Electronic Ferroelectricity in the Falicov-Kimball Model

C. D. Batista

Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545

(Dated: Received March 22, 2022)

I show that a spontaneous electric polarization exists in the solution of the Falicov-Kimball model by mapping the strong coupling limit of this Hamiltonian into an $xxz$ spin 1/2 model with a magnetic field. In this way, I determine the phase diagram of the strongly interacting model and show the existence to a transition to a mixed valence regime containing two phases: an orbitally ordered state and a Bose-Einstein condensation of excitons with a built-in electric polarization.

PACS numbers: 71.27.+a, 71.28.+d, 77.80.-e

The Falicov-Kimball model (FKM) was introduced to explain semiconductor-metal transitions and has been extensively used to describe valence transitions in heavy fermion compounds. Its original version contains a dispersive band of itinerant $d$ electrons interacting with localized $f$ orbitals via an on-site Coulomb interaction. If hybridization between both bands is included, the $f$ charge occupation is no longer a good quantum number, and it is possible to build coherence between the $d$ electrons and the $f$ holes. Based on a mean field solution of the FKM with a hybridization term, Portengen et al. proposed that this coherence gives rise to a spontaneous electric polarization associated with a Bose-Einstein condensate (BEC) of $d-f$ excitons.

Ferroelectrics are of considerable theoretical and technological interest because of their highly unusual properties. The ferroelectric (FE) transitions have traditionally been considered as a subgroup of the structural phase transitions. As in the case of superconductivity, the existence of ferroelectrics based on a purely electronic mechanism would provide a new set of physical properties and technological applications; for instance, it would open the possibility of controlling optical properties with magnetic fields.

The proposal of electronic ferroelectricity in the FKM was recently tested theoretically using different techniques. An analytical calculation in infinite dimension for the weak coupling limit did not confirm its existence. By using numerical methods to solve finite-size chains, Farkašovský arrived at the same conclusion for the intermediate and the strong coupling regimes. Recently, Zlatić et al. calculated the spontaneous polarization in the FKM from its exact solution in infinite dimensions. They found that the spontaneous hybridization susceptibility diverges when the temperature goes to zero, indicating a possible non-zero polarization of the ground state.

Hybridization between the bands however is not the only way to develop $d-f$ coherence. An $f-f$ hopping also induces it. Furthermore, I will show that in the mixed valence regime, the ground state of the FKM with $f-f$ hopping is either an orbitally-ordered (chessboard) state or a BEC of electron-hole pairs (excitons). In particular, the condensate has a built-in spontaneous FE or antiferroelectric (AFE) polarization induced by a pure electronic mechanism. The FE or AFE character of the solution depends on the relative sign of the $d-d$ and the $f-f$ hoppings.

I obtain the complete phase diagram of the extended FKM by mapping the original Hamiltonian into an effective spin model. The mapping is exact in the strong coupling limit and the resulting spin Hamiltonian is a spin 1/2 $xxz$ model with an applied magnetic field along the $z$ axis. This spin model is exactly solvable in one dimension and its phase diagram has been determined very accurately for two dimensional ($D = 2$) systems (the exact solution has been numerically obtained for a $96 \times 96$ square lattice). In this way, the results obtained in this paper prove that the phase diagram of the extended FKM contains FE and AFE phases induced by an electronic mechanism.

Recently, high dielectric constants were observed in oxides of the type ACu$_3$Ti$_4$O$_{12}$. In particular, the largest dielectric constant ever observed is exhibited by CaCu$_3$Ti$_4$O$_{12}$ ($\epsilon_0 \approx 80000$ for single-crystal samples at room temperature). In addition, high resolution x-ray and neutron powder diffraction measurements of CaCu$_3$Ti$_4$O$_{12}$ rule out a conventional FE structural phase transition. The electronic ferroelectricity proposed by Portengen et al. was also ruled out due to the large value of the optical gap ($\Delta \sim 1.5 eV$). The strong coupling theory introduced in this paper shows that the excitons condense in the presence of a large gap.

I will consider an extended FKM for spinless fermions on a $D$-dimensional hypercubic lattice:

$$H = c_d \sum_i n_i^d + \epsilon_f \sum_i n_i^f + t_d \sum_{\langle i,j \rangle} d_i^\dagger d_j + U_f d_i^\dagger n_i^f n_i^f + t_f \sum_{\langle i,j \rangle} f_i^\dagger f_j,$$  

(1)

where $n_i^d = d_i^\dagger d_i$, and $n_i^f = f_i^\dagger f_i$ are the occupation numbers of each orbital. For historical reasons, I denote the orbitals by $f$ and $d$ but in general they can represent any pair of atomic orbitals with different parity. For instance, in CaCu$_3$Ti$_4$O$_{12}$ there are $d$ states which are hybridized with $p$ bands. This fact is another important motivation to include a non-zero $t_f$.

The Hamiltonian $H$ can be rewritten as an asymmetric Hubbard model if the orbital flavor is represented by a pseudospin variable. A spin 1/2 is required to describe the two orbitals (flavors) on each site:

$$c_i^\dagger = d_i^\dagger \quad c_i^\dagger = d_i, \quad c_i^\dagger = f_i^\dagger \quad c_i^\dagger = f_i,$$  

(2)

arXiv:cond-mat/0207331v2 [cond-mat.str-el] 26 Feb 2004
where the pseudospin generators are:

\[
\tau^x_i = \frac{1}{2}(d_i^\dag f_i + f_i^\dag d_i),
\]

\[
\tau^y_i = \frac{i}{2}(f_i^\dag d_i - d_i^\dag f_i),
\]

\[
\tau^z_i = \frac{1}{2}(n_i^d - n_i^f).
\]

(3)

The expression for \(H\) in the new language is:

\[
H = e_d \sum_{i,\sigma} n_{i\sigma} + \sum_{(i,j),\sigma} t_{\sigma}(c_{i\sigma}^\dag c_{j\sigma} + c_{j\sigma}^\dag c_{i\sigma}) + U^{fd} \sum_i n_{i\uparrow} n_{i\downarrow} + B_z \sum_i \tau^z_i,
\]

(4)

where \(e_d = \frac{1}{2}(\epsilon_d + \epsilon_f)\) and \(B_z = \epsilon_d - \epsilon_f\). The new version of \(H\) is a Hubbard model with different hoppings for each spin flavor, \(t_\uparrow = t_d\) and \(t_\downarrow = t_f\), plus a Zeeman coupling with a magnetic field \(B_z\). Both terms break the \(SU(2)\) symmetry of the original Hubbard model \((t_\uparrow = t_d\) and \(B_z = 0\)). The remaining symmetries are the \(U(1)\) groups associated with the conservation of the total charge and the total \(\tau^z\). In the original language, these \(U(1)\) symmetries correspond to the conservation of the total number of particles in each band \((\langle H, \sum_i n_i^\dag \rangle = \langle H, \sum_i n_i^\dag \rangle = 0\).

I will consider from now on the half filled case, i.e., one particle per site. For this concentration, it is well known that the Hubbard model in the strong coupling limit can be reduced to an effective Heisenberg model. In a similar fashion, I can reduce \(H\) to an effective spin model when \(t_\sigma \ll U^{fd}\). The lowest energy subspace for infinite \(U^{fd}\) is the one generated by states having one particle at each site, i.e., the charge degrees of freedom are frozen (the system is a Mott insulator) and an effective spin is localized at each site. In this limit there is a complete spin degeneracy because the energy does not depend on the orientation of each spin. To lift this degeneracy it is necessary to consider the lowest order processes in \(t_\sigma/U^{fd}\). This can be done by a canonical transformation which eliminates the linear terms in the hopping \(t_\sigma\) and keeps the terms of quadratic order. Up to an irrelevant constant \(C = -NZJ_\perp/8\), where \(Z\) is the coordination number and \(N\) is the number of sites, the resulting effective spin Hamiltonian is [12]:

\[
H_{\text{eff}} = \sum_{(i,j)} J_z \tau^z_i \tau^z_j + J_\perp (\tau^x_i \tau^x_j + \tau^y_i \tau^y_j) + B_z \sum_i \tau^z_i.
\]

(5)

with \(J_z = \frac{2(t_\uparrow^2 + t_\downarrow^2)}{U^{fd}}\) and \(J_\perp = \frac{4t_\uparrow t_\downarrow}{U^{fd}}\). \(H_{\text{eff}}\) is a spin 1/2 \(xxz\) model with an applied magnetic field along the \(\hat{z}\) direction. The model is Ising-like \((J_z > J_\perp)\). However it is important to consider the whole phase diagram because the ratio \(J_z/J_\perp\) can take any value if non-zero nearest-neighbor repulsions are added to \(H\).

\(H_{\text{eff}}\) has been exactly solved in one dimension by means of the Bethe ansatz technique [13]. The one dimensional (1D) quantum phase diagram is similar to the 2D one that I describe below. The only important difference is that, as required by the Mermin-Wagner theorem [15], the excitonic condensate is critical at zero temperature (power law correlations) for the 1D case. The phase diagram of \(H_{\text{eff}}\) has been determined recently for 2D systems by solving up to \(96 \times 96\) lattices with quantum Monte Carlo loop algorithm [7]. The zero temperature phase diagram is shown in Fig. 1 and the corresponding name of each phase translated back to the original language of the FKM. Since \(H_{\text{eff}}\) is symmetric under a reflection in the \(xy\) plane, the phase diagram must be symmetric under a change of sign of the magnetic field. The fully polarized solutions, obtained for large values of \(|B_z|\), correspond to a full \(f\) band for positive \(B_z\) \((\epsilon_f \ll \epsilon_d)\) and a full \(d\) band for \(B_z\) negative \((\epsilon_f \gg \epsilon_d)\). The spectrum of both phases has a finite charge transfer (pseudospin gap) \(\Delta_{\text{CT}} = |B_z - Z(J_\uparrow + J_\perp)/2|\). This gap vanishes at the quantum critical points \(|B_z^c| = \frac{2}{Z}(|J_\uparrow| + J_\perp)\), which are the boundaries for the mixed valence phase that emerges when the \(f\) and \(d\) bands are sufficiently close: \(\epsilon_f - \epsilon_d \ll \frac{2}{Z}(|J_\uparrow| + J_\perp)\). If \(J_\perp > J_\uparrow\) two phases are possible within the mixed valence regime. For small values of \(|B_z|\), the \(J_\perp\) term dominates and induces a longitudinal antiferromagnetic (AFM) phase (chessboard state in the original language). When \(|B_z|\) is larger than a critical value, the magnetic field suppresses the Ising-like ordering and the \(J_\perp\) term induces a magnetic ordered state in the \(xy\) plane (BEC of electron-hole pairs). The line separating the orbital ordered state and the BEC corresponds to a first order transition. This line ends at the Heisenberg point \((J_z = J_\perp)\) where both phases coexist. For \(J_\perp < J_\uparrow\), the only phase in the mixed valence regime is the BEC. In a real material, changing \(B_z = \epsilon_d - \epsilon_f\) can be achieved by applying pressure or alloying.

![Staggered Orbital (Chessboard) Ordering](image-url)

**FIG. 1:** Two dimensional quantum phase diagram of \(H_{\text{eff}}\) obtained from Ref. [7]. The small circle indicates the position of the Heisenberg point. The dashed line denotes the quantum phase transition between the mixed valence (non-shadowed) and the non-mixed valence regimes.

The \(d - f\) exciton condensate has a built-in electric polarization [2]. This can be easily seen by realizing that the spin version of the order parameter for the BEC is the uniform \(xy\) magnetization for negative \(J_\perp\) (condensation at \(k = 0\) and
the staggered \(xy\) magnetization for positive \(J_\perp\) (condensation at the AFM wave vector \(k = Q\)):

\[
M^\perp = \sum_i (\tau_i^x \hat{x} + \tau_i^y \hat{y}) \quad \text{for} \quad J_\perp < 0
\]

\[
M^\perp_{ST} = \sum_i e^{iQ \cdot r_i} (\tau_i^x \hat{x} + \tau_i^y \hat{y}) \quad \text{for} \quad J_\perp > 0. \quad (6)
\]

Since \(M^\perp\) is a two dimensional vector, it can also be represented by a complex number \(|M^\perp|e^{i\phi}\) (\(\tan \phi = M^x/M^y\)) which is the usual expression for the order parameter of the BEC. The sign of \(J_\perp\) is determined by the relative sign of \(t_d\) and \(t_f\). On the other hand, the uniform polarization operator is \(\mathcal{P}\):

\[
\mathcal{P} = \mu \sum_i (d_i^\dagger f_i + d_i f_i^\dagger) = \frac{2\mu}{\Omega} M^x,
\]

where \(\mu\) is the inter-band dipole matrix element and \(\Omega\) is the volume of the system. Therefore, the condensate has a built-in electric polarization which is proportional to \(\hat{x}\) (real) component of its order parameter. For positive \(J_\perp\), the condensate becomes AFE because the staggered electric polarization:

\[
\mathcal{P}_{ST} = \mu \sum_i e^{iQ \cdot r_i} (d_i^\dagger f_i + d_i f_i^\dagger) = \frac{2\mu}{\Omega} M^x_{ST}, \quad (8)
\]

is proportional to \(M^x_{ST}\).

The three dimensional (3D) quantum phase diagram of \(H_{eff}\) \(^{14}\) is similar to the two dimensional (2D) one shown in Fig.1. The same is not true for the finite temperature phase diagrams due to the Mermin-Wagner theorem \(^{15}\). The transition temperature associated to the BEC is finite only for the 3D case. From the finite temperature phase diagram obtained in Ref. \(^7\), the BEC of electron-hole pairs undergoes a Kosterlitz-Thouless phase transition in a 2D system.

I will now analyze the effect that a time dependent electric field \(E e^{i\omega t}\) induces in our FE or AFE condensate of excitons. The coupling term between the electric field and the uniform polarization:

\[
H_I = E \cdot \mathcal{P} e^{i\omega t} = \mu \sum_i (d_i^\dagger f_i + d_i f_i^\dagger), \quad (9)
\]

corresponds, in the spin language, to the application of a uniform time dependent magnetic field \(\mathbf{B}_I(t) = 2E \cdot \mathcal{P} e^{i\omega t} \hat{x}/\Omega\). From the point of view of the spin variables this is like a magnetic resonance experiment since \(H_{eff}\) already includes a uniform static field \(B_z \hat{z}\). Therefore, the equivalent magnetic system will have a resonant absorption at the frequency which tends to \(\omega_0 = B_z/\hbar\) when \(B_z\) tends to zero. Back to the original language, this means that for small electric fields the optical absorption will be resonant at \(\hbar \omega_0 = \epsilon_d - \epsilon_f\). This is an experimental fingerprint of the excitonic condensate.

Since the above theory is only valid in the strong coupling limit, it is natural to ask whether the chessboard ordering and the excitonic condensate survive in the intermediate and weak coupling regimes. To answer this question it is more convenient to use the Hubbard-like representation of \(H\) (see Eq. \(^{3}\)). The dispersion relation for the non-interacting part of \(H\) \((U^{fd} = 0)\) is: \(\epsilon_k(\sigma) = \epsilon_d + B_z \sigma + 2t_\sigma \sum_\nu \cos(k_\nu)\). At half filling and for \(B_z = 0\) the Fermi surface of the non-interacting problem nests at \(k = Q\). This indicates that an infinitesimal value of \(U^{fd}\) is sufficient to induce an AFM (chessboard ordering in the original language) instability. Again the presence of a non-zero magnetic field will induce a transition from the orbitally ordered state to the BEC of excitons. For the 3D case, if \(U^{fd} < U^{fd}_{crit} \sim 2.85(|t_a| + |t_b|)\) the magnetic field \(B_z\) induces an insulator-metal transition before the saturation of the magnetization (non-mixed valence regime) is reached \(^{14}\). This means that for weak coupling a new metallic phase appears between the BEC of excitons and the non-mixed valence regime (see Fig.1). For these reasons, I expect the phase diagram of \(H\) to contain an electric polarized BEC in the weak and intermediate coupling regimes as well. This subject will be studied more extensively in Ref. \(^{17}\).

What happens if we consider electrons instead of spinless fermions? In this case each orbital can be occupied by two electrons and therefore it is natural to include local Coulomb repulsions \(U^{ff}\) and \(U^{dd}\). By doing so the FKM is replaced by a two orbital Hubbard model and the large \(U^{\alpha,\beta}\) expansion gives rise to a Kugel-Khomskii like model \(^{13}\) containing spin \(s\) (magnetic) and pseudospin \(\tau\) (orbital) degrees of freedom. If \(t_a = -t_b = t\) and \(U^{ff} = U^{dd} = U\) (the most general case will be analyzed in Ref. \(^{19}\)), the effective spin Hamiltonian is:

\[
H_{eff}^{s,\tau} = \frac{J_0}{2} \sum_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j + (J_z - J_0) \sum_i \tau_i^z \tau_j^z + B_z \sum_i \tau_i^z
\]

\[
+ 2 \sum_{i,j} [J_0 \tau_i^z \tau_j^x - J_\perp (\tau_i^x \tau_j^x + \tau_i^y \tau_j^y)](\mathbf{S}_i \cdot \mathbf{S}_j + \frac{1}{4}),
\]

where \(J_0 = 4t^2/U\). The ground state of \(H_{eff}^{s,\tau}\) is ferromagnetic (FM) if \(J_0 < J_0^c\). For the FM solution, \(H_{eff}^{s,\tau}\) reduces to \(H_{eff}^{ff}\) because all the electrons have the same spin orientation and hence can be considered as spinless fermions. Therefore the charge degrees of freedom (\(\tau\)) of the FM solution are exactly described by \(H_{eff}^{ff}\), and the phase diagram is the one of Fig.1; i.e., ferromagnetism coexists with chessboard ordering or a FE BEC of excitons. If \(J_0 > J_0^c\), the system becomes AFM. In this case the effective transverse coupling for the pseudospins variables, \(J^{eff}_{\perp} = -2J_\perp \langle (\mathbf{S}_i \cdot \mathbf{S}_j + \frac{1}{4}) \rangle\), changes its sign because \(\langle (\mathbf{S}_i \cdot \mathbf{S}_j + \frac{1}{4}) \rangle\) turns to be negative. For this reason the AFM solution coexists with an AFE condensate. This means that when a magnetic field induces a transition from an AFE phase to a FM one, it simultaneously changes the electric polarization from AFE to FE. This important property gives rise to new technological applications.

From now on I will continue with the spinless case just to isolate the basic mechanism for FE and AFE which is associated with the charge degrees of freedom. An important aspect of this analysis is the inclusion of a non-zero hybridization.
produced by structural phase transitions. The different signs in the hybridization terms are due to the different parities of the two orbitals. The crystal has inversion symmetry.) By adding $H_V$ to $H$, we get the following additional terms for $H_{\text{eff}}$ (large $U$ expansion):

$$H_{\text{eff}} = J' \sum_{\nu,i} (\mathbf{\tau}_i \cdot \mathbf{\tau}_{i+\mathbf{\hat{e}_x}} + J'_{\perp} \sum_{\nu,i} (\mathbf{\tau}_i \cdot \mathbf{\tau}_{i+\mathbf{\hat{e}_x}} - \mathbf{\tau}_i \cdot \mathbf{\tau}_{i+\mathbf{\hat{e}_y}})),$$

$$- 2J' \sum_{\nu,i} \mathbf{\tau}_i \cdot \mathbf{\tau}_{i+\mathbf{\hat{e}_x}},$$

where $J' = 4V^2/U_{fd}$ and $J'_{\perp} = 4V(t_a + t_b)/U_{fd}$. Let me now consider the perturbative effects of the hybridization ($J', J'_{\perp} \ll J_z, J_L$) on the phase diagram of Fig. 1 for the FE case ($J_L < 0$). The first term is a Heisenberg interaction which just produces a renormalization of $J_z$ and $J_L$. The mean value of the second term is zero in the FE phase (BEC of excitons) and therefore they do not make any contribution. The last term introduces an easy axis anisotropy along the $\mathbf{\hat{x}}$ direction and lifts the $U(1)$ degeneracy. The BEC then is replaced by an Ising-like FE state characterized by the breaking of the remaining $Z_2$ symmetry. Therefore, the spontaneous ferroelectricity remains when the hybridization is included perturbatively; however, the resonant response to a time dependent electric field disappears (see Eq. [9]) due to the absence of Goldstone modes. In other words, the hybridization makes the electronically induced FE phase similar to the ones induced by structural phase transitions.

In summary, I derived the phase diagram of the FKM with a $t_f$ hopping term in the strong coupling limit. The insulating phase obtained at half filling has a transition from a non-mixed valence to a mixed valence regime as a function of the energy difference between the centers of both bands. Two different phases are present in the mixed valence regime: a BEC of excitons with a built-in electrical polarization which starts just at the valence transition and an orbitally ordered (chessboard) state which appears when the centers of the bands are sufficiently close. These results were extended to the intermediate and weak coupling regimes due to the nesting property of the Fermi surface of hypercubic lattices. I also mentioned the effect of including spin degrees of freedom in $H$: the interplay between magnetic and charge degrees of freedom gives rise to the coexistence of FE and FM phases which are coupled to each other. This opens the possibility of controlling optical properties by applying magnetic fields or controlling magnetic properties by applying electric fields.

The effect of a non-zero hybridization was also considered. The main conclusion is that the $U(1)$ degeneracy associated to the BEC of excitons is lifted by the hybridization and replaced by an Ising-like FE state (broken $Z_2$ symmetry). Then, the resonant response to a time dependent electric field disappears because the Goldstone modes acquire a finite mass (gap).

These results indicate that the following characteristics are favorable to the formation of an electronically driven FE state: a) The system must be in a mixed-valence regime and the two bands involved must have different parity. b) It is best, though not necessary, if both bands have similar bandwidths. c) A local Coulomb repulsion ($U_{fd}$) between the different orbitals is required. d) The hybridization between the bands must be small compared to their bandwidths.

I wish to thank L. Sham, J. E. Gubernatis, J. Thompson, J. Sarrao, N. Kawashima, and A. A. Aligia for stimulating discussions. This work was sponsored by the US DOE under contract W-7405-ENG-36.

[1] L. M. Falicov and J. C. Kimball, Phys. Rev. Lett. 22, 997 (1969).
[2] T. Portengen, Th. Östreich and L. J. Sham, Phys. Rev. Lett. 76, 3384 (1996); Phys. Rev. B 54, 17452 (1996).
[3] C. Kittel, Introduction to Solid State Physics, John Wiley and Sons, Inc., New York (1996).
[4] G. Czycholl, Phys. Rev. B 59, 2642 (1999).
[5] P. Farkašovský, Phys. Rev. B 59, 9707 (1999); P. Farkašovský, Phys. Rev. B 65, 081102 (2002).
[6] V. Zlatić, J.K. Freericks, R. Lemanski and Czycholl, Phil. Mag. B 81, 1443 (2001).
[7] G. Schmid et al., Phys. Rev. Lett. 88, 167208-1 (2002).
[8] M. A. Subramanian et al., J. Solid State Chem. 151, 323 (2000).
[9] A. P. Ramirez et al., Solid State Commun. 115, 217 (2000).
[10] C. C. Homes et al., Science 293, 673 (2001).
[11] L. He et al., Phys. Rev. B 65, 214112 (2002).
[12] G. Fáth et al., Phys. Rev. B 52, 13910 (1995).
[13] C. N. Yang and C. P. Yang, Phys. Rev. 150, 321 (1966).
[14] M. E. Fisher and D. R. Nelson, Phys. Rev. Lett. 29, 1350 (1974).
[15] N. D. Mermin and H. Wagner, Phys. Rev. Lett. 17, 1133 (1966).
[16] P. G. van Dogen and V. Janiš, Phys. Rev. Lett. 72, 3258 (1994).
[17] C. D. Batista and J. E. Gubernatis, in preparation.
[18] K. I. Kugel and D. I. Khomskii: Sov. Phys. Usp. 25, 231 (1982).
[19] C. D. Batista, in preparation.