Doping-Induced Ferromagnetism and Possible Triplet Pairing in $d^4$ Mott Insulators

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We study the effects of electron doping in Mott insulators containing $d^4$ ions such as Ru$^{4+}$, Os$^{4+}$, Rh$^{5+}$, and Ir$^{5+}$ with $J = 0$ singlet ground state. Depending on the strength of the spin-orbit coupling, the undoped systems are either nonmagnetic or host an unusual, excitonic magnetism arising from a condensation of the excited $J = 1$ triplet states of $t_{2g}$. We find that the interaction between $J$-excitons and doped carriers strongly supports ferromagnetism, converting both the nonmagnetic and antiferromagnetic phases of the parent insulator into a ferromagnetic metal, and further to a nonmagnetic metal. Close to the ferromagnetic phase, the low-energy spin response is dominated by intense paramagnon excitations that may act as mediators of a triplet pairing.

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A distinct feature of Mott insulators is the presence of low-energy magnetic degrees of freedom, and their coupling to doped charge carriers plays the central role in transition metal compounds [1]. In large spin systems like manganites, this coupling converts parent antiferromagnet (AF) into a ferromagnetic (FM) metal and gives rise to large magnetoresistivity effects. The doping of spin one-half compounds like cuprates and tinateis, on the other hand, suppresses magnetic order and a paramagnetic (PM) metal emerges. In general, the fate of magnetism upon charge doping is dictated by spin-orbital structure of parent insulators.

In compounds with an even number of electrons on the $d$ shell, one may encounter a curious situation when the ionic ground state has no magnetic moment at all, yet they may order magnetically by virtue of low-lying magnetic levels with finite spin, if the exchange interactions are strong enough to overcome single-ion magnetic gap. The $d^4$ ions such as Ru$^{4+}$, Os$^{4+}$, Rh$^{5+}$, and Ir$^{5+}$ possess exactly this type level structure [2] due to spin-orbit coupling $\lambda (\mathbf{S} \cdot \mathbf{L})$: the spin $S = 1$ and orbital $L = 1$ moments form a nonmagnetic ground state with total $J = 0$ moment, separated from the excited level $J = 1$ by $\lambda$. A competition of the exchange and spin-orbit couplings results then in a quantum critical point (QCP) between nonmagnetic Mott insulator and magnetic order [3]. Since magnetic order is due to condensation of the virtual $J = 1$ levels and hence “soft”, the amplitude (Higgs) mode is expected. The corollary of the “$d^4$ excitonic magnetism” [3] is the presence of magnetic QCP that does not require any special lattice geometry, and the energy scales involved are large. The recent neutron scattering data [4] in $d^4$ Ca$_2$RuO$_4$ seem to support the theoretical expectations.

As we show in this Letter, unusual magnetism of $d^4$ insulators, where the “soft” $J$-spins fluctuate between 0 and 1, results also in anomalous doping effects that differ drastically from conventional cases as manganites and cuprates. Indeed, while common wisdom suggests that the PM phase with yet uncondensed J-moments near QCP would get even “more PM” upon doping, we find that mobile carriers induce long-range order instead. The order is of FM type and is promoted by carrier-driven condensation of $J$-moments. By the same mechanism, the exchange dominated AF phase also readily switches to FM metal, as observed in La-doped Ca$_2$RuO$_4$ [5, 6]. The theory might be relevant also to electric-field-induced FM of Ca$_2$RuO$_4$ [6] and FM state of the Ru$_2$O$_7$ planes in oxide superlattices [7]. Further doping suppresses any magnetic order, and we suggest that residual FM correlations may lead to a triplet superconductivity (SC).

Model.– There are a number of $d^4$ compounds, magnetic as well nonmagnetic, with various lattice structures [8, 9]. To be specific, we consider a square lattice $d^4$ insulator lightly doped by electrons. Assuming relatively large spin-orbit coupling (SOC), the relevant states are pseudospin $J = 0$, 1 states of $t_{2g}$ and $J = 1/2$ states of $t_{2g}$ [see Fig. 1(a)]. The $d^4$ singlet $s$ ($J = 0$) and triplet $T_{0,\pm 1}$ ($J = 1$) states obey the Hamiltonian derived in Ref. [6]. Adopting the Cartesian basis $T_x = (T_1 - T_{-1})/\sqrt{2i}$, $T_y = (T_1 + T_{-1})/\sqrt{2}$, and $T_z = iT_0$, it can be written as

\[
H_{d^4} = \lambda \sum_i T_i^z \cdot T_i + \frac{1}{4} \sum_{\langle ij \rangle} \left[ s_i s_j^z (T_i^x \cdot T_j^x + \frac{1}{3} T_i^z T_j^z - \frac{1}{3} T_i^z T_j^z) - s_i^z s_j^z (\frac{1}{2} T_i^z T_j^z T_{ij}) + \text{H.c.} \right],
\]

(1)

where $\gamma$ is determined by the bond direction. The model shows AF transition due to a condensation of $T$ at a critical value $K_c = \frac{\lambda}{4i} \lambda$. The degenerate $T_{x,y,z}$ levels split upon material-dependent lattice distortion, affecting the details of the model behavior [10]. We will consider the cubic symmetry case and make a few comments on the possible effects of the tetragonal splitting.

The $d^4$ system is doped by introducing a small amount of $d^0$ objects – fermions $f_0$ carrying the pseudospin $J = 1/2$ of $t_{2g}$. The on-site constraint $n_s + n_T + n_f = 1$ is
implied. The Hamiltonian describing the correlated motion of $f$ is derived by calculating matrix elements of the nearest-neighbor hopping $\hat{T}_{ij} = -t_0(a_{i\sigma}^\dagger a_{j\sigma}^{} + b_{i\sigma}^\dagger b_{j\sigma}^{})$ between multielectron configurations $\{d_i^d d_j^d | T_{ij}| d_i^d d_j^d\}$. Here $a$ and $b$ are the $t_{2g}$ orbitals active on a given bond, e.g. $xy$ and $zx$ for $x$-bonds. The resulting hopping Hamiltonian comprises three contributions, $\mathcal{H}_{d^1-d^5} = \sum_{ij} (h_1 + h_2 + h_3)^{ij}$. The first one, depicted schematically in Fig. (1b,c), is a spin-independent motion of $f$, accompanied by a backflow of $s$ and $T$:

$$h_1^{(\gamma)} = -t f^\dagger f \sum_{ij} \left[ s_j^\dagger s_i^\dagger + \frac{1}{4} v(t_j^\dagger T_i^\dagger T_j^\gamma T_i^\gamma) \right].$$

(2)

The second contribution is a spin-dependent motion of $f$ generating $J = 0 \leftrightarrow J = 1$ magnetic excitation in the $d^4$ background [see Fig. (1d)]:

$$h_2^{(\gamma)} = \frac{i t}{\hbar} \left[ \gamma^{ij} \left( s_j^\dagger T_i^\dagger s_i^\dagger - T_i^\dagger T_j^\gamma s_j^\dagger - \frac{3}{4} \sigma_{ij} \cdot \left( s_j^\dagger T_i^\dagger s_i^\dagger - T_i^\dagger T_j^\gamma s_j^\dagger \right) \right) \right].$$

(3)

Here, $\sigma_{ij} = f^\dagger f \tau_{ij}^\sigma f_{j\beta}$ with Pauli matrices $\tau$ denotes the bond-spin operator. The derivation for the cubic symmetry gives $t = \frac{1}{4} t_0$ and $\hat{t} = \frac{1}{\sqrt{6}} t_0$ with the ratio $\hat{t}/t \approx 1$. However, these values are affected by the lattice distortions (via the pseudospin wave functions) and $f$-band renormalization reducing the effective $t$. We thus consider $\hat{t}/t$ as a free parameter and set $\hat{t} = 1.5 t$ below. The last contribution to $\mathcal{H}_{d^1-d^5}$ reads as coupling between the bond-spins residing in $f$ and $T$ sectors: $h_3^{(\gamma)} = \frac{i t_0}{\hbar} \left( \gamma^{ij} \left( J_{ji}^\dagger T_i^\dagger s_i^\dagger - \frac{3}{4} \sigma_{ij} \cdot J_{ji}^\dagger \right) \right)$, where $J_{ji} = -i(T_j^\dagger J_j^\dagger T_i^\gamma T_i^\gamma)$ at small doping and near QCP where the density of $T$ excitons is small, the scattering term $h_3$ can be neglected.

Phase diagram.— We first inspect the phase behavior of the model as a function of doping $x$ and interaction parameters $K$ and $\hat{t}$. The magnetic order is linked to the condensation of triplons induced by their mutual interactions and the interaction with the doped fermions $f$. In contrast to the cubic lattice where all the $T$ flavors are equivalent, on the two-dimensional square lattice the $T_2$ flavor experiences the strongest interactions and is selected to condense, provided that it is not suppressed by a large tetragonal distortion. We thus focus on $T_2$ and omit the index $z$.

Following the standard notation for spin-1 condensates, we express complex $T = u + iv$ using two real fields $u, v$. The ordered dipolar moment residing on Van Vleck transition $s \leftrightarrow T$ is then $m = 2\sqrt{6} v [3]$. Assuming either FM order (condensation prescribed by $T \rightarrow iv$) or AF order ($T \rightarrow \pm iv$ in a Néel pattern), we evaluate the classical energy of the $T$-condensate and add the energy of the $f$-bands polarized due to the condensed $T$. Doing so, we replace $s_i$ by $\sqrt{1 - x - v^2}$ to incorporate the constraint on average. The resulting total energy $E(v) = E_T + E_{\text{band}}$ is minimized with respect to the condensate strength $v$ and compared for the individual phases: FM, AF, and PM ($v = 0$). The condensate energy amounts to $E_T = [\frac{\lambda}{2} + \frac{1}{4} K (1 - x - v^2)] v^2$, with the $+/-$ sign for FM/AF phase, respectively. The band energy $E_{\text{band}} = \sum_{k \sigma} \varepsilon_{k\sigma} n_{k\sigma}$ is calculated for a particular doping level $x = \sum_{k \sigma} n_{k\sigma}$ using the band dispersion $\varepsilon_{k\sigma} = -4(t_1 - \sigma t_2) \gamma_k$ where $\gamma_k = \frac{1}{2} (\cos k_x + \cos k_y)$. The hopping parameter $t_1$ stemming from $h_1$ reads as $t_1 \simeq t(1-x)$ and $t_k \simeq t(1-x - 2v^2)$ for FM and AF, respectively. This captures the double-exchange nature of $h_1$ — only FM-aligned $T$ allow for a free motion of $f$, while AF order of $T$ blocks it. The parameter $t_2$ quantifies the polarization of the bands by virtue of $h_2$ and is nonzero in FM case only: $t_2 = \frac{2}{3} \lambda v \sqrt{1-x-v^2}$.

Shown in Fig. (2) are the resulting phase diagrams along with the total ordered moment $m_{\mu B} = 2\sqrt{6} v + n_+ - n_-$. In both phase diagrams for constant $\hat{t}/\lambda$ [Fig. (2a,b) at $x = 0$ we recover the QCP of the $d^4$ model. Nonzero doping causes a suppression of the AF phase via the double-exchange mechanism in $h_1$, and an appearance of FM phase strongly supported by $h_2$ that directly couples the moment $m \sim v$ of $T$ exciton to the fermionic spin $\sigma_{ij}$, promoting magnetic condensation. With increasing $\hat{t}$ the FM phase quickly extends as seen also in Fig. (2c,d).
containing the phase diagrams for constant $K/\lambda = 0.65$ (selected to roughly reproduce experimental value $1.3 \mu_B$ for Ca$_2$RuO$_4$ [18]) and $K/\lambda = 0.30$. The constant $\tilde{t}/\lambda$ cut in Fig. 2(c) is strongly reminiscent of the phase diagram of La-doped Ca$_2$RuO$_4$ [6, 7, 20], where the AF phase is almost immediately replaced by the FM phase present up to a certain doping level. To estimate realistic values of $\tilde{t}/\lambda$, we assume $t_0 \approx 300$ meV. Large SOC in $d^4$ Ir$^{5+}$ with $\lambda \sim 200$ meV [22, 23] leads to $\tilde{t}/\lambda \sim 1$ and places it strictly to the AF/PM (c) or PM/PM (d) regime. In contrast to this, moderate $\lambda \sim 70 - 80$ meV in Ru$^{4+}$ [2, 25] makes the FM phase easily accessible.

Spin susceptibility, emergence of paramagnons.—The tendency toward FM ordering naturally manifests itself in the dynamic spin response of the coupled T-exciton and f-band system. Here we study it in detail for the PM phase, focusing again on $T_z$ being the closest to condense. The magnetic moment $m$ is carried mainly by the fermionic component $\psi = (T - T')/2i$ of triplons so that the dominant contribution to the spin susceptibility is given by the $v$-susceptibility $\chi(q, \omega)$. To evaluate it, we replace $s_\uparrow \rightarrow \sqrt{1 - x} - n_{\uparrow\uparrow}$, and decouple $h_1$ [2] into $f$ and $T$ parts on a mean-field level. This yields a fermionic Hamiltonian $\mathcal{H}_f = \sum_{\sigma \sigma'} \varepsilon_k f_{\sigma}^\dagger f_{\sigma'}$ with $\varepsilon_k = -4t(1 - x)\gamma_k$, and a quadratic form for $T_z$ boson: $\mathcal{H}_T = \sum_q [A_q T_q^\dagger T_q - \frac{1}{4}B_q (T_q T_{-q} + T_{-q} T_q^\dagger)]$.

Here, $A_q = \lambda + 4t(n_{ij}) (1 - \gamma_q) + K(1 - \gamma_q)$, $B_q = \frac{1}{2}K(1 - x)\gamma_q$, and $\langle n_{ij} \rangle = \sum_{\sigma \sigma'} \gamma_k n_{k\sigma}$. Bogoliubov diagonalization provides the bare triplon dispersion $\omega_q = (A_q^2 - B_q^2)^{1/2}$ and the bare $v$-susceptibility $\chi_0(q, \omega) = \frac{1}{2}(A_q - B_q)/[\omega_q^2 - (\omega + i\delta]^2]$. The susceptibility is further renormalized by the coupling $h_2$ [3], which can be viewed as an interaction between a dipolar component $v$ of the triplons and the Stoner continuum of $f$-fermions:

$$\mathcal{H}_{\text{int}} = g \sum_q v_q \sigma^- - q, \quad \mathcal{H}_{\text{int}} = \sum_{kq} \Gamma_{kq} f_{k+q}^\dagger \tau^z_{\alpha\beta} f_{k,\beta}.$$  \hfill (4)

The coupling constant $g = \frac{2}{\tilde{t}}\sqrt{1 - x}$, and the vertex $\Gamma_{kq} = \frac{1}{2}(\gamma_k + \gamma_{k+q})$ is close to 1 in the limit of small $k$, $q$. By treating this coupling on a RPA level, we arrive at the full $v$-susceptibility $\chi = \chi_0/(1 - \chi_0 \Pi)$ with the $v$-selfenergy

$$\Pi(q, \omega) = g^2 \sum_{kq} \Gamma_{kq} \frac{n_{k\sigma} - n_{k+q\sigma}}{\varepsilon_{k+q} - \varepsilon_k - \omega - i\delta}. \hfill (5)$$

The interplay of the coupled excitonic and band spin responses is demonstrated in Fig. 3. The high-energy component of $\chi$ linked to $\chi_0$ follows the bare triplon dispersion $\omega_q$. In an undoped system, due to the AF $K$-interaction, $\omega_q$ has a minimum at $q = (\pi, \pi)$ and $\chi_0$ would be most intense there. By doping, the double exchange mechanism in $h_1$ disfavoring AF correlations pushes $\omega_q$ up near $(\pi, \pi)$. Further, due to a dynamical mixing [21, 22] of triplons with the fermionic continuum, the low-energy component of $\chi$ gains spectral weight as $\tilde{t}/\lambda$ approaches the critical value, and a gradually softening FM-paramagnon is formed [see Fig. 3(b)]. The emergence of the paramagnon and the increase of its spectral weight is shown in detail in Fig. 3(c). Finally, once the critical $\tilde{t}/\lambda$ is reached, triplons, whose spectral weight was pulled down by the coupling to the Stoner continuum, condense and the FM order sets in, signaled by the divergence of $\chi(q = 0, \omega = 0)$ [cf. 3(c,d)].

Triplet pairing.—Intense paramagnons emerging in the proximity to the FM phase may serve as mediators of a triplet pairing interaction [2]. In the following, we perform semiquantitative estimates for this triplet SC. While the dominant contribution to the pairing strength is due to the $v_z$-fluctuations, in order to assess the structure of the triplet order parameter, the full coupling $\mathcal{H}_{\text{int}} = g \sum_q v_q \sigma^- - q$ leading to the effective interaction $-\frac{1}{2}g^2 \sum_{q_0} \chi_0(q, \omega = 0) \sigma^a_q \sigma^a_{-q}$ has to be considered. The $v_z$-susceptibility $\chi_0$ for $\alpha = x, y$ may be calculated in the same way as $\chi_2$ above, using now $A_q^2 = A_q^2 + \frac{1}{2}(\gamma_k + \gamma_{k+q})$ cos $q_k$ and $B_q = B_q^2 - \frac{1}{2}K(1 - x) \cos q_k$. The coupling vertex for $v_x$ and $v_y$ obtains an additional contribution, $\Gamma_{q} = \Gamma_{k} - \frac{1}{2} \cos k_x + \cos (k_y + q_y)$. The resulting BCS interaction in terms of $\tilde{t} + \tilde{t}_k = f_{k\uparrow} f_{k\downarrow}^\dagger$, $t_0k = \frac{1}{\sqrt{2}}(f_{k\uparrow} f_{-k\uparrow}^\dagger + f_{k\downarrow} f_{-k\downarrow})$. 

![](image-url) FIG. 2. (Color online) (a,b) Phase diagrams and the ordered magnetic moment value for varying doping $x$ and $K/\lambda$ keeping fixed $\tilde{t}/\lambda$ of 1.7 and 2.5. (c) Phase diagram for varying doping and $K/\lambda$ and fixed $K = 0.65\lambda$ above the critical $K_c = \frac{\pi}{2}\lambda$ of the $d^3$ system. Bottom panel shows $m(x)$ along the cut at $\tilde{t}/\lambda = 3.0$. (d) The same for $K = 0.3\lambda$ and the cut at $\tilde{t}/\lambda = 3.0$. 

![Diagram](image-url)
and \( t_{-1k} = f_{k+} f_{k-} \) takes the form

\[
\mathcal{H}_{\text{BCS}} = -\frac{1}{2} \sum_{k, k'} \left[ V_z \left( t^+_k t_1^+ + t^-_{1k'} t_{k'} + \right. \right.
\]

\[
\left. \left. + (V_x - V_y) (t^+_k t^-_{1k'} + t^-_{1k} t^+_k) + (V_x + V_y - V_z) t^+_k t^+_0 \right] \right],
\]

(6)

where \( V_{\alpha} \) denotes the properly symmetrized \( V_{\alpha k k'} = g^2 (\Gamma_{\alpha k k'} - k')^2 \frac{1}{2} \left[ \chi_{\alpha}(k - k') - \chi_{\alpha}(k + k') \right] \). Decomposed into the Fermi surface harmonics, the BCS interaction is well approximated by \( V_{\alpha k k'} \approx 2V_0 \cos(\phi_k - \phi_{k'}) \) and \( (V_x - V_y) k k' \approx 2V_1 \cos(\phi_k + \phi_{k'}) \) with \( V_{0,1} > 0 \) [see Fig. 3(d) and Fig. 4(a)]. The relatively small \( V_1 \ll V_0 \) fixes the relative phase of the \( t_{-1k} \) and \( t_{-1k'} \) pairs so that the SC order parameter becomes \( \Delta_{\pm 1k} = \Delta_0 \pm \phi_k \). This ordering type is captured by the \( d \)-vector \( \mathbf{d} = -i \Delta \sin(\phi_0, \cos(\phi_0, 0) \rightarrow \tilde{b}_{k_0} + y_{k_0} \) shown in Fig. 3(b). In the classification of Ref. 28, it forms the \( \Gamma_4 \) irreducible representation of tetragonal group \( D_{4h} \). However, this

result applies to cubic symmetry case. Lattice distortions that cause splitting among \( T_{x,y,z} \) and modify the pseudospin wave functions may in fact offer a possibility to “tune” the symmetry of the order parameter. If distortions favor \( T_{x,y} \), the potentials \( V_{x,y} \) are expected to dominate in Eq. 6, supporting the chiral \( t_0 \)-pairing represented by the last term in (6).

Data in Fig. 4(c,d) serve as a basis for a rough \( T_c \) estimate. Fig. 4(c) shows the BCS parameter \( \lambda_{\text{BCS}} = V_0 / V \) (\( N \) is DOS per spin component of the \( f \)-band) which attains sizable values near the FM phase boundary, where the paramagnons are intense. To avoid complex physics near the very vicinity of the FM QCP [29, 31], we take a conservative upper limit \( \lambda_{\text{BCS}} \approx 0.5 \). Extending \( V_0 \) by the \( \omega \)-dependence of the underlying \( \chi_{\alpha}(\mathbf{q}, \omega) \), we define \( \lambda_{\text{BCS}}(\omega) \). Its imaginary part to be understood as the conventional \( \lambda_{\text{BCS}}(\omega) = \frac{\chi_{\alpha}(\mathbf{q}, \omega)}{2} \) is plotted in Fig. 4(d) yielding an estimate of the BCS cutoff \( \Omega \approx 0.1 \lambda \). With \( \lambda \approx 100 \text{ meV} \), this gives \( T_c \approx \Omega e^{-1/\lambda_{\text{BCS}}} \) of about 10 K.

In conclusion, we have explored the doping effects in spin-orbit \( d^3 \) Mott insulators. The results show that the doped electrons moving in the \( d^3 \) background firmly favor ferromagnetism, explaining e.g. the observed behavior of La-doped Ca$_2$RuO$_4$. In the paramagnetic phase near the FM QCP, the incipient FM correlations are manifested by intense paramagnons that may provide a triplet pairing.

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