Hybridization effect in the Falicov-Kimball model

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The extended Falicov-Kimball model which contains hybridization between localized level and conduction band has been studied using the exact diagonalization method. We obtain the single-particle density of states and the valency from this method and analyze the behaviors of valence transition and activation gap. We find that the valence transition is continuous due to hybridization, while the activation gap closes discontinuously. Moreover, the onset of the valence transition and the closing point of the activation gap mismatch each other. Our result is well consistent with the recent experiment on SmB$_6$.

I. INTRODUCTION

During last several decades, extensive studies have been done to understand two-band models such as Anderson model, Kondo model, and Falicov-Kimball model(FKM). These models are especially useful to explain many features of lanthanides and actinides since these materials have broad conduction band(s,d-band) and well localized valence band(f-band) near Fermi level. These materials show some typical strong correlation effects, for example large effective mass, non-integer valency, and small activation gap.

We can categorize various two-band models into two groups according to their interband interactions. The first group includes hybridization between valence and conduction band. Anderson model, periodic Anderson model, and Kondo model are well-known examples emphasizing hybridization. Models taking interband Coulomb interaction into account fall into the second group. This interband Coulomb interaction is often called Falicov-Kimball term since they considered this interaction most crucial in understanding many features on lanthanides and actinides. FKM has been studied to explain valence transition and metal-nonmetal transition in non-integer valent rare-earth compounds.

SmB$_6$ and many other non-integer valent systems show phase transitions in valence and electric property when temperature or pressure varies. Increasing temperature makes d-electron more itinerant and external or internal pressure reduces lattice constant and enhances crystal field splitting. These two effects broaden conduction band and lower the energy of d-electron. As a result, f-level crosses d-band and the system undergoes valence transition. Variation of these parameters also changes the configuration of localized f-electron and itinerant d-electron, which may causes metal-nonmetal transition.

These transitions have been explained using the hybridization gap theory in the periodic Anderson model. According to this theory, the valence transition is due to the overlap between f- and d-band, and the appearance of semiconducting gap is the result of the hybridization between two bands. The width of the semiconductor gap is proportional to the characteristic energy scale, the so-called Kondo temperature $T_K$, and the gap disappears continuously as temperature or pressure increases. In other words, the hybridization gap theory predicts the second order metal-nonmetal transition.

A generalized two-band model, the so-called extended Falicov-Kimball model(EFKM) considering both interband Coulomb interaction and hybridization was proposed. Though much efforts have been devoted to this model for last two decades, no settled result on the nature of EFKM exists as far as we know. The most controversial point in EFKM is its valence transition behavior. It is well known that FKM shows discontinuous valence transition as pressure changes. Some authors argued that this discontinuity still remains for small hybridization. Others, however, have reported that there is no discontinuous transition in EFKM. The only consensus is that the valence transition behavior in EFKM is so sensitive to the approximation used that only approximation-free solution can clarify above controversy.

In this paper, we study EFKM to show the valence transition behavior when hybridization exists and to elucidate metal-nonmetal transition which has been given by Cooley et al. recently. They measured for that the activation gap of SmB$_6$, which is a well-known non-integer valent material, closes discontinuously. This result makes the hybridization gap theory suspicious since it predicts continuous gap closing.

The transition behavior shown by Cooley et al. is strikingly similar to that of Mott-Hubbard transition. It is natural to suppose that the Coulomb interaction may play an important role in SmB$_6$ and other non-integer valent materials. The simplest model, which includes Coulomb interaction between localized level and conduction band, may be the Falicov-Kimball model(FKM).

Recently Farkašovský has tried to explain the experimental results of Cooley et al. using FKM. He showed using the exact diagonalization method that the Mott-Hubbard type of metal-nonmetal transition appears in FKM when Coulomb interaction is small. This fact suggests that FKM may be considered as a possible microscopic model for non-integer valent materials such as SmB$_6$. 
Since the valencem, i.e. the expectation value of f-electron number operator in the ground state, must be an integer in FKM, non-integer valency is the result of statistical average of the mixtures of different integer valency. To have intermediate valency, the system must include the hybridization between the localized level and conduction band.

We use the Lanczos exact diagonalization method to remove the artifacts of approximation in studying this model. Due to the limitation of the numerical method, we treat 1-dimensional chain of 8 lattice sites. For this system, we first get the DOS of FKM depending on energy scale εf, and introduce the effective gap Δ_{eff} to explain valence transition in terms of the DOS. We find that only continuous valence transition is allowed when hybridization exists. From the DOS of EFKM, we find that the activation gap shows sudden disappearance at a particular εf as in the case of FKM, while the valence changes continuously. Moreover, the onset of the valence transition and the closing of activation gap show clear mismatch. This is well consistent with the experiment on SmB6.

In section II, we introduce briefly the models and method. We present our results on DOS, valence transition, and the activation gap in section III. Section IV is devoted to the summary and conclusion.

II. MODEL

The FKM is a model explaining the properties of 2-level system competing among binding of f-electron(εf), itinerancy of d-electron(t), and on-site Coulomb interaction between f- and d-electron(U). Ignoring spin degree of freedom, the Hamiltonian of FKM is written as

\[ H_0 = -t \sum_{\langle i,j \rangle} (d_i^\dagger d_j + d_j^\dagger d_i) + U \sum_i n_i^f n_i^d + \epsilon_f \sum_i n_i^f \]  

(1)

where \( d_i^\dagger (d_i) \) creates(annihilates) a spinless d-electron at i-site. \( n_i^f \) and \( n_i^d \) denotes the i-site occupation number operator of f- and d-electron, respectively.

In Eq. (1), we must note that \( n^f = \sum_i n_i^f \) and \( n^d = \sum_i n_i^d \) commute with the Hamiltonian. This commutativity implies that their expectation values, \( \langle n^f \rangle \) and \( \langle n^d \rangle \), are good quantum numbers of this model. Therefore \( \langle n^f \rangle \) and \( \langle n^d \rangle \) remain some natural numbers from the beginning to the end, and all \( \langle n_i^f \rangle \) and \( \langle n_i^d \rangle \) are 0 or 1.

Due to this simplicity, there are several rigorous theorems and many numerical results about FKM (see ref. [3] and references therein). These are worthy of note since FKM can be applied to various systems having f- and d-electrons. For example, FKM has been regarded as a simplified version of the single band Hubbard model [19-22], the crystalline formation model [3] and the binary alloying model [23].

Ignoring the hybridization, however, could lead to an oversimplification in describing non-integer valent systems. In particular, it seems unreasonable to disregard hybridization in non-integral valent systems where the energy difference between f- and d-level is very small. If we remind that hybridization plays a key role in the periodic Anderson model, it is natural to add the hybridization term to Eq. (1). This leads us to an extended model

\[ H = H_0 + V \sum_i (f_i^\dagger d_i + d_i^\dagger f_i) \]  

(2)

where V is the transition amplitude between f- and d-level. This is the Hamiltonian of EFKM.

Using Hartree-Fork approximation, Avignon and Ghatak insists that EFKM shows discontinuous valence transition as well as continuous one by decreasing the energy gap between two levels for a finite f-d hybridization. Da Silva and Falicov also reported that they found first and second order valence transitions in EFKM using Green’s function method with mean field approximation and zero conduction band width. According to their result, discontinuous valence transition appears when \( U/V \geq 2.5 \). Kanda et al. showed the same result with Da Silva and Falicov within Hartree-Fork approximation but non-zero conduction band width. Recently, Giesekus and Falicov also reported using Hartree-Fork approximation that EFKM has first order valence transition for particular parameter range.

However, there are some contradictory results to those mentioned above. Using Hartree-Fork approximation and taking the periodicity of the system into account, Leder argued that there is no discontinuity in valence transition in EFKM. Baecck and Czycholl also reported using different decoupling method that first order valence transition does not exist in EFKM. Depending on the approximation used, some of results show discontinuity in valence transition but others do show only continuous transition. This is why we use the Lanczos exact diagonalization method to get rid of the effect of approximation. At first, we use the modified Lanczos method to get the ground state. Then using the Lanczos method, we investigate the ground state valency \( \langle \psi_g | n_f | \psi_g \rangle \), and the DOS

\[ D_{\sigma}(\omega) = \sum_{\vec{k},n} \left| \langle \psi^N_{\vec{k},\sigma} | \psi^N_{\vec{k},\sigma} \rangle \right|^2 \delta(\omega - E^N_{\vec{k}} + E^N_{\vec{k}+1}) \]  
\[ = \sum_{\vec{k}} S_\sigma(\vec{k},\omega) \]  

(3)

and

\[ D_{\sigma}(\omega) = \sum_{\vec{k},n} \left| \langle \psi^N_{\vec{k},\sigma} | \psi^{N+1}_{\vec{k},\sigma} \rangle \right|^2 \delta(\omega + E^N_{\vec{k}} - E^{N+1}_{\vec{k}}) \]  
\[ = \sum_{\vec{k}} S_\sigma(\vec{k},\omega) \]  

(4)
where subscript ‘o’ and ‘e’ mean ‘occupied’ and ‘empty’, respectively. \( S(\mathbf{k}, \omega) \), the spectral function, means the partial DOS of momentum \( \mathbf{k} \). \( S(\mathbf{k}, \omega) \) can be compared with the angle resolved photoemission spectroscopy data.

### III. RESULTS

The \( f \)- and \( d \)-electron DOS of FKM depending on \( \epsilon_f \) are shown in Fig.1. We put in the figure the activation gap \( \Delta_{\text{act}} \) corresponding to the energy gap between filled \( f \)-band and empty \( d \)-band and the effective gap \( \Delta_{\epsilon ff} \) corresponding to the energy gap between empty \( f \)-band and empty \( d \)-band.

![FIG. 1. The DOS for FKM with \( V=0 \) and \( U=1.5 \). Fermi surfaces are located in between two large \( f \)-peaks in all cases.](image)

The ground state electron configuration in real space for \( \epsilon_f \leq 0.47 \) is the alternating type such as \(-f-d-f-d-\). There is no sign of change in electron configuration from \( \epsilon_f = 0 \) (a), to \( \epsilon_f = 0.47 \) (c). The only change in DOS is shifting of \( f \)-DOS, to high-frequency side. On the contrary, Fig.1 (d) is quite different from Fig.1 (a)-(c), which implies that sudden change takes place in between \( \epsilon_f = 0.47 \) and \( \epsilon_f = 0.48 \). This is clear from Fig.2 which shows \( f \)-electron valency \( \langle n_f \rangle \) depending on \( \epsilon_f \). In Fig.2 (b) for \( U=1.5 \), valence transition occurs at \( 0.47 < \epsilon_f < 0.48 \), where \( \Delta_{\epsilon ff} = 0 \).

Therefore it is clear that \( \Delta_{\epsilon ff} \) is the effective gap governing the valence transition in FKM. The difference between \( \Delta_{\text{act}} \) and \( \Delta_{\epsilon ff} \) is resulted from onsite electron-hole binding and proportional to the onsite interband Coulomb interaction strength \( U \). This interpretation is well consistent with the original idea of Falicov and Kimball [2] about the origin of discontinuous valence transition in two band system. Thus \( \Delta_{\epsilon ff} \) corresponds to the shrinking gap

\[
\Delta_{\epsilon ff} = \Delta_{\text{act}} - 2U(1 - \langle n_f \rangle)
\]

suggested by Falicov and Kimball [2].

![FIG. 2. \( \langle n_f \rangle \) depending on \( \epsilon_f \) for \( U=0.6 \) (a), 1.5 (b), and 3.0 (c). Hybridization effect is shown in each case with \( V=0, 0.02, \) and 0.06. Hybridization effect is more clear within large \( U \) or large \( \epsilon_f \) region.](image)

Fig.2 shows the type of valence transition. For \( V=0 \) the \( f \)-electron valency shows steps as \( \epsilon_f \) increases, which is the well-known discontinuous valence transition in FKM. The hybridization effect in the valence transition is also clearly shown in Fig.2. Within all parameter range, all edges of \( V=0 \) disappear for any small hybridization. This disappearance clarifies continuous valence transition in all \( U \) for \( V \neq 0 \). It is interesting to see that the hybridization effect is more prominent in large \( U \) and large \( \epsilon_f \). This is consistent with the reduction of \( \Delta_{\epsilon ff} \), which is corresponds to the length of plateau in Fig.2 as \( U \) or \( \epsilon_f \) increases. Eq.3 clearly explains these behaviors of \( \Delta_{\epsilon ff} \).

The continuous transition can be confirmed via analyzing DOS. We present the change of DOS with \( \epsilon_f \) for a finite hybridization \( V=0.02 \) in Fig.3. Comparing Fig.3 with Fig.2, we find that small \( f \)-peak indicated by arrow in (c) grows as we increase \( \epsilon_f \) from 0 to 0.47. This new creation of \( f \)-peak make \( \Delta_{\epsilon ff} = 0 \). Therefore \( \Delta_{\epsilon ff} \) is not defined in the hybridization-induced valence transition or \( \Delta_{\epsilon ff} \) is always zero for \( V \neq 0 \), and this means the transition is continuous. As this \( f \)-peak grows, valence electrons can transfer more easily to conduction band and we observe continuous change of valency as a result.

We now study the transport property of the system in terms of the activation gap \( \Delta_{\text{act}} \) which has been measured by Cooley et al. [3]. We calculate the activation gap \( \Delta_{\text{act}} \) from DOS. We find that \( \Delta_{\text{act}} \) decreases linearly as \( \epsilon_f \) increases in the constant valence regions which correspond to plateaus in Fig.3. This is quite natural since
1. the effect of $\epsilon_f$ on DOS is shifting of the $f$-DOS with $d$-DOS as rigid background. Calculation has been done for $U=0.6$ and $V=0.02$ and the result is shown in Fig. 4. $U=0.6$ is the value for which Farkašovský has shown metal-nonmetal transition for $V=0$.

Our result demonstrates that the activation gap closes not at the onset of valence transition but at the end of valence transition. This is the well-known mismatching showing in the experiment of Cooley et al.

IV. CONCLUSION

In this paper, we consider a generalized two band model, the so-called extended Falicov-Kimball model which includes both the Coulomb repulsion and hybridization between valence band and conduction band. The behaviors of valence transition and metal-nonmetal transition in EFKM have been studied using the Lanczos method.

First, we give a remark on the energy gaps. The activation gap $\Delta_{act}$ governs transport properties of the system, while the effective gap $\Delta_{eff}$ governs the valence transition. The latter is the effective gap suggested by Falicov and Kimball and determines the condition of valence transition in FKM. Intrisite electron-hole pairing causes decreasing of $\Delta_{act} - \Delta_{eff}$. This is known as gap shrinking by Falicov and Kimball.

Secondly, we find that the valence transition becomes continuous even for small hybridization. The effect of hybridization in valence transition is determined by the competition between $\Delta_{eff}$ and $V$. For a fixed $V$, the hybridization effect becomes more prominent as $U$ or $\epsilon_f$ increases. Fig. 3 clearly shows the increasing of $U$ or $\epsilon_f$ causes smoother transition. The DOS of Fig. 3 shows that hybridization makes the valence transition continuous by showing the growing of small $f$-peak as $\epsilon_f$ increases, which makes the effective gap vanishes. Continuous growth of this $f$-peak reflects continuous valence transition when $V \neq 0$.

Finally, we show that the exotic metal-nonmetal transition behavior of SmB$_6$ can be explained by EFKM. Due to finite hybridization the valence transition takes place continuously, while $\Delta_{act}$ decreases linearly as $\epsilon_f$ increases until the system meets new valence phase. $\Delta_{act}$ closes suddenly at the point of valence change. These features of EFKM are well consistent with Cooley et al.’s experimental result on SmB$_6$.

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