Existence of a ferroelectric ground state with a spontaneous polarization in the Falicov-Kimball model

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The extrapolation of small-cluster exact-diagonalization calculations is used to examine the possibility of electronic ferroelectricity in the one-dimensional spinless and spin-one-half Falicov-Kimball model (FKM). It is found that neither the spinless nor the spin-one-half version of the FKM allows for a ferroelectric ground state with a spontaneous polarization, i.e., there is no nonvanishing $\langle d^+ f\rangle$ expectation value for vanishing hybridization V. [S0163-1829(99)05015-8]

In the last few years the Falicov-Kimball model[1] (FKM) has been extensively studied in connection with the exciting idea of electronic ferroelectricity.[2–4] It is generally supposed that the ferroelectricity in mixed-valent compounds is of purely electronic origin, i.e., it results from an electronic phase transition, in contrast to the conventional displacive ferroelectricity due to a lattice distortion. Since the FKM is probably the simplest model of electronic phase transitions in rare-earth and transition-metal compounds it was natural to test the idea of electronic ferroelectricity just on this model.

The FKM is based on the coexistence of two different types of electronic states in a given material: localized, highly correlated ioniclike states and extended, uncorrelated, Bloch-like states. It is 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. Taking into account only the intra-atomic Coulomb interaction between the two types of states, the Hamiltonian of the spinless FKM with hybridization can be written as the sum of four terms:

$$H=\sum_{ij} t_{ij}d_i^\dagger d_j+U_{df}\sum_i f_i^\dagger f_i d_i^\dagger d_i+E_f\sum_i f_i^\dagger f_i + V\sum_i d_i^\dagger f_i+\text{H.c.}, \tag{1}$$

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

The first term of Eq. (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 $n_d=(1/L)\Sigma_i d_i^\dagger d_i$ 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 whose sharp energy level is E_f. The last term represents the hybridization between the itinerant and localized states.

In spite of the fact that many of the ground-state properties of the spinless FKM (the nature of the ground state,[7] the picture of valence and metal-insulator transitions,[5,6] etc.) are well understood at present, the problem of electronic ferroelectricity remains still an open question. Very recently Portengen *et al.*[2,3] studied the FKM with a k-dependent hybridization in the Hartree-Fock approximation and found, in particular, that a nonvanishing excitonic $\langle d^\dagger f\rangle$ expectation value exists even in the limit of vanishing hybridization $V\rightarrow 0$. As an applied (optical) electrical field provides for excitations between d and f states and thus for a polarization expectation value $P_{df}=\langle d_i^\dagger f_i\rangle$, the finding of a spontaneous P_{df} (without hybridization or electric field) has been interpreted as evidence for electronic ferroelectricity. However, analytical calculations within well-controlled approximation (for U_{df} small) performed by Czycholl[4] in infinite dimensions do not confirm this conclusion. In contrast to results obtained by Portengen *et al.*[2,3] he found that the symmetric ($E_f=0,n_f=n_d=0.5$) FKM does not allow for a ferroelectric ground state with a spontaneous polarization, i.e., there is no nonvanishing $\langle d^\dagger f\rangle$ expectation value in the limit of vanishing hybridization.

In order to shed some light on this controversy we have decided to study the problem of electronic ferroelectricity in the FKM using the small-cluster exact-diagonalization method that was so successful in describing valence and metal-insulator transitions in this model.[5,6] It should be noted that for a given L the full-Hilbert space of the spinless FKM consists of 4^L quantum states, thereby strongly limiting numerical computations. Although the number of states can be reduced considerably by the use of symmetries of H, there is still a limit ($L\sim 10$) on the size of clusters that can be studied using small-cluster exact-diagonalization calculations. However, we will show later that due to small sensitivity of the FKM on L (for a wide range of parameters), already such small clusters can describe satisfactory the behavior of the $\langle d^\dagger f\rangle$ expectation value that lies in the center of our interest.

To compare our numerical results with Czycholl's,[4] obtained for small Coulomb interactions, we have started our investigation in the weak-coupling limit and half-filled band

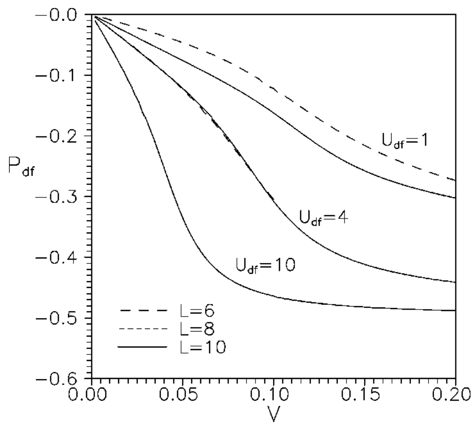

FIG. 1. Hybridization dependence of the d-f-polarization $P_{df} = \langle d_i^\dagger f_i \rangle$ in the spinless FKM calculated for three different values of U_{df} and L. The symmetric case $E_f=0$.

case ($n_f=n_d=0.5$). The weak-coupling numerical results for P_{df} obtained using the modified Lanczos method[8,9] are displayed in Fig. 1. To reveal the finite-size effects on P_{df}, numerical calculations have been performed for three finite clusters of $L=6$, 8, and 10 sites. It is seen that there are nonzero finite-size effects on the $\langle d^\dagger f \rangle$ expectation value in the weak-coupling limit, however they do not change qualitatively the behavior of P_{df} in the limit $V \to 0$ that is crucial for the verification of spontaneous polarization. In all cases the $\langle d^\dagger f \rangle$ expectation value vanishes in the limit $V \to 0$, so there is no spontaneous polarization in the spinless FKM. Thus, in accordance with Czycholl's weak-coupling results we can conclude that the spinless FKM does not allow for a ferroelectric ground state with a spontaneous polarization at least for U_{df} small.

Unlike the method used by Czycholl that is restricted to small interactions, we can proceed in the numerical study of the FKM at arbitrary U_{df}. The strong-coupling numerical results for P_{df} are displayed in Fig. 1 for $U_{df}=4$ and $U_{df}=10$. Obviously the one-dimensional FKM does not exhibit a ferroelectric ground state with a spontaneous polarization in the strong-coupling limit. For both values of U_{df} the $\langle d^\dagger f \rangle$ expectation value vanishes for $V \to 0$, and it is demonstrated that this result is independent of L. Thus, the strong-coupling results can be satisfactorily extended to large systems and they should be considered as definite.

Of course, the absence of the ferroelectric ground state in the spinless FKM does not exclude that some other models could exhibit such a ground state. The spinless FKM is not too realistic model of a rare-earth compound, because any real-Fermi system has at least a spin degeneracy. Therefore, it is natural to ask if the spin-one-half FKM would not allow for the ferroelectric ground state with a spontaneous polarization.

Numerically the problem can be easily solved since the numerical method used for the spinless FKM can be straightforwardly generalized also for the spin-one-half FKM. Unfortunately, including spins will result in further reduction of the size of clusters that can be analyzed using the exact-diagonalization method. In order to compensate partially for the small size of clusters we next examine the model only for strong d-f interactions that (as was shown for the spinless FKM) minimize considerably the finite-size effects.

The Hamiltonian of the spin-one-half FKM can be obtained directly from the spinless model by including the spins for both d and f electrons and by adding the on-site Coulomb interaction U_{ff} that acts between two f electrons of opposite spins (the last term):

$$H=\sum_{ij\sigma} t_{ij} d^\dagger_{i\sigma} d_{j\sigma} + U_{df} \sum_{i\sigma\sigma'} f^\dagger_{i\sigma} f_{i\sigma} d^\dagger_{i\sigma'} d_{i\sigma'} + E_f \sum_{i\sigma} f^\dagger_{i\sigma} f_{i\sigma} + V \sum_{i\sigma} d^\dagger_{i\sigma} f_{i\sigma} + \text{H.c.} + \frac{U_{ff}}{2} \sum_{i\sigma} f^\dagger_{i\sigma} f_{i\sigma} f^\dagger_{i-\sigma} f_{i-\sigma}. \qquad (2)$$

The ground-state properties of this model for $V=0$ have been investigated in our preceding paper.[10] We have found that numerical results depend strongly on f-f interaction strength U_{ff}, but they are relatively insensitive to d-f interaction strength U_{df} (for $U_{df}>2$). Therefore, to represent the typical behavior of the model at nonzero V, and to minimize finite-size effects we choose in the next study the value $U_{df}=3$ that is sufficiently large to stabilize the system. Another advantage of this selection is that the ground-state phase diagram of the spin-one-half FKM without hybridization is well understood[10] for large values of U_{df}. Particularly, in the strong-interaction limit $U_{ff}>4/\pi$ the ground state is insulating for $E_f<-4/\pi$ and metallic for $E_f>-4/\pi$. At $E_f=-4/\pi$ the model exhibits a discontinuous insulator-metal transition that is accompanied by an integer-valence transition from $n_f=1$ ($n_d=0$) to $n_f=0$ ($n_d=1$). The same behavior exhibits the model also in the opposite limit $U_{ff}<4/\pi$: the ground state is insulating for $E_f<E_c(U_{ff})$ and metallic for $E_f>E_c(U_{ff})$. However, a discontinuous insulator-metal transition that takes place at $E_f=E_c(U_{ff})$ realizes now between an integer-valence state $n_f=1$ and an inhomogeneous intermediate-valence state $n_f \neq 0$. These results show that there are only three physically different ground states in the spin-one-half FKM without hybridization, and, namely, an insulating integer-valence ground state with $n_f=1$, a metallic integer-valence ground state with $n_f=0$, and a metallic intermediate-valence ground state with $0<n_f<1$. Here we examine whether these ground states are stable against a small, finite hybridization or whether some new ground states are obtained if one starts from a finite hybridization and studies the $V \to 0$ limit of the model. Again the special attention is devoted to the question if the model can exhibit a ferroelectric ground state with a spontaneous, nonvanishing polarization $P_{df}=\langle d^\dagger_{i\sigma} f_{i\sigma} \rangle$.

The strong-coupling ($U_{ff}=10$) numerical results for P_{df} obtained on finite clusters of 4 and 6 sites are displayed in Fig. 2. It is seen that for both $E_f<-4/\pi$ (for $V=0$ an insulating integer-valence state) and $E_f>-4/\pi$ (for $V=0$ a metallic integer-valence state) the $\langle d^\dagger f \rangle$ expectation value vanishes in the limit $V \to 0$ indicating that there is no spontaneous polarization in the spin-one-half FKM. It should be noted that this result is expected since approximate solutions[11] lead also to $P_{df}=0$ for the integer-valence states with $n_f=1$ and $n_f=0$. A less trivial situation is expected in the intermediate-valence state with $0<n_f<1$. As was discussed above, this state exists in the spin-one-half FKM without hybridization for $U_{ff}<4/\pi$ and $E_f>E_c(U_{ff})$. Particularly, for $L=4$, $U_{df}=3$ and $U_{ff}=0.4$ we have found

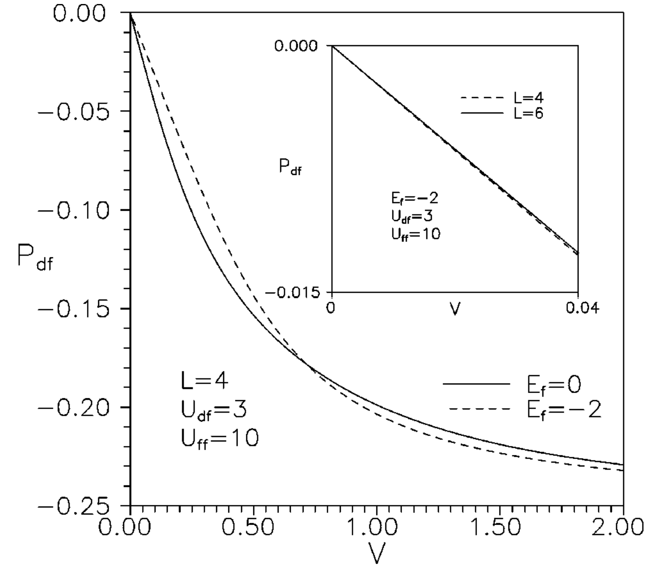

FIG. 2. Hybridization dependence of the *d-f* polarization $P_{df} = \langle d^{\dagger}_{i\sigma} f_{i\sigma} \rangle$ in the spin-one-half FKM calculated for $E_f = -2$ (for $V=0$ an insulating integer-valence state) and $E_f=0$ (for $V=0$ a metallic integer-valence state). Inset: Hybridization dependence of P_{df} in the limit of vanishing V for $L=4$ and 6.

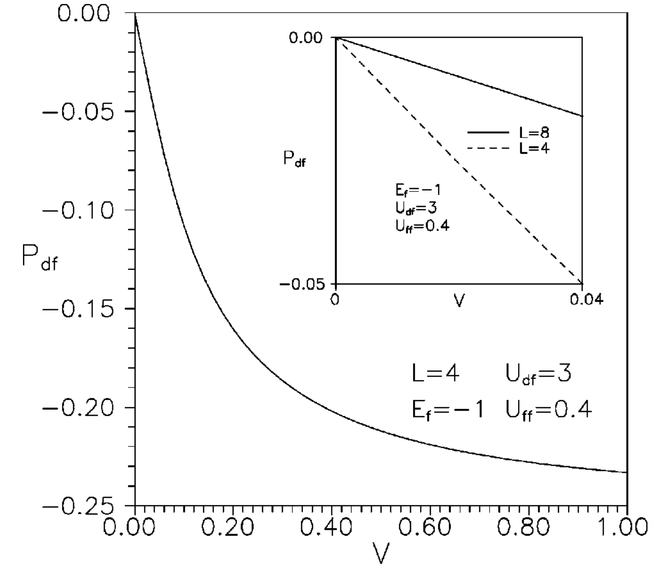

FIG. 3. Hybridization dependence of the *d-f* polarization $P_{df} = \langle d^{\dagger}_{i\sigma} f_{i\sigma} \rangle$ in the spin-one-half FKM calculated for $E_f=-1$ (for $V=0$ an intermediate-valence state). Inset: Hybridization dependence of P_{df} in the limit of vanishing V for $L=4$ and 8.

that $n_f=1$ for $E_f<-1.35$, $n_f=0.5$ for $-1.35<E_f<-0.65$, and $n_f=0$ for $E_f>-0.65$. To examine the stability of intermediate-valence state against a small, finite hybridization we chose the value $E_f=-1$ for numerical calculations. The results obtained for P_{df} are shown in Fig. 3. Again the $\langle d^{\dagger} f \rangle$-expectation value vanishes in the limit $V \to 0$ indicating the absence of spontaneous polarization. We have verified this important result also for $L=8$ (see inset in Fig. 3). Unfortunately, due to the memory limitations we were not able to continue with numerical computations on larger lattices (the memory requirement of the Lanczos method for clusters larger than $L=8$ is beyond the reach of present day computers) to exclude definitely the existence of spontaneous polarization in the spin-one-half FKM. However, in accordance with results obtained for the spinless FKM we do not expect that the behavior of P_{df} for $V \to 0$ could be qualitatively changed on larger lattices.

In summary, we have used the extrapolation of small-cluster exact-diagonalization calculations to study the possibility of electronic ferroelectricity in the one-dimensional spinless and spin-one-half FKM. It was found that neither the spinless nor spin-one-half version of the FKM allows for a ferroelectric ground state with a spontaneous polarization, i.e., there is no nonvanishing $\langle d^{\dagger} f \rangle$ expectation value for vanishing hybridization V.

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[1] L.M. Falicov and J.C. Kimball, Phys. Rev. Lett. **22**, 997 (1969).
[2] T. Portengen, T. Östreich, and L.J. Sham, Phys. Rev. Lett. **76**, 3384 (1996).
[3] T. Portengen, T. Östreich, L.J. Sham, Phys. Rev. B **54**, 17 452 (1996); **59**, 2642 (1999).
[4] G. Czycholl, cond-mat/9805363 (unpublished).
[5] P. Farkašovský, Phys. Rev. B **51**, 1507 (1995).
[6] P. Farkašovský, Phys. Rev. B **52**, R5463 (1995).
[7] C. Gruber and N. Macris, Helv. Phys. Acta **69**, 850 (1996).
[8] E. Dagotto, Rev. Mod. Phys. **66**, 763 (1994).
[9] P. Farkašovský, Z. Phys. B **104**, 553 (1997).
[10] P. Farkašovský, Phys. Rev. B **54**, 11 261 (1996).
[11] For an overview, see T. Portengen and L.J. Sham, Superlattices Microstruct. **23**, 531 (1998).