unstable phases in each region. These differences tend to be very small when the hopping parameters are small. For instance, the energies of the AFII and FM-AFO phases completely coincide in the limit $t=t' \rightarrow 0$. Thus, narrow-band systems are likely to show phase coexistence due to inhomogeneities. In addition, we cannot rule out the appearance of more complex phases in a small region of parameters for which $E_{\text{FM-AFO}} \sim E_{\text{AFII}}$. One candidate is a phase in which orbitals display FM order in one direction (say x) and AF order in the y direction, while the spins are ordered antiferromagnetically in the x direction and ferromagnetically in the y direction.

VI. THE DOPED SYSTEM

RuO₂ planes in RuSr₂(Eu, Gd)Cu₂O₈ are expected to have electron doping corresponding in our effective Hamiltonian H to a fraction below 20% of Ru sites with four electrons. Depending on the ratio Δ/J , there are three possibilities for the ground state of the local Hamiltonian $H_I^i + H_{\text{CF}}^i$ for four electrons (see Table I):

(1) $\Delta < 0$: The ground state is the spin triplet $|i4a_21M\rangle$ (e.g., $|i4a_211\rangle = d_{ixy}^\dagger d_{ixy}^\dagger d_{iyz}^\dagger d_{izx}^\dagger |0\rangle$).

(2) $0 < \Delta < \Delta_c (\sqrt{41}-1)J/2 \approx 2.70J$: The ground state is the spin triplet and orbital doublet $|i4x1M\rangle$, $|i4y1M\rangle$.

(3) $\Delta > \Delta_c$: The ground state is the spin singlet and orbital doublet $|i4x0\rangle$, $|i4y0\rangle$.

Treating the hopping term in first-order degenerate perturbation theory, and combining with the results of Sec. IV, we can construct effective Hamiltonians H_{eff} for the doped case. We begin by considering $|\Delta/J| < \sqrt{15} \approx 3.87$, as suggested by the observed robust AF order,¹³ and the results of Sec. V. Then the ground state of $H_I^i + H_{\text{CF}}^i$ for three electrons is the spin quadruplet with symmetry B_{1g} .

A. $-\sqrt{15}J < \Delta < 0$

In this case, the problem of finding H_{eff} reduces to calculating matrix elements of $d_{ixy\sigma}^\dagger d_{ixy\sigma}$ (all others vanish by symmetry) in the basis of $|i3b_{1/2}M_1\rangle$ and $|i4a_21M_0\rangle$. For brevity we shall denote these states as $|i\frac{3}{2}M_1\rangle$ and $|i1M_0\rangle$. Using the

Wigner-Eckart theorem, all matrix elements can be calculated in terms of one of them (e.g., that for maximum projections, which is easily calculated), and Clebsch-Gordan coefficients $\langle J_0 j M_0 m | J_1 M_1 \rangle$ for the combination of angular momenta J_0 and j to give J_1 . A similar approach was used before in problems of valence fluctuation with two magnetic configurations.³⁹ Including the second-order terms described before [Eq. (6)], H_{eff} becomes

$$H_{\text{eff}}^{(1)} = -t' \sum_{i\delta\{M\}} \left\langle 1\frac{1}{2}M_0\sigma \left| \frac{3}{2}M_1 \left\langle 1\frac{1}{2}M'_0\sigma \left| \frac{3}{2}M'_1 \right. \right. \right. \\ \times \left. \left. \left. \left(i + \delta \right) \frac{3}{2}M'_1 \right\rangle \langle (i + \delta)1M'_0 || i1M_0 \rangle \left\langle i\frac{3}{2}M_1 \right. \right. \right. \\ \left. \left. \left. + K \sum_{\langle ij \rangle} \left(\mathbf{S}_i \cdot \mathbf{S}_j - \frac{9}{4} \right) \right. \right. \right. \quad (18)$$

where $\{M\}$ denotes the set M_0, M_1, M'_0, M'_1 . Using the same method as above, it can be easily shown that this model is equivalent to a double-exchange model with infinite *antiferromagnetic* coupling J_{de} between localized and itinerant electrons:

$$H_{\text{eff}}^{\text{de}} = -t' \sum_{\langle ij \rangle \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) + J_{\text{de}} \sum_i \mathbf{s}_i \cdot \mathbf{S}_i \\ + K \sum_{\langle ij \rangle} \left(\mathbf{S}_i \cdot \mathbf{S}_j - \frac{9}{4} \right). \quad (19)$$

Here, $c_{i\sigma}^\dagger$ is the operator creating an itinerant electron of spin σ at site i , and $\mathbf{s}_i = \sum_{\alpha\beta} c_{i\alpha}^\dagger \boldsymbol{\sigma}_{\alpha\beta} c_{i\beta}$ gives the spin of this electron.

The physics of this model is expected to be quite similar to that of the model with FM exchange, as long as both Ru⁺⁵ and Ru⁺⁴ ground-state configurations are magnetic, which is this case. In fact, treating the spins classically as in Ref. 14, the sign of J_{de} is irrelevant for the electron dynamics, and only affects the effective magnetic moment of Ru⁺⁴. Thus, these results bring support to the model that successfully explained the magnetic properties of RuSr₂(Eu, Gd)Cu₂O₈.¹⁴

B. $0 < \Delta < \Delta_c$

The $4d^4$ configuration has orbital degeneracy in addition to spin degeneracy. Proceeding as before, H_{eff} can again be written as a double-exchange model, but now there are two types of carriers, each hopping only in one direction:

$$H_{\text{eff}}^{(2)} = -t \sum_{i\sigma} (x_{i+\hat{x},\sigma}^\dagger x_{i\sigma} + y_{i+\hat{y},\sigma}^\dagger y_{i\sigma} + \text{H.c.}) + J' \sum_i \mathbf{s}_i \cdot \mathbf{S}_i \\ + K \sum_{\langle ij \rangle} \left(\mathbf{S}_i \cdot \mathbf{S}_j - \frac{9}{4} \right). \quad (20)$$

While the magnetic properties of $H_{\text{eff}}^{(2)}$ should display some similarities to those of the previous $H_{\text{eff}}^{\text{de}}$, anisotropic properties and the formation of stripes are more clearly expected here. No evidence of stripes in this system has been reported so far. A preferential direction was not observed in neutron experiments.¹³ However, an equal amount of small

domains with stripes oriented in the x and y directions cannot be completely ruled out by these experiments. Furthermore, although we explore here, for completeness, all the possibilities of our model, the available experimental results seem to indicate that $\Delta < 0$.

C. $\Delta_c < \Delta < \sqrt{15}J$

In this case, the first-order effective hopping vanishes. It is necessary to go to third order in H_h to effectively exchange a $4d^3$ spin quadruplet with a $4d^3$ spin singlet and orbital doublet. Thus, the added electrons are essentially localized, and the observed magnetic properties would be difficult to explain within this picture.

D. $|\Delta| > \sqrt{15}J$

Now, for any sign of Δ , the ground state of $H_1^i + H_{CF}^i$ for $n=3$ is the spin and orbital doublet $|i3x_{\frac{1}{2}}M\rangle$, $|i3y_{\frac{1}{2}}M\rangle$. We assume that the system is in the AFII phase to be consistent with neutron experiments, in spite of the different magnitude of the localized moment. Thus, the orbital degree of freedom is ferromagnetically frozen in the direction $\gamma=x$ or y . For negative Δ , H_{eff} turns out to be equivalent to a double-exchange model with itinerant electrons coupled ferromagnetically to the localized spins $\frac{1}{2}$, and one-dimensional hopping in the direction *perpendicular* to γ . Instead, for positive $\Delta > \sqrt{15}J$, the resulting H_{eff} is equivalent to a $t-J$ model with isotropic hopping and anisotropic exchange.

VII. DISCUSSION

We have studied the electronic structure of RuO_2 planes in $\text{RuSr}_2(\text{Eu}, \text{Gd})\text{Cu}_2\text{O}_8$ using a strong-coupling approach to describe the $4d$ t_{2g} orbitals of Ru and their interactions. For undoped planes (corresponding to formal valence +5 for Ru ions), we find three possible phases. Two of them are favored for large tetragonal crystal field (of any sign), and have orbital degrees of freedom which order at zero temperature (also at finite temperatures if hopping along the tetragonal axis were included). The spins order either ferromagnetically or in a particular AF order with very small staggered magnetic moment compared to the experimentally observed one $m \sim 1.2 \mu_B$,¹³ due to strong one-dimensional fluctuations. The dominant phase for small crystal-field splitting consists of spins $\frac{3}{2}$ which order antiferromagnetically, with nearest-neighbor spins pointing in opposite directions, as observed in neutron experiments.¹³ One might wonder whether the effective measured staggered moment $\sim 1.2 \mu_B$ is closer to that of a localized spin $\frac{1}{2}$ rather than $\frac{3}{2}$. However, for both

mentioned AF phases, there are several physical ingredients that reduce the measured moment: (i) spin fluctuations that reduce the sublattice magnetization, (ii) effective Ru-Ru charge fluctuations (that are easily calculated within our perturbative approach), (iii) Ru-O charge fluctuations,²⁶ and (iv) doping, particularly if FM polarons are formed.¹⁴

When the system is doped with electrons, there are two main possibilities depending on the sign of the tetragonal crystal-field parameter Δ . If it is negative (as it seems to be the case²⁵ in Sr_2RuO_4), the additional carriers are described by a double-exchange model with infinite AF coupling with the localized $S=3/2$ spins. This model is able to qualitatively explain the apparent contradiction between observed AF order, magnetic field dependence of the magnetization, and temperature dependence of the magnetic susceptibility.¹⁴ It is also consistent with the observed magnetoresistance.^{18,19} Using previous results of the effective double exchange model,¹⁴ the experimental positive Curie constant $\Theta = 100 \pm 3$ K suggests that the xy hopping $t' \sim 0.25$ eV. A more quantitative description of the magnetic properties requires an accurate calculation of the magnetic moment. It is also possible that the double-exchange model should be supplemented by interatomic Coulomb repulsions of a moderate range,¹⁵ since the number of carriers in the system is low, particularly taking into account the low superconducting critical temperature. In addition, previous studies of the double-exchange model suggest that there is macroscopic phase separation at small doping^{21,40} which is inhibited by long-range Coulomb repulsion.

If Δ is positive, the effective model for the doped case is similar, but the carriers have an orbital degree of freedom, as in manganites,^{41,42} which might lead to the observation of orbitons by Raman scattering⁴³ for enough doping. We also expect the formation of stripes in this case. However, there is no experimental evidence of stripes so far in the system, and fitting of optical properties of another layered ruthenate Sr_2RuO_4 suggests that Δ is small and negative.²⁵ More detailed studies of the effects of doping would be possible if the superconducting critical temperature T_S could be further enhanced, either by appropriate substitution of the rare earth or by applied pressure.

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