A ground state phase diagram of a spinless, extended Falicov–Kimball model on the triangular lattice

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Abstract
Correlated systems with hexagonal layered structures have come to the fore with renewed interest in cobaltates, transition metal dichalcogenides and GdI2. While superconductivity, unusual metal and possible exotic states (prevented from long-range order by strong local fluctuations) appear to come from frustration and correlation working in tandem in such systems, they freeze at a lower temperature to crystalline states. The underlying effective Hamiltonian in some of these systems is believed to be the Falicov–Kimball model and therefore, a thorough study of the ground state of this model and its extended version on a non-bipartite lattice is important. Using a Monte Carlo search algorithm, we identify a large number of different possible ground states with charge order as well as valence and metal–insulator transitions. Such competing states, close in energy, give rise to complex charge order and other broken symmetry structures as well as the phase segregations observed in the ground state of these systems.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
Systems such as transition metal dichalcogenides [1–3], cobaltates [4], GdI2 [5, 6] and its doped variant GdI2H, [7] have attracted considerable attention recently as they exhibit a number of remarkable cooperative phenomena, such as valence and metal–insulator transitions, charge and magnetic order, excitonic instability [1] and possible non-Fermi liquid states [6, 8]. The underlying geometric frustration of the triangular lattice, coupled with strong quantum fluctuations, gives rise to a large degeneracy at low temperatures and competing ground states close by in energy. A consequence of this is a fairly complex ground state magnetic phase diagram [7] and the presence of soft local modes strongly coupled to the conduction electrons [6].

These systems are characterized by the presence of localized and itinerant electrons confined to the two-dimensional triangular lattice. The electronic coherence along the perpendicular direction is negligible owing to the presence of large intervening ions (like iodine in GdI2) between the layers of rare earth or transition metal ions. It has been suggested recently that these correlated systems may very well be described by an effective Falicov–Kimball model (FKM) on a triangular lattice. The nearly degenerate manifold of d-states close to the Fermi level, seen in LSDA calculations [7], breaks down into a narrow, core-like state pushed below the Fermi level and an extended state crossing it, due to the strong local correlations in the d-band manifold [6]. The situation is similar to the well-known FKM [9], if electrons in this narrow, localized band are assumed to possess a very large effective mass. In the usual FKM one considers only the kinetic energy of the itinerant electrons and the local Coulomb interaction between the itinerant and localized electrons. This model has a long history, and has been used to study metal–insulator transition, magnetism in correlated systems and, in the version where the interaction is attractive (the sign of the interaction is irrelevant in a particle–hole symmetric case), it can be used to model crystallization in solids [10]. Most of the studies are mean-
field in nature. There are only a few exact results, which are almost entirely on bipartite lattices [11–14] and are in lower dimensions [15].

A very important question, in this context, is the nature of the ground states in such a system. Most of the systems described above show charge and orbital order at low temperatures. The layered material Na$_x$CoO$_2$ which shows superconductivity on hydration, reveals a $\sqrt{3} \times \sqrt{3}$ superlattice [4] at low temperatures due to spacial modulation of charge/orbital densities. Transition metal dichalcogenides mostly freeze into charge density wave states [16], both commensurate and incommensurate (on doping some of them become superconductors at low temperature). Superlattice spots have also been seen in GdI$_2$ in x-ray scattering at low temperatures. Regions of phase segregations have been seen in many of these systems [17] as the density of electrons is changed via doping or intercalation (both the localized and itinerant electron densities can be varied). Phase separation is a major attribute of all the different manganites and a host of other correlated systems. Phase segregation in correlated electrons and the routes to achieve and control it have indeed been hotly debated subjects for over a decade now [17].

Modeling the low-energy physics of some of these materials in an effective FKM naturally leads to such ordered states at low temperature. The FKM is known to support various kinds of ordered or phase segregated [12, 18] ground states on a bipartite lattice. Some of these ordered structures appear in the ground state of a triangular lattice as well [18]. There are hardly any rigorous results for the ground state of FKM on a triangular lattice. Most of the results are perturbative [18, 19], valid for large $U$. The combined effects of correlation and geometric frustration on the ground state phase diagram have not been investigated extensively using numerical methods on finite size lattices either. With the appearance of charge ordered states as the low-energy broken symmetry ground states in the systems described above, it is imperative to look for the solutions of the FKM at low temperatures. In this work, therefore, we numerically study the FKM in its spinless version for all ranges of interaction, and explore the ground state charge ordering on a triangular lattice.

It may be noted that in some rare earth compounds (especially the mixed valence compounds), the rare earth ions with two different ionic configurations $f^n$ and $f^{n-1}$ have different ionic radii. The contraction of d-orbitals in ions having the $f^{n-1}$ configuration, for reduced screening of nuclear charge, leads to their increased localization. This implies that the d-orbital overlap between nearest neighbors depends on local f-electron configurations of neighboring ions, resulting in a correlated hopping of d-electrons. Such a correlated hopping term also appears in the first principles calculation [20] of the tight binding Hamiltonian, and is usually neglected in Hubbard type models as being smaller compared to the on-site term. Its significance in superconductivity has already been emphasized [21, 22] and in the context of FKM, it has been considered by several authors [19, 23, 24] using various approximations. We, therefore, extend the model to include a correlated hopping term in the Hamiltonian for the itinerant electrons.

$$
H = -\sum_{\langle ij \rangle} \left( t_{ij} + \mu \delta_{ij} \right) d_i^\dagger d_j + E_1 \sum_i f_i^\dagger f_i + U \sum_i f_i^\dagger f_i + \sum_{\langle ij \rangle} \left( f_i^\dagger \left( f_j^\dagger + f_j \right) \right) d_i^\dagger d_j.
$$

Here $d_i^\dagger, d_i \ (f_i^\dagger, f_i)$ are, respectively, the creation and annihilation operators for itinerant d-electrons (localized f-electrons) at the site $i$. The first term in equation (1) is the kinetic energy of d-electrons on a triangular lattice: only nearest-neighbor hopping is considered. The second term represents the dispersionless energy level $E_1$ of the f-electrons, while the third term is the on-site Coulomb repulsion between d- and f-electrons. The last term, a correlated hopping term, is an extension over the usual FKM as discussed above. In the context of GdI$_2$ (or the transition metal dichalcogenides), the f-electrons represent the localized (or valence) band below the Fermi level, while d-electrons cross the Fermi level in the effective low-energy model alluded to earlier [6, 25].

2. Methodology

The Falicov–Kimball Hamiltonian (1), conserves the local f-electron occupation number $n_{\text{f}} = f_i^\dagger f_i$, owing to its local $U(1)$ gauge invariance in the absence of f–d hybridization. Therefore, $[n_{\text{f}}, H] = 0$ and $o_i = f_i^\dagger f_i$ is a good quantum number taking values only 0 or 1. The gauge symmetry also implies [26]$^3$ the interband excitonic averages of the type $\langle d_i^\dagger f_j \rangle$ are identical zero at any finite temperature (implying an absence of homogeneous mixed valence) and the f-electron level remains dispersionless $\langle f_i^\dagger f_j \rangle = 0, \text{ for } i \neq j$. On a non-bipartite lattice, as we consider here, there is no particle–hole symmetry either. The local conservation of f-electron number implies that the Hamiltonian may be written as

$$
H = \sum_{\langle ij \rangle} h_{ij} (\omega) d_i^\dagger d_j + E_1 \sum_i o_i
$$

where $h_{ij} (\omega) = [ -t_{ij} + t_{ij} (\omega_i + \omega_j) ] + ( U \omega_i - \mu ) \delta_{ij}$.

We set the scale of energy with $t_{ij} = 1$. The Hamiltonian equation (2) represents a non-interacting d-electron moving in an annealed disordered background of the f-electrons [27]. The interactions among the electrons is, therefore, kinematical in nature, coming entirely from the Fermi statistics for a given f-electron configuration. It suffices therefore to obtain the spectrum of this Hamiltonian for different configurations $\omega = \{ \omega_1, \omega_2, \ldots, \omega_N \}$ of f-electrons by numerically diagonalizing the Hamiltonian over different $\omega$ and annealing over the configurations. We perform this on a triangular lattice of finite size with periodic boundary conditions (PBC). Although this entails a tremendous simplification over solving a full interacting quantum Hamiltonian, even for a relatively small lattice size (in this work we considered $L \times L$ lattice with $L = 12$ and checked the results at larger $L$ values in test cases), the number of different f-electron configurations is

$^3$ In the context of FKM, the absence of homogeneous mixed valence is explicitly worked out in Subramaniam and Barma [26].
exponentially large and it may not be feasible to explore all the configurations within a reasonable computer time. For example, even for \( N = 36 \) and \( N_f = 18 \), the number of configurations \( N_{\text{conf}} \sim 10^{10} \).

Therefore, one needs efficient search algorithms and can explore only a relatively small subset of the entire f-electron configurations. We have used a Monte Carlo sampling method to achieve this goal. We work at half-filling, i.e., \( N_f + N_d = N \), where \( N_f, N_d \) are the total number of f- and d-electrons and \( N = L^2 \) is the number of sites. For a lattice of \( N \) sites, the basis is chosen as \( d_0^\dagger \langle 0 \rangle, \ldots, d_N^\dagger \langle 0 \rangle \) and \( H \) (in equation (2)) is now an \( N \times N \) matrix for a fixed configuration \( \omega \). The partition function is, therefore,

\[
Z = \prod_i \left( \sum_{\omega_j=0,1} \text{Tr} e^{-\beta H(\omega_j)} \right)
\]

where the trace is taken over the d-electrons, and \( \beta = \frac{1}{kT} \). The trace can be calculated from the eigenvalues \( \lambda_i \) (\( i = 1 \cdots N \)) of the matrix \( h \) (first term in \( H \) (equation (2))) quite easily. \( h \) is diagonalized by a unitary transformation \( U^\dagger h U = K \), where \( K \) is a diagonal matrix with \( \lambda_i \) its diagonal elements. The unitary rotation gives the diagonal basis (in which \( h \) is diagonal) represented by the eigenvectors \( v_i^\dagger \langle 0 \rangle, \ldots, v_N^\dagger \langle 0 \rangle \). Defining the operator \( \hat{n}_i = v_i^\dagger v_j \) and writing \( n_i \) to denote the corresponding eigenvalues of \( \hat{n}_i \), the trace above can be identified with

\[
\text{Tr} e^{-\beta h} = \sum_{n_1 \cdots n_N} \langle n_1 \cdots n_N | e^{-\beta h} | n_1 \cdots n_N \rangle
= \sum_{n_1 \cdots n_N} \langle n_1 \cdots n_N | e^{-\beta \sum_i \lambda_i n_i} | n_1 \cdots n_N \rangle.
\]

This reduction of the exponential to a c-number is the essential simplification that makes the problem amenable to a classical MC calculation. The partition function can, therefore, be recast in the form

\[
Z = \prod_i \left( \sum_{\omega_j=0,1} e^{-\beta E(\omega_j)} \right) \prod_{j=1}^N (\text{Tr}_j e^{-\beta \lambda_j n_j})
= \prod_i \left( \sum_{\omega_j=0,1} e^{-\beta E(\omega_j)} \right) \prod_{j=1}^N (1 + e^{-\beta \lambda_j}).
\]

An average of any operator operating on the d-electrons is then calculated using the usual statistical mechanical procedure \( \langle \hat{A} \rangle = \text{Tr} (\hat{A} e^{-\beta h}) / \text{Tr} (e^{-\beta h}) \). Indeed, the intensive part of the calculation involves finding the eigenvalues of \( h \). The summations over the static variables \( \{\omega_j\} \) are evaluated using a classical Monte Carlo simulation. In order to get the ground state, a simulated annealing is employed, ramping the temperature down from a high to a very low value. The process, therefore, involves the following steps: (i) for a lattice of size \( L (N = L^2) \), choose a particular value of \( N_f (0 \leq N_f \leq N) \), and \( N_d = N - N_f \). (ii) For a fixed \( N \) and \( N_f \), we choose a random configuration \( \omega = \{\omega_1, \omega_2, \ldots, \omega_N\} \). (iii) Choosing values for \( t', U \) and \( E_c \), we find the eigenvalues \( \lambda_i \) of \( H(\omega) \) and the corresponding total free energy \( F(\omega) = -kT \log Z \). The chemical potential \( \mu \) is used to fix the d-electron number \( N_d \). The corresponding total energy is then \( E(\omega) = \lim_{T \to 0} F(\omega) \).

(iv) Generate a new random configuration \( \omega' \) and calculate the new energy \( E(\omega') \). (v) Find \( \Delta E = E(\omega) - E(\omega') \), compare \( s = e^{-\Delta E/kT} \) with a random number \( r_n \) (\( 0 < r_n < 1 \)); if \( r_n < \min(1, s) \), accept the new configuration \( \omega' \); else it is rejected. The steps (ii)–(v) are repeated until convergence is reached at a temperature \( T \). The temperature is then ramped down slowly to a very low (compared, again, to typical \( \Delta E \)) value and at each step of \( T \), the same routine is performed. Repeating this over a few times usually leads to a unique low-energy state to the lowest temperatures searched. Although this is still a finite temperature state, the nearest excitation \( \Delta E \) was checked to be higher than \( kT \), indicating that this is the likely ground state. This procedure converges to the ‘ground state’ faster (even for the largest lattice sizes we studied) in contrast with other methods [24] and makes it possible to test our results in larger lattices. There are, of course, the usual problems of simulated annealing that one needs to take care of. While ramping down in \( T \), it often gets stuck in a local minimum even when the ramping is made ever slower at lower \( T \). Different kinds of moves, and at times simultaneous moves involving several sites (and at longer ranges), were employed to drive the system out of the quench. The procedure has been successfully used in the search for complex ground state structures in manganites [17]. It allows us to work in a much smaller sample space of the whole configuration space, and any physical variable may be obtained by averaging over this sample space. A similar approach was earlier employed in the study of the phase transitions in FKM on a bipartite lattice [28, 29].

3. Results and discussion

Perturbative results for large \( U \) indicate that to order \( 1/U \), the FKM can be mapped onto an Ising antiferromagnet (AFM) in a magnetic field \( H_{d} = \sum_{i} \frac{1}{2} s_i \left( s_i + \frac{1}{2} \right) (\mu + E_c) \sum_j s_j + \text{ constant terms} \), where \( s_i = 2 \omega_i - 1, s_i = -1, 1 (\omega_i) \) is the local f-electron occupation defined above). The Ising AFM state on a triangular lattice is frustrated and leads to large degeneracies at low temperature, as discussed above. It turns out that this frustration is lifted [18] in the higher order perturbation in \( 1/U \). It is therefore quite intriguing that one would expect the effects of frustration to bear on the ground states as \( U \) and the chemical potentials are varied. Different regions of the phase space are, therefore, controlled by different dominant effects. We studied the ground state configurations and the possible valence transitions as a function of a range of values of \( U \), and filling \( n_f = N_f/N \) using the method outlined in section 2. \( N_d \) is constrained to \( N - N_f \) at half-filling, while the Hamiltonian conserves \( N_f \) and \( N_d \) separately, allowing us to work with fixed \( N_d \) and \( N_f \) [14, 28, 30]. As mentioned at the beginning, phase diagrams in the experimental systems are obtained by controlling the density of electrons, making the canonical ensemble a natural choice. We look at the effect of correlated hopping of d-electrons on these phases and obtain the ground state configuration for several values of \( t' \in [-1, 1] \) at a fixed \( U \).

In figure 1 we present the phase diagram in the \( n_f-t' \) plane at three representative free energy values \( (U = 1, 3 \) and 5). We observe
that the ground state configurations of f-electrons for a fixed filling are significantly affected by the correlated hopping $t'$ and undergo several phase transitions at lower $U$ values. At larger $U$, the ground states remain nearly independent of $t'$. The various ground state phases encountered in figure 1 are mainly: (a) **Regular phase**: found around $n_f = \frac{1}{4}$ (figure 2(a) columns 1, 2), where the filled sites are arranged in a long-range ordered pattern over the three sublattices (A, B, C). Following the definitions on a square lattice [27], in this phase, $s_i = \epsilon_\alpha(-1)^x$. Here $\alpha$ is the row number, $\epsilon_\alpha = 0$ (1) for $\alpha$ odd (even) and $x = 0$ for $i \in A$ and 1 otherwise. There are also situations where a nearly regular pattern with few defects appear (see figure 2(b), first column). These have been dubbed as ‘quasi-regular’ [30] earlier. (b) **Bounded phase**: where there are separated regions of empty sites (several domains of empty sites surrounded by filled sites on all sides), observed (see footnote 4) around $n_f = \frac{1}{2}$ (figures 2(c) and (d), first column). There is no apparent spatial order in this state and it is found to shrink as $U$ increases. (c) **Hexagonal phase**: (figure 2(d) second column) where f-electrons form hexagonal structures, are observed at all investigated $U$ values. They appear at $n_f = \frac{1}{3}$ and $\frac{4}{3}$. As in the regular phase, there is a long-range order here, the correlation function $\langle s_i s_j \rangle = 1$ for $i, j \in A, B$ and $-1$ if only one of the $i, j$ belongs to $C$. We get a nearly hexagonal phase slightly away from these commensurate values of $n_f$. (d) **Segregated phase**: where domains of sites occupied by f-electrons are segregated from the unoccupied sites (figure 2 column 3 shows four such configurations). (e) **Stripe phase**: the filled sites form diagonal stripes (figure 2(c) second column). This phase is observed at higher values of $U$ (above $U \sim 5$) at $n_f = 1/2$. Interestingly, such stripes are seen in manganites at commensurate fillings as well. The stripe phase is found to be stable at finite $t'$ ranging from $-1$ to 0.8, beyond which there is phase segregation. Comparing our results with earlier results at the $t' = 0$ limit [30], we find that there can be phase segregation now at a lower value of $U$ (for example, $U \simeq 1$) as the parameter $t'$ is tuned. The $t'$ term would, therefore, play an important role in driving phase segregation even in weakly correlated systems. This could be understood by looking at the position of the localized f-electron level ($E_f$) with respect to the d-electron band. At large $U$, the d-band is strongly renormalized and the modulation of the d-band due to the $t'$ term becomes insignificant. It is also noticed that $t' = 1$ is a special point, as at this point hopping takes place only between pairs of sites having identical f-electron occupation (near-neighbor

Figure 1. $n_f-t'$ phase diagram for $U = 1, 3$ and $5$. In the $U = 5$ phase diagram there is a **stripe** phase exactly at $n_f = 1/2$ from $t' = -1$ to 0.8 (shown by a horizontal line from $t' = -1$ to 0.8).
Figure 2. The ground state configurations for various values of $U$, $t'$ and $n_f$. Filled circles correspond to sites occupied by f-electrons and open circles correspond to unoccupied sites.

configurations $\{0, 0\}$ and $\{1, 1\}$, though, occupying different regions of the Brillouin zone. This enhances the formation of inhomogeneous phases where a pair of f-electrons (or a pair of empty sites) tend to occupy neighboring places on the lattice, as in figure 2 column 3. If the coherence of the f-electrons is restored, this would lead to the formation of interband excitons involving near-neighbor sites (at finite f–d mixing). In the context of the Hubbard model, where d (f)-electrons represent up (down) spins, the correlated hopping would, therefore, tend to enhance the extended s-wave superconducting order parameter (OP) fluctuations.

Shown in figure 2 are some of the ground state patterns mentioned above and their dependence on the correlated hopping parameter $t'$ as well as the Coulomb correlation strength $U$. Figure 2(a) (top panel) reveals the variety of ground state patterns at $n_f = 1/4$, starting from regular structures to phase segregated regions on changing the value of $t'$ from $-1$ to $+1$ at $U = 1$. This is also observed at $n_f = 1/3$, where on varying either $U$ or $t'$ one could go from a quasi-regular pattern to phase segregated regions. At $n_f = 1/2$ (panel (c)) we have shown three patterns corresponding to three different sets of values for $U$ and $t'$ (i.e., bounded, stripe and phase segregated). On changing the value of $U$ from 1 to 5, keeping $t'$ fixed at $-1$, a transition from a bounded phase to a stripe phase occurs, whereas on changing the value of $t'$ from $-1$ to $+1$ at a fixed $U = 1$, we arrive at a phase segregated state. Finally in panel (d) we present the phases observed at $n_f = 2/3$, ranging from bounded, hexagonal to phase segregated regions at three different $t'$. It is clear from the figure that a non-zero $t'$ facilitates phase segregation in the ground state as it favors simultaneous occupation of f-electrons (or simultaneous occupation of vacancies, depending on the value of $t'$) in the neighboring sites. Phase segregations have been the key to the physics of many correlated systems hotly pursued in the last decade [17] and this correlated hopping term seems to open up another route to the phase segregation scenario in certain correlated systems. A ground state phase diagram in the $t'$–$U$ plane could be drawn now, based on the structures obtained in figure 2. We show this at $n_f = 2/3$ in figure 3. One can identify the three different phases, namely, bounded, hexagonal and segregated. The reasonably large region of phase segregations at the upper part of the phase diagram primarily owes its origin to $t'$, as discussed earlier. At large $U$, of course, the hexagonal phase dominates. At this filling, no other phases were found in the range of parameters studied.
In order to identify if there is a metal to insulator transition in the above phase diagrams, we look at the d-electron spectrum (figure 4) and observe the gap at the Fermi level at various values of $U$ and $t'$ in the corresponding density of states (DOS). In figure 4(a) is shown the DOS for three distinct phases observed at $n_f = 2/3$, keeping $U$ fixed while changing $t'$. Figure 4(b) shows the DOS for different values of $U$, $t'$ in two different phases at $n_f = \frac{1}{3}$. We find that the hexagonal phase at $U = 5$ is insulating with a large gap, the bounded phase at low $U$ is also insulating but with a small gap, while the phase segregated regions appear to have a very small (or vanishing) gap. Although the charge excitation gap continues to increase with $U$ in the insulating phases, a 'spin' excitation involving exchange between vacant and occupied f-electron sites has a lower energy scale $\sim \frac{1}{U}$ at large $U$. In this context, we note the evolution of the spectrum and the corresponding DOS in figure 4(b) at a lower $n_f = 1/4$. It is clear that the DOS in the regular phases ($U = 1, t' = -1$ and $U = 5, t' = -1$) have two-peak like structures above and below Fermi energy $E_F$ (in the phases with a clear gap at the Fermi level) and the gap at the Fermi level increases with $U$. The band spreads out towards higher energy as expected. But the segregated phase ($U = 1, t' = 1$) here is observed to have an almost gapless spectrum. Whether a very tiny gap still exists is not clear from this finite size calculation, but within our numerical accuracy it appears to have closed. Such observations are reported earlier, albeit on a square lattice away from half-filling [13]. It is possible that due to the segregation of f-electrons in one part of the lattice, d-electrons find a percolative path in the rest of the lattice and move freely from one end of the lattice to the other without appreciable effects of correlation in the segregated phase.

It is clear that the degeneracies as well as the separation between the energy levels increase as $U$ rises and lead to incompressible states at specific values of the filling (or, equivalently, the chemical potential) in the thermodynamic limit. The FKM is known to show first order transitions and consequent phase separations in the bipartite lattices, and it appears that similar physics holds good in a large part of the phase diagram for a triangular lattice as well. In order to glean a physical picture of the local electron occupancies in different regimes, we have drawn the density of the d-electrons on the real lattice (figure 5) where the radii of the circles are proportional to the d-electron density at that site (a color coding is also used). A change of $t'$ from 1 to $-1$ leads to an increase in d-electron density on the unoccupied sites (sites without an f-electron) as discussed above. For $t' = 1$ there is a reasonable weight of the d-electrons in the occupied sites at smaller $U$. As $U$ increases, the wavefunctions spread out from occupied sites. Thus the competition between localization and itinerancy is clearly visible from these figures.

The FKM is known to have transitions [12] involving states with different $n_f$ values. We have looked at these
**Figure 5.** d-electron densities are shown on each site for $U = 1$, $t' = -1.0$, $n_f = 1/4$; $U = 5$, $t' = -1.0$, $n_f = 1/4$ and $U = 1$, $t' = 0.4$, $n_f = 2/3$. The color coding and the radii of the circles indicate the d-electron density profile. The dark dot indicates $\omega_i = 1$ at that site.

**Figure 6.** $n_f$–$E_f$ phase diagrams for $U = 1$ and different values of $t' = -1.0$, -0.6, 0, 0.6 and 1 respectively. We observe that as $t'$ increases from -1.0 to +0.6, the valence transition (i.e. $n_f$-transition) (i) occurs at smaller values of $E_f$ and (ii) becomes sharper. However, as shown in figure 6(e), the $n_f$-transition becomes smoother again for $t' = 1.0$. We observe that the transition width (the range of $E_f$ over which $n_f$ goes from 1.0 to 0.0) decreases as $t'$ increases from -1.0 to 0.6. This could be explained from the fact that at $t' = -1.0$, the position of $E_f$, where $n_f$ starts decreasing (from its maximum value 1.0) is located far below the center of the d-band. As $t'$ increases towards zero, the position of $E_f$, at which $n_f$ starts decreasing, moves towards the center of the d-band. The dark dot indicates $\omega_i = 1$ at that site.

Transitions as a function of $N_f$ (keeping $N_f + N_d = N$) depending on the relative position of the f-electron level ($E_f$) and the Fermi level of the d-electrons. If $E_f$ lies above the Fermi energy ($E_F$), then $N_d = N$ and the f-states are empty. In the opposite limit, we are in a classical mixed-valent regime. For a given set of $t'$, $U$ and $E_f$, one can easily find the values of $N_f$ for which the ground state has minimum energy. We have plotted $n_f$ in figure 6 as a function of $E_f$ for a set of values of $t'$ and $U$.
For $t' > 0.6$, the corresponding position of $E_f$ again moves below the center of the d-band. So the effective width of the d-band is maximum for $t' = -1.0$, is minimum around $t' = 0.5$ and increases again for $t' > 0.5$. In figures 7(a)–(c) we show the same for $U = 1.5, 10$ with $t' = -0.6, 0$ and 0.4. We observe here that the transition width decreases as the value of $U$ increases. The value of $E_f$ where major change in $n_l$ occurs hardly depends on the value of $U$. For all values of $U$, the $n_l$-transition is relatively smooth for $t'$ around $-0.6$, becoming steep for $t'$ around 0.4. These features are easily understood from an analysis of the spectrum of d-electrons.

As an interesting aside, we note that although the extended FKM studied here has $U > 0$, the corresponding ground state phase diagram for $U < 0$ is obtainable from the following symmetry: if $\{\omega_i\}$ is the ground state for a particular $\mu, E_f$ and $U$, then $\{\bar{\omega}_i\}$ is the ground state for $\mu, -E_f, -t'$ and $-U$, where $\bar{\omega}_i = 1 - \omega_i$. The negative $U$ FKM was introduced by Lieb [10] as a model for the study of the formation of crystalline solids. In that context, the heavy f-electrons can be thought to represent the ions in a solid, and their ordered structure implies a crystalline arrangement of the lattice.

It is in order now to discuss the numerical results obtained above in the context of the systems where such models are expected to be useful, under simplifying assumptions, in certain regions of their phase diagrams. Figure 1 gives a good account of the complexity of phases obtainable from an FKM on a triangular lattice. The model produces charge ordered states of varying periodicities and phase segregated states as filling, $U$ and $t'$ are changed, also observed in dichalcogenides, cobaltates and GdI$_2$. The hexagonal structure close to $n_l = 2/3$ is reminiscent of the superlattice structure in Na$_x$CoO$_2$ (at $x = 2/3$ in figure 3(c) of [4]). The CDW in 2H-TaS$_2$ is incommensurate [3], while it is commensurate in TiSe$_2$ [2], though the superlattice periodicity is dictated by special relations between the nearly flat valence band and the conduction band [1, 2], rather than the geometry of the underlying lattice, since the CDW in TiSe$_2$ is likely to be excitonic in origin [1]. Stripes in correlated systems tend to appear at special fillings [17] due to commensurability effects in bipartite lattices, while we observe its formation here (e.g.,

at $n_l = 1/2$) even if the underlying lattice is non-bipartite. Stripes have not yet been seen experimentally in the systems we discussed, but appear to be a distinct possibility if carefully investigated. The phases revealed here clearly shows the intricate nature of the competing states alluded to earlier—correlation and frustration working together on a triangular lattice in unraveling such a rich phase diagram. This underlines the need for a thorough experimental investigation of these systems to delineate both the ordered and inhomogeneous phases as filling and parameters change.

As discussed earlier, a common feature among systems like dichalcogenides [2, 3] and Na$_x$CoO$_2$ [4] is the competition between a charge density order and superconductivity, where slight changes in symmetry, or a small perturbation, may lead to a transition from one to the other. Off-diagonal long-range order (ODLRO) is absent in the FK model, unless of course the f-electrons become dispersive. In the limit of infinitely heavy down-spin electrons ($t_{ij,↓} = 0$), the Hubbard model reduces to the (symmetric) FKM. With any symmetry-breaking perturbation (pressure [1], doping/hydration [2, 4, 3] etc), as $t_{ij,↓}$ shifts away from zero, the charge order or phase segregation may disappear [32] and superconductivity could appear: s-wave for the attractive-U model and extended s-wave in the repulsive-U case, due explicitly to the $t'$ term [21]. The nature of superconductivity in both these systems should, therefore, shed considerable light on the underlying microscopic mechanism operating here. Although there is a suggestion of high angular momentum superconducting OP in doped dichalcogenides [8], the symmetries of OP in hydrated cobaltate and doped dichalcogenides are not resolved yet and should be probed thoroughly.

In GdI$_2$ a phase segregation appears to preempt the formation of a long-range order. While phase segregation has been shown to appear in FKM on bipartite lattices [32, 14], it requires a fairly strong $U$. GdI$_2$ falls in the intermediate coupling range and the phase segregation seen in GdI$_2$ at low temperatures even for a low $U$ could be facilitated by the presence of $t'$, as shown above. The correlated hopping term helps in tuning the balance between states close in energy, and therefore, plays a significant role in non-bipartite lattices where nearly degenerate states proliferate at low temperatures. We note that a quantitative modeling in detail, including first principles band structure and Fermi surface topologies, is beyond the present model. Such a study would indeed be very

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Note that in the FK model for both Na$_x$CoO$_2$ and GdI$_2$, the localized level is actually two-fold degenerate, and decorating the hexagonal pattern in figure 2(d) (column 2) accordingly, we get the $\sqrt{5} \times \sqrt{5}$ charge order of Na$_x$CoO$_2$ from a simulation with two degenerate f-orbitals ([31]).
useful and left for the future. We believe our present study already sheds light on certain important aspects of the ground state phenomenology and will motivate new experiments.

In conclusion, we have studied the Falicov–Kimball model on a non-bipartite lattice and found several ordered ground states. Extending the model to include a correlated hopping term leads to new effects: in particular, it strongly facilitates phase segregation in the ground states even in the weak correlation limit. We also identify several valence transitions as state phenomenology and will motivate new experiments. These observations are quite relevant for the ground state order and phase segregation observed recently in correlated systems with triangular lattices such as GdI$_2$, dichalcogenides and cobaltates.

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