Electronic phase transitions in the spin-$\frac{1}{2}$ Falicov-Kimball model

Pavol Farkašovský
Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 043 53 Košice, Slovakia
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The spin-$\frac{1}{2}$ Falicov-Kimball model for electronically driven valence and metal-insulator transitions is studied in one dimension using small-cluster exact diagonalization calculations. The resultant exact solutions are used to examine the f-state occupation (n_f) as a function of f-level energy (E_f), d-f interaction strength G, and f-f interaction strength U. It is shown that for sufficiently large values of G ($G>2$) the model can describe two types of discontinuous valence transitions: the insulator-metal transitions from an integer-valence ground state ($n_f=1$) into an inhomogeneous intermediate-valence ground state ($0<n_f<1$) and the insulator-metal transitions from $n_f=1$ to $n_f=0$. In the weak-coupling limit ($G<1$) the model undergoes a few consecutive discontinuous and continuous intermediate-valence transitions. In addition, the local pairing of f electrons and some other features of the spin-$\frac{1}{2}$ Falicov-Kimball model are discussed. [S0163-1829(96)02940-2]

Since its introduction in 1969, the Falicov-Kimball model[1] has become an important standard model for a description of valence and metal-insulator transitions observed in a wide group of substances (transition-metal and rare-earth oxides, halides, sulfides, and borides) when some external parameters such as pressure or temperature are varied.[2–4] The model is based on the coexistence of two different types of electronic states in given materials: localized, highly correlated ioniclike states and extended, uncorrelated, Blochlike states. It is generally accepted that insulator-metal transitions result from a change in the occupation numbers of these electronic states, which remain themselves basically unchanged in their character. The Hamiltonian of the model can be written as the sum of four terms

$$H=\sum_{i,j,\sigma} t_{ij} d^{\dagger}_{i\sigma} d_{j\sigma} + G \sum_{i,\sigma,\sigma'} f^{\dagger}_{i\sigma} f_{i\sigma} d^{\dagger}_{i\sigma'} d_{i\sigma'} + E_f \sum_{i,\sigma} f^{\dagger}_{i\sigma} f_{i\sigma} + \frac{U}{2} \sum_{i,\sigma} f^{\dagger}_{i\sigma} f_{i\sigma} f^{\dagger}_{i-\sigma} f_{i-\sigma}, \quad (1)$$

where $f^{\dagger}_{i\sigma}, f_{i\sigma}$ are the creation and annihilation operators for an electron of spin σ in the localized state at lattice site i with binding energy E_f and $d^{\dagger}_{i\sigma}, d_{i\sigma}$ are the creation and annihilation operators of the itinerant electrons in the d-band Wannier state at site i.

The first term of (1) is the kinetic energy corresponding to quantum-mechanical hopping of the itinerant d electrons between sites i and j. These intersite hopping transitions are described by the matrix elements t_{ij}, which are $-t$ if i and j are the nearest neighbors and zero otherwise (in the following all parameters are measured in units of t). The second term represents the on-site Coulomb interaction between the d-band electrons with density $n_d=N_d/L=(1/L)\Sigma_{i\sigma} d^{\dagger}_{i\sigma} d_{i\sigma}$ and the localized f electrons with density $n_f=N_f/L=(1/L)\Sigma_{i\sigma} f^{\dagger}_{i\sigma} f_{i\sigma}$, where L is the number of lattice sites. The third term stands for the localized f electrons whose sharp energy level is E_f. The last term represents the intraatomic Coulomb interaction between the localized f electrons.

In spite of the fact that the Falicov-Kimball model is one of the simplest examples of interacting fermionic system, the theoretical picture of metal-insulator and valence transitions still remains uncertain in the framework of this model. Even in the existing literature on this model different answers can be found on the fundamental question whether or not the Falicov-Kimball model can describe the discontinuous transition of the f- (d-) electron occupation number n_f (n_d) as a function of the f-level energy E_f. Depending on the type of approximations used, both positive answers[1,5] and negative answers[6] were found for the Falicov-Kimball model. Discontinuous transitions were obtained within Hartree-Fock treatments, while in treatments based on the coherent-potential approximation only continuous transitions were obtained. Since experimentally one sees both discontinuous and continuous transitions it has been generally accepted that the Falicov-Kimball could yield the correct physics for describing these transitions. Unfortunately, many controversies have been found in approximate solutions. Even within the same approximation the details of the first-order phase transitions strongly depend on the form of the conduction band (the density of states). For example, for the case of a semielliptic density of states $\rho(E)=4\pi^{-1}[1-2(E/W)^2]^{1/2}$ the mean-field approximation of the type[2]

$$d^{\dagger}_i d_i f^{\dagger}_i f_i \rightarrow \langle d^{\dagger}_i d_i \rangle f^{\dagger}_i f_i + \langle f^{\dagger}_i f_i \rangle d^{\dagger}_i d_i - \langle f^{\dagger}_i f_i \rangle \langle d^{\dagger}_i d_i \rangle \quad (2)$$

yields the continuous transitions for $G<\pi W/16$; for $\pi W/16<G<[1-(4/3\pi)]W/2$ there are discontinuous transitions from $n_f \neq 1$ to $n_f=0$ and for large G the transition goes from $n_f=1$ to $n_f=0$. The same approximation for a rectangular density of states $\rho(E)=W^{-1}$ leads to continuous transitions for $G<W/4$, while for $G>W/4$ discontinuous transitions from $n_f=1$ to $n_f=0$ take place at $E_f=W/4$. It is characteristic of the mean-field treatment of the Falicov-Kimball model that the discontinuous transitions go to pure valence metallic state for simple band densities of states. These results indicated that the study of valence and metal-insulator transitions may be successful only with methods that are relatively insensitive to the type of approximation used and, of course, with exact methods.

In our previous papers,[7,8] we have investigated the spinless version of the Falicov-Kimball model by extrapolation of small-cluster exact-diagonalization calculations. Unlike

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the approximate results we have found that the f-electron occupation number n_f as a function of the f-level energy E_f exhibits a few intermediate-valence transitions at $T=0$. We have found discontinuous insulator-insulator transitions for sufficiently strong interactions[7] and a discontinuous insulator-metal transition for weak interactions.[8]

In this paper we study the problem of valence and metal-insulator transitions in the spin-$\frac{1}{2}$ Falicov-Kimball model when the same method, extrapolation of small-cluster exact-diagonalization calculations, is used. We have performed the exhaustive study of the E_f dependence of the f-state occupation (n_f) for a wide range of parameters. Typical examples are then chosen from a large number of available results to represent interesting cases.

Since the f-electron density operators $f^{\dagger}_{i\sigma}f_{i\sigma}$ of each site i commute with the Hamiltonian (1), the f-electron occupation number n_f is a good quantum number, taking only three values $w_i=0,1,2$ according to whether the site i is unoccupied or occupied by one or two localized f electrons. Therefore the Hamiltonian (1) can be replaced by

$$H=\sum_{i,j,\sigma} h_{ij}d^{\dagger}_{i\sigma}d_{j\sigma}+E_f\sum_i w_i+UD, \tag{3}$$

where $h_{i,j}=t_{ij}+Gw_i\delta_{ij}$ and D is the total number of doubly occupied sites.

Thus, for a given f-electron configuration $w=\{w_1,w_2,\ldots,w_L\}$ defined on a one-dimensional lattice with periodic boundary conditions, the Hamiltonian (3) is the second-quantized version of the single-particle Hamiltonian $h(w)=T+GW$, so the investigation of the model (3) is reduced to the investigation of the spectrum of h for different configurations of f electrons. (From the numerical point of view there is only one difference between the spin-$\frac{1}{2}$ and spinless version of the Falicov-Kimball model, namely, that w_i takes now three instead of two values.) Since the d electrons do not interact among themselves, the numerical calculations preceed directly in the following steps [we consider only the case $N_f+N_d=L$, which is the point of the special interest for valence and metal-insulator transitions caused by promotion of electrons from localized f orbitals ($f^n\rightarrow f^{n-1}$) to the conduction band states]. (i) Having G,U,E_f, and $w=\{w_1,w_2,\ldots,w_L\}$ fixed, find all eigenvalues λ_k of $h(w)=T+GW$. (ii) For a given $N_f=\Sigma_i w_i$ determine the ground-state energy $E(w)=\Sigma_{k=1}^{L-N_f}\lambda_k+E_fN_f+UD$ of a particular f-electron configuration w by filling in the lowest $N_d=L-N_f$ one-electron levels (the spin degeneracy must be taken into account). (iii) Find the w^0 for which $E(w)$ has a minimum. Repeating this procedure for different values of E_f, one can immediately study the dependence of the f-electron occupation number $N_f=\Sigma_i w_i^0$ on the f-level position E_f.

First we have investigated the spin-$\frac{1}{2}$ Falicov-Kimball model for the small finite clusters (up to 24 sites) and for all possible configurations of the localized f electrons. The small-cluster exact-diagonalization calculations have been performed for the following set of U and G values: $U=0,0.1,0.2,\ldots,1.5$, $G=1.5,2,3,4,5,10$. We summarize our results with some observations. (i) For $U>2$ the results do not depend sensitively upon d-f interaction strength G.

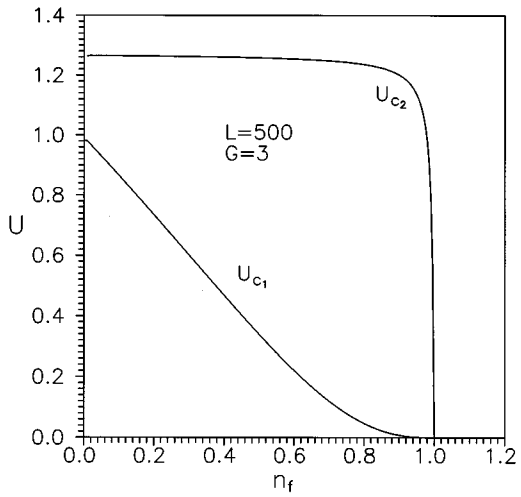

FIG. 1. Critical interaction strengths U_{c_1} and U_{c_2} as a function of n_f calculated for $L=500$ and $G=3$.

(Next the value $G=3$ is chosen to represent the typical behavior of the model in the strong coupling limit.) (ii) The ground state for $U=0$ is the segregated configuration of the local f pairs[9] ($w_p=\{22\cdots200\cdots0\}$ for N_f even and $w_p=\{22\cdots2100\cdots0\}$ for N_f odd). (iii) For a given N_f the segregated configuration w_p persists as the ground state for $U<U_{c_1}$. (iv) For $U_{c_1}<U<U_{c_2}$ the number of local f pairs is reduced with increasing U. (v) For $U>U_{c_2}$ the ground state is the segregated configuration with singly occupied sites ($w_s=\{11\cdots100\cdots0\}$).

In addition, we have found that the transition from w_p to w_s realizes through the steps

$$\begin{aligned} w_p=\{2\cdots20\cdots0\}&\rightarrow\{12\cdots210\cdots0\}\\ &\rightarrow\{112\cdots2110\cdots0\}\rightarrow\cdots\{1\cdots10\cdots0\}=w_s \end{aligned} \tag{4}$$

or

$$\begin{aligned} w_p=\{2\cdots210\cdots0\}&\rightarrow\{12\cdots2110\cdots0\}\\ &\rightarrow\{112\cdots21110\cdots0\}\rightarrow\cdots\{1\cdots10\cdots0\}=w_s. \end{aligned} \tag{5}$$

Since no exceptions have been observed for $L\leqslant 24$, we conjecture that for sufficiently large G ($G\geqslant 2$) the ground states of the spin-$\frac{1}{2}$ Falicov-Kimball model are only the configurations of type (4) or (5).

The last observation is very important for the extrapolation of small-cluster exact-diagonalization calculations since it allows us to avoid technical difficulties associated with a large number of configurations and consequently to study much larger systems. Figure 1 presents numerical results for the critical interaction strengths U_{c_1} and U_{c_2} as functions of the f-electron occupation number n_f obtained for $G=3$ and $L=500$. It is seen that there is a relative large region of U values where the configurations with a nonzero number of local f pairs are the ground states. The fact that the f electrons form the local f pairs, in spite of a relative large repulsive interaction U, indicates that there is an attractive interaction that is able to overcome this direct repulsion. One of

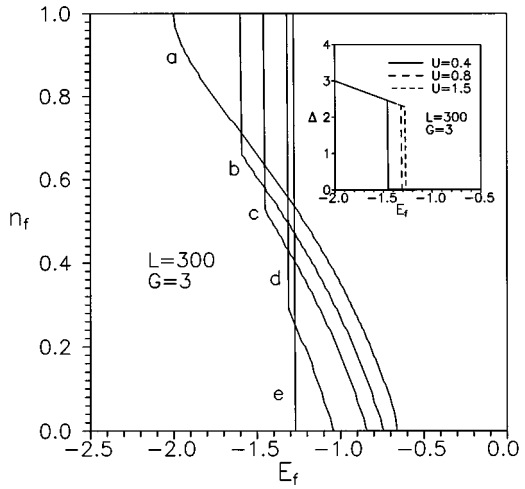

FIG. 2. Dependence of the f-electron occupation number n_f [calculated for all configurations of the type (4) and (5)] on the f-level position E_f for $L=300, G=3$, and five different values of U: a, $U=0$; b, $U=0.2$; c, $U=0.4$; d, $U=0.8$; and e, $U=1.5$. Inset: dependence of the energy gap Δ on the f-level position E_f calculated for $L=300, G=3$, and three different values of U.

the most important results for the spin-$\frac{1}{2}$ Falicov-Kimball model is that the interaction of the localized f electrons with the itinerant d-band electrons leads to an effective on-site attraction between the localized f electrons. It is interesting to study whether this feature changes the picture of valence and metal-insulator transitions found for the spinless version of the model. The numerical results for E_f dependence of n_f [calculated for configurations of type (4) and (5)] are plotted in Fig. 2 for $G=3$ and different values of U. They lead to the following conclusions. (i) The transition is continuous for $U=0$. (ii) For $0<U<U_c$ ($U_c \sim 1.273$) there are discontinuous transitions from an integer-valence state $n_f=1$ into an inhomogeneous intermediate-valence state $n_f \neq 1$ at $E_f=E_c(U)$. (iii) For $U>U_c$ the transitions are discontinuous from $n_f=1$ to $n_f=0$. They take place at $E_c=-U_c$ independent of U.

The last result can be directly compared with the above-mentioned mean-field solutions that exhibit the same behavior for large G and $U\rightarrow\infty$. Since the mean-field solutions strongly depend on the form of the conduction band, we have calculated the mean-field ground-state energy

$$E_{\mathrm{MF}}=\int_{-\infty}^{\infty} E\rho(E)dE+E_f n_f+Gn_f\int_{-\infty}^{\infty}\rho(E)dE \qquad (6)$$

using the exact density of state $\rho(E)=\pi^{-1}\mathrm{Re}(4-E^2)^{-1/2}$ in one dimension. We have found that discontinuous transitions take place at $E_c=-4/\pi=-1.2732\ldots$, which is in very good agreement with our numerical value $E_c=-1.273$. Next we will show that the mean-field decoupling of the type (2) reproduces very well the exact numerical results also for small values of G.

In order to examine possibilities for the insulator-metal transitions at E_c, we have computed the energy gaps[10] of ground-state configurations corresponding to E_f. The inset in Fig. 2 presents results obtained for $G=3$ and different values of U. It is seen that below E_c the gaps have a finite width, while above E_c the gap apparently vanishes: the discontinuous insulator-metal transition takes place at E_c. Since no finite-size effects have been found we can conclude that the spin-$\frac{1}{2}$ Falicov-Kimball model in the pressure induced case can describe two types of discontinuous valence transitions: the insulator-metal transitions from an integer-valence ground state ($n_f=1$) into an inhomogeneous intermediate-valence ground state ($n_f\neq 1$) and the insulator-metal transitions from an integer-valence state ($n_f=1$) into another integer-valence state ($n_f=0$). Note that these results are in very good agreement with experimental studies of insulator-metal transitions in the samarium monochalcogenides.[11] This fact indicates that the Falicov-Kimball model could yield the correct physics for describing these transitions. However, one might expect $U>G$ in the Falicov-Kimball and thus the application of these results for a description of intermediate-valence transitions of real materials is possible only if there is an additional mechanism that reduces the values of U. Such a mechanism should be the electron-phonon interaction.[12]

TABLE I. Typical examples of the ground-state configurations that form the structure of valence transitions in the weak-coupling limit ($G=0.5, U=1$, and $L=24$).

N_f	w
4	100001000000100001000000
6	100100001001000010010000
8	100100100100100100100100
10	110010011001001001100100
12	110011001100110011001100
14	111001110011100111001100
16	111100111100111100111100
18	111111001111110011111100
20	111111111100111111111100

Let us now study the problem of valence and metal-insulator transitions in the weak-coupling limit. First we have performed numerical calculations on finite clusters (up to 24 sites) for all f-electron configurations and $G=0.5$. We have found that the local f pairs are now stable only in a very narrow region near $U=0$ and that outside this region the valence transitions are formed by configurations w_h of only one kind (see Table I). In these configurations the pairs of consecutive unoccupied sites are distributed in such a manner that the distances between two consecutive pairs are either d or $d+1$. Furthermore, the distribution of the distances of d and $d+1$ has to be mostly homogeneous. The valence transition calculated for these configurations w_h is shown in Fig. 3 together with the exact numerical results obtained for all f-electron configurations. The comparison of these results confirms our conjecture made in a previous paper,[8] namely, that the valence transition is formed by the primary structure corresponding to configurations w_h with the smallest periods and the secondary structure corresponding to remaining configurations. The primary structure is almost independent of L (see Fig. 4), while the secondary structure is suppressed with inreasing L and for sufficiently large L it forms a gradual transition between two configurations with small periods. However, unlike the spinless version we have found no discontinuous insulator-metal transi-

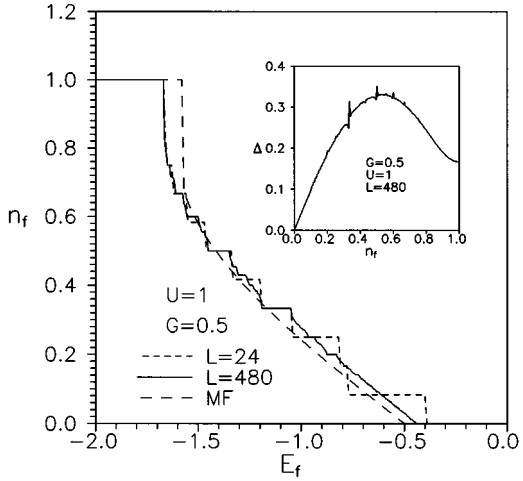

FIG. 3. Dependence of the f-electron occupation number n_f on the f-level position E_f for $G=0.5$ and $U=1$. The behavior for $L=24$ has been calculated for all possible f-electron configurations, for $L=480$ only the configurations w_h have been considered, and the MF curve represents the mean-field result obtained using the exact density of states. Inset: energy gaps corresponding to configurations w_h.

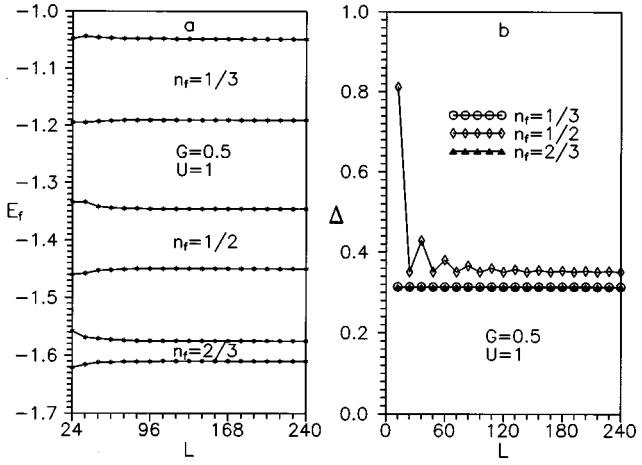

FIG. 4. L dependence of (a) the exact numerical bounds and (b) the energy gap calculated for three selected configurations with small periods, which form the primary structure of the valence transition.

tions in the spin-$\frac{1}{2}$ Falicov-Kimball model for small values of G. The transition to pure valence state ($n_f=0$) is a continuous insulator-metal transition (see Fig. 3) and the transitions that realize between two states with $n_f\neq 0$ are insulator-insulator transitions. For comparison we have displayed in Fig. 3 also the results that have been obtained using the mean-field approximation of the type (2) with the exact density of states. The results are again in good agreement and both exhibit discontinuous transition from an integer-valence state ($n_f=1$) into an intermediate-valence state ($n_f\neq 0,1$). This result shows how crucial it is to use the exact density of states for description of valence transitions in the mean-field approximation.

In summary, the spin-$\frac{1}{2}$ Falicov-Kimball model for electronically driven valence and metal-insulator transitions was studied using small-cluster exact-diagonalization calculations. It was shown that for sufficiently large values of the interaction strength G ($G>2$) the model can describe two types of discontinuous valence transitions: the insulator-metal transitions from an integer-valence ground state ($n_f=1$) into an inhomogeneous intermediate-valence ground state ($0<n_f<1$) and the insulator-metal transitions from $n_f=1$ to $n_f=0$. In the weak-coupling limit the model undergoes a few consecutive discontinuous and continuous intermediate-valence transitions. The transition to pure valence state ($n_f=0$) is a continuous insulator-metal transition and transitions that realize between two states with $n_f\neq 0$ are insulator-insulator transitions. In addition, the local f-electron pairing (even in the presence of direct repulsive interactions) was found.

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