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Pressure-induced insulator-metal transitions in the spinless Falicov-Kimball model

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The possibilities for pressure-driven insulator-metal transitions in the spinless Falicov-Kimball model are studied using small-cluster exact-diagonalization calculations. It is shown that for small values of the interaction strength U the Falicov-Kimball model undergoes an insulator-metal transition, which is accompanied by a discontinuous change of the energy gap. Thus, in the pressure-induced case, the model is capable of describing the insulator-metal transitions observed in some rare-earth compounds, e.g., in SmB_6. In the general case, the valence transitions for small U have a staircase structure formed by the most homogeneous configurations with the smallest periods; however, the transitions between two such configurations (unlike the case of large U, where they are very sharp) are now gradual.

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. These transitions are observed in a wide group of substances formed by transition-metal as well as rare-earth oxides, halides, sulfides, and borides, when some external parameters (like pressure or temperature) are varied.[2,3] Although the experimental aspects of valence and metal-insulator transitions have been well established, particularly in the samarium monochalcogenides,[4] the theoretical picture of transitions is still uncertain. One of the most controversial questions for models of correlated electrons that describe valence and metal-insulator transitions is whether or not the f (d) -electron occupation number n_f (n_d) exhibits a discontinuity as a function of the f-level energy E_f. This question is indeed crucial for the systems mentioned above, since, supposing[2] that the external pressure shifts the energy level E_f, the valence changes observed in some rare-earth and transition-metal compounds (SmS, TmTe, SmB_6, Ti_2O_3, and so on) could be understandable purely electronically, if $n_f(E_f)$ really has discontinuities. Depending on the type of approximation 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 if the intra-atomic interaction term was decoupled in a form that was diagonal in the f and d creation and annihilation operators, while in treatments based on the coherent-potential approximation no sign of any discontinuity was obtained. Thus, within the Hartree-Fock treatments, the Falicov-Kimball model can describe the first-order transition from $n_f=1$ to $n_f=0$; however, the valence, i.e., the average number of localized f electrons n_f, remains an integer and does not attain intermediate values. Although this shortcoming can be removed by including the hybridization of localized states with the band states, the theoretical picture of the transitions is still uncertain, since different approximations, again, produce controversial results.[7,8] From this short survey it is clear 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 paper,[9] we investigated the Falicov-Kimball model by strong-coupling perturbation theory and extrapolation of small-cluster exact-diagonalization calculations. We found that for sufficiently large U the spinless Falicov-Kimball model undergoes only a few discrete intermediate-valence transitions. Thus, in the pressure-induced case, it can describe both the valence transitions from an integer valence ground state ($n_f=0$ or 1) into an inhomogeneous intermediate-valence ground state ($n_f \neq 0,1$) and the transitions from one inhomogeneous intermediate-valence state with n_f into another inhomogeneous intermediate-valence state with $n_f' \neq n_f$. These results showed that the Hartree-Fock picture[2] of valence transitions yielding one or even neither discontinuous valence transition is incorrect for large U. On the other hand, it should be noted that the intermediate-valence transitions mentioned above are insulator-insulator transitions, since they are realized between the insulating ground states corresponding to the most homogeneous configurations, which are the ground states in this region.[10] Thus, the Falicov-Kimball model in the strong-coupling limit can describe only one kind of the experimentally observed intermediate-valence transitions, namely, the insulator-insulator transition (TmSe), while the picture of insulator-metal transitions (e.g., SmB_6, SmS) still remains uncertain in the framework of the Falicov-Kimball model. However, the numerical results of Gruber *et al.*,[11] obtained for a restricted set of configurations, show that there exists a region, namely, the weak-coupling limit, in which this deficiency of the model could be corrected. Therefore, to study the possibilities for the insulator-metal transitions in the Falicov-Kimball model, we turn our attention to the case $U<1$.

The Hamiltonian of the Falicov-Kimball model is

$$H=\sum_{ij} t_{ij} d_i^\dagger d_j + U \sum_i f_i^\dagger f_i d_i^\dagger d_i + E_f \sum_i f_i^\dagger f_i , \qquad (1)$$

where $f_i^\dagger$ and f_i are the creation and annihilation operators for an electron in the localized state at lattice site i with binding energy E_f and $d_i^\dagger$, d_i are the creation and annihilation operators of the itinerant spinless electrons in the d-band Wannier state at site i.

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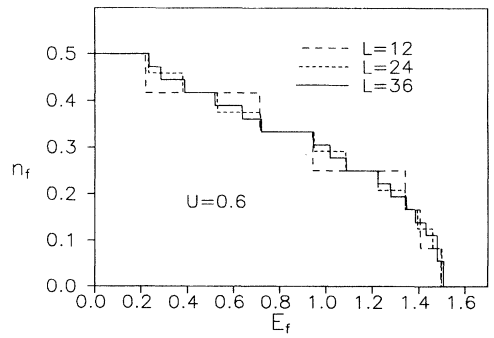

FIG. 1. Dependence of the f-electron occupation number n_f (calculated for all configurations) on the f-level position E_f for $L=12$ (long-dashed line), $L=24$ (short-dashed line), $L=36$ (solid line), and $U=0.6$.

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 -1 if i and j are the nearest neighbors and zero otherwise. The second term represents the on-site Coulomb interaction between the d-band electrons with density $n_d=(1/L)\Sigma_i d_i^\dagger d_i$ and the localized f electrons with density $n_f=(1/L)\Sigma_i f_i^\dagger f_i$, where L is the number of lattice sites. The third term stands for the localized f electrons with sharp energy level E_f.

Since in this spinless version of the Falicov-Kimball model without hybridization the f-electron occupation number $f_i^\dagger f_i$ of each site i commutes with the Hamiltonian (1), the f-electron occupation number is a good quantum number, taking only two values, $w_i=1$ or 0, according to whether or not the site i is occupied by the localized f electron.

Now the Hamiltonian (1) can be written as

$$H=\sum_{ij} h_{ij}d_i^\dagger d_j+E_f\sum_i w_i, \tag{2}$$

where $h_{ij}(w)=t_{ij}+Uw_i\delta_{ij}$.

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 (2) is the second-quantized version of the single-particle Hamiltonian $h(w)=T+UW$, so the investigation of the model (2) is reduced to the investigation of the spectrum of h for different configurations of f electrons. Since the d electrons do not interact among themselves, the numerical calculations precede directly in the following steps (we consider only the half-filled band case $N_f+N_d=L$, which is the point of special interest for the mixed-valence phenomena). (i) Having U, E_f, and $w=\{w_1,w_2,\ldots,w_L\}$ fixed, find all eigenvalues λ_k of $h(w)=T+UW$. (ii) For a given $N_f=\Sigma_i w_i$, determine the ground-state energy $E(w,U,E_f)=\Sigma_{k=1}^{L-N_f}\lambda_k+E_fN_f$ of a particular f-electron configuration w by filling in the lowest $N_d=L-N_f$ one-electron levels. (iii) Find the w^0 for which $E(w,U,E_f)$ 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.

Figure 1 presents the exact numerical results obtained for $U=0.6$ and the complete set of f-electron configurations on the finite lattices of 12, 24, and 36 sites.[12] It is seen that some fundamental features of the valence transitions found for large U (Ref. 9) hold for $U<1$ too. The valence transitions have, again, a staircase structure, where one can easily recognize the primary structure (formed by the most homogeneous configurations with the smallest periods), which is almost independent of L and the secondary structure depending strongly on L. However, there are some important physical differences. At first, the ground-state configurations for small values of N_f are already not the most homogeneous configurations but are the configurations consisting of at least $L/2$ consecutive unoccupied sites. For example, for $N_f=2$ ($L=24, U=0.6$) the ground state is the configuration 1_20_{22}, consisting of 2 occupied sites followed by 22 unoccupied sites, and for $N_f=3$ the ground state is the configuration $1_20_51_10_{16}$ [the lower index denotes the number of consecutive sites occupied (unoccupied) by f electrons]. These results show that, for $U<1$ and sufficiently small f-electron densities, the ground-state configurations could be mixtures of two configurations (one of which is the empty configuration). In order to verify such a separation, we have performed small-cluster exact-diagonalization calculations for a large number of finite lattices. For given L, the energies of all f-electron configurations have been computed and the ground-state configurations (GSC's) selected. We have found that for each $U<1$ and $L\geq 16$ there exists a critical value of the f-level position $E_c(U)$ [f-electron occupation number $N_c(U)$] such that for $E_f<E_c(U)$ [$N_f>N_c(U)$] the GSC's are the most homogeneous configurations, while for $E_f\geq E_c(U)$ [$N_f\leq N_c(U)$] the GSC's are the mixtures of the empty configuration of a length $l\geq L/2$ and a configuration w of a length $l\leq L/2$. The GSC's, which are the ground states for $E_f\geq E_c(U)$ as well as the critical values of $E_c(U)$ [$N_c(U)$] calculated for $U=0.6$ and different values of L, are shown in Table I.

To show the possibilities for the insulator-metal transitions at E_c, we have computed the energy gaps[13] of all the most homogeneous configurations (which are the ground states above n_c) and the GSC's listed in Table I (which are the ground states below n_c). Figure 2 presents results obtained for the largest ($L=48$) finite lattice, which we have been able to consider numerically. Note that, from reasons discussed below, we have plotted the dependence of the energy gap on the deviation from the symmetric case $n_f=n_d=1/2$ rather than the f-electron concentration n_f. Although the results still contain finite size effects, they show that below $\delta_c=1/2-n_c$ the energy gap has a finite width (we know already[9] that the ground states corresponding to the most homogeneous configurations, which are the ground states in this region, are insulating), while above δ_c the gap is apparently suppressed and vanishes, probably discontinuously. To verify this guess, and to exclude the finite size effects, we have computed the energy gaps of selected configurations in the thermodynamic limit using the exact expression for the density of states,[14] which allows us to perform exact numerical calculations for the periodic configurations with the smallest periods. With regard to our numerical results obtained on small lattices, we have chosen the following set of configurations: Above n_c, the most ho-

TABLE I. The critical values of the f-electron occupation number N_c, f-level position E_c, and the ground-state configurations (GSC's) below N_c calculated for $U=0.6$ and different values of L. Here the lower index denotes the number of consecutive sites occupied (unoccupied) by f electrons in a GSCs.

L N_c E_c	GSC
16 2 1.4149	$1_2 0_{14}$
18 2 1.2922	$1_2 0_{16}, 1_2 0_4 1_1 0_1 1$
20 3 1.3440	$1_2 0_{18}, 1_2 0_5 1_1 0_{14}$
22 3 1.3711	$1_2 0_{20}, 1_2 0_4 1_1 0_{15}$
24 3 1.3957	$1_2 0_{22}, 1_2 0_5 1_1 0_{16}$
26 4 1.3675	$1_2 0_{24}, 1_2 0_6 1_1 0_{17}, 1_2 0_3 1_2 0_{19}$
28 5 1.3091	$1_2 0_{26}, 1_2 0_6 1_1 0_{19}, 1_2 0_4 1_2 0_{20}, 1_2 0_3 1_2 0_3 1_1 0_{17}$
30 5 1.3399	$1_2 0_{28}, 1_2 0_7 1_1 0_{20}, 1_2 0_4 1_2 0_{22}, 1_2 0_3 1_2 0_4 1_1 0_{18}$
32 5 1.3532	$1_2 0_{30}, 1_2 0_7 1_1 0_{22}, 1_2 0_4 1_2 0_{24}, 1_2 0_3 1_2 0_4 1_1 0_{20}$
34 5 1.3678	$1_2 0_{32}, 1_2 0_7 1_1 0_{24}, 1_2 0_4 1_2 0_{26}, 1_2 0_4 1_2 0_4 1_1 0_{21}$
36 6 1.3485	$1_2 0_{34}, 1_2 0_8 1_1 0_{25}, 1_2 0_5 1_2 0_{27}, 1_2 0_4 1_2 0_5 1_1 0_{22}, 1_2 0_3 1_2 0_3 1_2 0_{24}$
48 8 1.3434	$1_2 0_{46}, 1_3 0_{45}, 1_2 0_6 1_2 0_{38}, 1_2 0_5 1_2 0_6 1_1 0_{32}, 1_2 0_4 1_2 0_4 1_2 0_{34}, 1_2 0_4 1_2 0_4 1_2 0_4 1_1 0_{29}, 1_2 0_3 1_2 0_3 1_2 0_3 1_2 0_{28}$

mogeneous with the smallest periods, i.e., $w=\{10\ldots\}$, $\{100\ldots\}$, $\{1000\ldots\}$, $\{10000\ldots\}$, $\{10100\ldots\}$; and below n_c, the incoherent mixtures of $[2|5]$ and $[2|6]$ configurations[15] with the empty configuration, which are the ground states on larger lattices for $n_f=1/6$ and $n_f=1/8$ (see Table I). The energy gaps calculated for these configurations correlate very well with the exact numerical results obtained for $L=48$ (see Fig. 2). Below δ_c (above n_c) the gap has a finite width, while above δ_c (below n_c) the gap vanishes —the insulator-metal transition takes place at n_c.

Let us mention an important consequence of such a picture. As was shown above (see Fig. 1), the change of n_f can be driven by a shift of E_f. It is, however, well known[2,8] that the f-level energy E_f shifts up when the external pressure p is applied to the system. Thus, in the pressure-induced case, the Falicov-Kimball model undergoes a discontinuous insulator-metal transition at $E_f=E_c$ ($p=p_c$). Such a behavior of the energy gap on the external pressure was really observed recently by Colley *et al.*[16] in SmB_6. Performing a more exhaustive resistivity study which was supplemented by Hall-effect measurements, they found that the energy gap does not vanish continuously as the previous resistivity studies indicated,[17] but discontinuously at ~ 50 kbar (see inset in Fig. 2). The average f-electron occupation number in SmB_6 at ambient pressure and $T\to 0$ is ~ 0.5,[18] which corresponds to the point $\Delta=0.6$, $\delta=0$ in the Falicov-Kimball model. In the pressure-induced case, when the f-level position is pushed upward the f-electron concentration n_f decreases (see Fig. 1) and the gap changes as shown in Fig. 2. At $\delta=\delta_c$ ($n_f=n_c$) the gap suddenly disappears, similar to SmB_6. Note that further evidence of the discontinuity of the energy gap at E_c follows directly from our small-cluster exact-diagonalization calculations. As we have mentioned above, the ground-state configurations above E_c are the incoherent mixtures of the empty configuration (whose length is at least $L/2$) and a configuration w (whose length is $l\leq L/2$). However, the ground states corresponding to such mixtures are always metallic, and so the transition is discontinuous at E_c. Thus, the E_f dependence of the energy gap yields a pressure-driven discontinuous insulator-metal transition, as well as a transition from an inhomogeneous intermediate-valence state into a homogeneous intermediate-valence state described in previous papers.[9,19] The Falicov-Kimball model is indeed a convenient model for describing

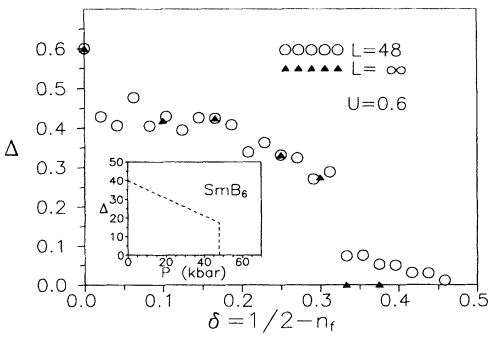

FIG. 2. Dependence of the energy gap on the f-electron concentration. Circles correspond to $L=48$ and triangles to $L=\infty$. Inset shows the fit of the pressure dependence of the energy gap in SmB_6 (Ref. 16).

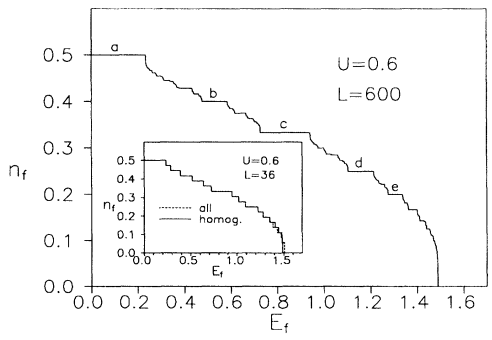

FIG. 3. Dependence of the f-electron occupation number n_f (calculated for the most homogeneous configurations) on the f-level position E_f for $L=600$ and $U=0.6$. The largest regions of stability correspond to the most homogeneous configurations with the smallest periods, i.e., $\{10\ldots\}$ (a), $\{10100\ldots\}$ (b), $\{100\ldots\}$ (c), $\{1000\ldots\}$ (d), $\{10000\ldots\}$ (e), etc. Inset: E_f dependence of n_f [calculated for all (dashed line) and the most homogeneous (solid line) configurations] on the finite lattice of 36 sites.

the valence and insulator-metal transitions in rare-earth compounds, particularly in SmB_6.

Of course, to fully confirm this picture of valence and insulator-metal transitions a much deeper analysis including larger lattices and higher dimensions should be performed.

Finally, let us mention another important difference between the valence transitions in the strong- and weak-coupling limit. Although in both cases the basic structure of the transition is formed by the primary structure corresponding to the most homogeneous configurations with the smallest periods, the secondary structure (corresponding to remaining configurations) behaves differently for large and small interactions. While for sufficiently large U the secondary structure is completely suppressed and only the primary structure forms the transition,[9] for small values of U the secondary structure is always present (see Fig. 3) and forms a gradual transition between two configurations with small periods. It should be noted that the behavior in Fig. 3, representing the complete picture of the valence transitions in the weak-coupling limit, has been calculated only for the most homogeneous configurations, which are only expected to be the ground-state configurations for $n_f > n_c$. However, a comparison (see inset in Fig. 3) of the exact numerical results which have been obtained for all configurations (dashed line) with the approximate results from the most homogeneous configurations (solid line) on the finite lattice of $L=36$ sites shows that the presented picture will be very close to the real one, since the region below n_c is very narrow and the transition is very steep for both cases.

In summary, using small-cluster exact-diagonalization calculations we have found that for small values of the interaction strength U the Falicov-Kimball model undergoes an insulator-metal transition, which is accompanied by a discontinuous change of the energy gap. Thus in the pressure-induced case the model is capable of describing the discontinuous insulator-metal transition observed recently in SmB_6. Similar to the large-U case, we have found that the valence transitions have a staircase structure formed by the most homogeneous configurations with the smallest periods. However, unlike the case of large U, where the transitions between two such configurations are very sharp, they are gradual for the small-U case.

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